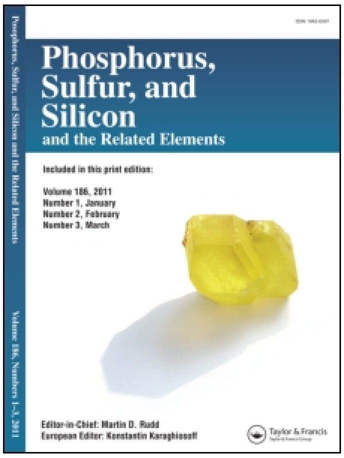

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ELEMENTAL SELENIUM REACTIONS WITH 2- AND 3-PICOLINE

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ELEMENTAL SELENIUM REACTIONS WITH 2- AND 3-PICOLINE

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Reactions of elemental selenium with 2- and 3-picoline have been studied at reflux temperatures under normal pressure in argon and in sealed ampuls at about 250°C. After removing unreacted reactants, the products were identified by GC-MS. With 2-picoline and 3-picoline, eleven and six reaction products, respectively, were identified.

Key words: Elemental selenium, 2-, 3-picolines, mass spectrometry-gas chromatography.

INTRODUCTION

This work is a continuation of our investigations into the reaction products of elemental sulfur and selenium with heterocyclic aromatic amines. The purpose of these investigations was to synthesize new, interesting derivatives of the amines. In the preceding papers, the products of the reactions of elemental sulfur with 2-, 3- and 4-picoline[1–3] and of selenium with 4-picoline[4] have been reported. It seemed now expedient to expand the studies by surveying the reactions of selenium with 2- and 3-picoline. Thus, the completed experimental evidence would enable to draw conclusions concerning the effect of substituent in the aromatic ring on the course of the reaction and the nature of the products formed. It would also be possible to compare the behavior of sulfur and selenium in respect of the aromatic amines studied.

RESULTS

The red modification of selenium obtained by reduction of SeO_2 with hydroxylamine was used throughout. Inspection of the reactions of 2-picoline and 3-picoline with selenium, conducted under atmospheric pressure under argon (following the procedure adopted for the reaction of 4-picoline[4] at reflux temperature (ca. 135°C) has shown that the two amines are markedly less reactive than 4-picoline. After 48 hrs, as much as 99% of selenium was recovered, as compared to 74% with 4-picoline. To increase the yield, the reactions were conducted in sealed ampuls. Under these conditions the temperature could be raised to 250°C. An excess of reactants was removed from the mixture. Table I illustrates the dependence between the extent of consumption of selenium and temperature as well as of duration of its reaction with

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TABLE I
The influence of the time and temperature on the extent of selenium transformation in the reaction with 2-picoline

Reaction number	Time of the reaction [h]	Temperature [°C]	mass of the product [mg]	Extent of Se transformation [%]
I	48	230	5.7	2.38
II	72	230	10.6	4.43
III	72	240	14.8	5.95
IV	72	250	28.8	11.62

2-picoline. To determine molecular masses of the products, their FD and EI mass spectra were recorded. Mixtures of the products were analyzed by gas chromatography-mass spectrometry (GC-MS). Gas chromatograms of the products of the reactions of 2-picoline and 3-picoline are shown in Figures 1 and 14, respectively. The results are presented in Tables II and III. The mass spectra together with the fragmentation patterns are shown in sucessive figures whereas the structures of the compounds and reaction pathways are seen in Schemes I and II.

DISCUSSION

2-Picoline

Figure 1 shows a gas chromatogram of the reaction products of 2-picoline, whereas successive figures show their mass spectra and fragmentation pathways. Peaks 1, 2 and 3 in the chromatogram can be assigned to compounds of the general formula $C_{12}H_{12}N_2$ (M = 184) which may have resulted from condensation of two picoline molecules. This reaction is likely to afford 1,2-dipyridylethane as well as four other products resulting from substitution of a hydrogen atom in the pyridine ring. The mass spectra of the compounds are shown in Figures 2, 3 and 4. None of the spectra exhibits an abundant peak at m/z = 92, characteristic of the cleavage of the β linkage relative to the ring in ethylpyridines. At the same time, all the spectra display a m/z 169 ion (M-15). Accordingly, none of the products can be identified as dipyridylethane.

The mass spectra do not allow to assign unambiguously the chromatographic peaks to a definite "nonlinear" isomer. However, it has been well established that during radical methylation of the 2-picoline ring, the most reactive is position 6 followed by 4.[5] Hence, the most abundant peak 2 in the chromatogram can be assigned to compound **1**, whereas peak 3 to compound **2** and the smallest one 1 to compound **3**. It is worth noting here that compound **1** was also obtained in the reaction of 2-picoline with sulfur.[1] Peaks 4, 5, 6, 7 and a more remote one 9 in the chromatogram have been assigned to compounds with molecular masses exceeding 184, as sup-

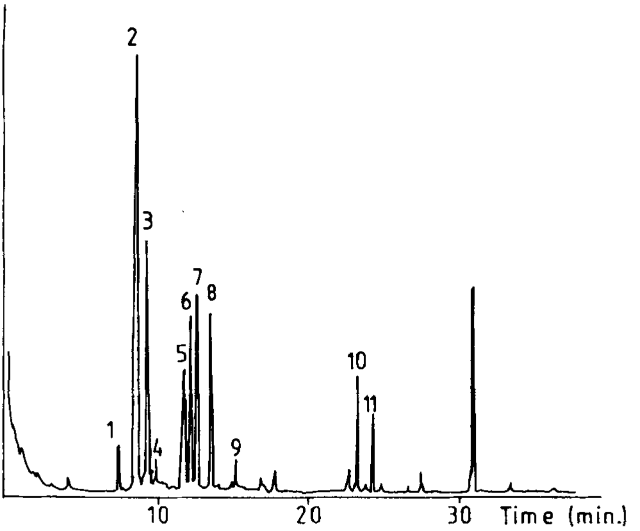


FIGURE 1 GC analysis of products of the reaction of 2-picoline with selenium, 3 μl. Initial temperature 100°C, 4°/min.

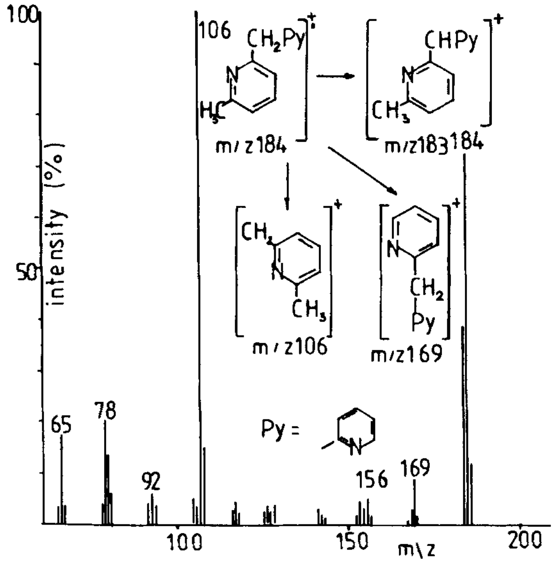


FIGURE 2 Mass spectrum and fragmentation pathways of compound 1.

ported by appearance of fragment ions at m/z 197 and 198 in their mass spectra (Figures 5–9). These products must have resulted from condensation of either at least three picoline molecules ($C_{18}H_{17}N_3$) or two picoline molecules and selenium. The identified organoselenium compound will be discussed later. Only two products (peaks 4 and 6) have molecular ions at m/z 275. However, the remaining ones were assigned molecular masses based on their retention times.

As shown in Figure 10, there is a variety of structures derived from the conden-

TABLE II

Products of the reaction of selenium with 2-picoline

Molecular mass (measured)	Elemental composition	Compound
184	$C_{12}H_{12}N_2$	2-methyl-6-(2-pyridyl)methylpyridine, **1**[*] 2-methyl-4-(2-pyridyl)methylpyridine, **2** 2-methyl-3-(2-pyridyl)methylpyridyne, **3**
182	$C_{12}H_{10}N_2$	1,2-di(2-pyridyl)-ethene, **4**
275	$C_{18}H_{17}N_3$	1,2,3-tri(2-pyridyl)propane, **5** 2-(2-pyridyl)methyl-6-[2'-(6-methyl)pyridyl]-pyridine, **6** 4-(2-pyridyl)methyl-6-[2'-(6'-methyl)pyridyl-pyridyne, **7** 1,2-di(2-pyridyl)-1-[6-(2-methyl)pyridyl]-ethane, **8** 1,2-di(2-pyridyl)-1-[4-(2-methyl)pyridyl]-ethane, **9**
273	$C_{18}H_{15}N_3$	1,2-di(2-pyridyl)-1-[6-(2-methyl)pyridyl]-ethene, **10**
344	$C_{12}H_{12}N_2Se_2$	2-methyl-6-[(2-piridyl)hydrodiselenomethyl]-pyridyne, **11**

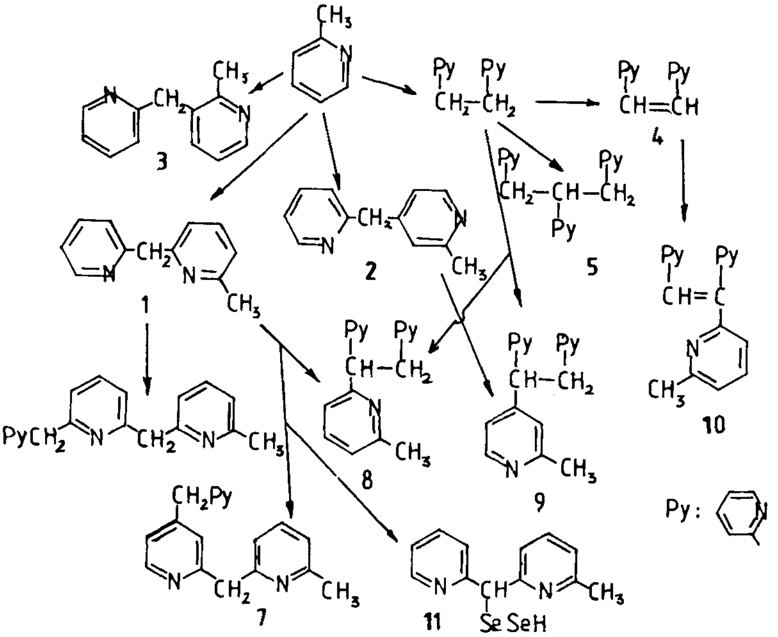
[*] The numbering of the compounds in Tables and figures is consistent with the numbering defined in the Scheme I and II.

sation of three picoline molecules. A compound giving rise to peak 4 in the chromatogram was identified as tripyridylpropane **5**. Its mass spectrum (Figure 5) is identical with that of a compound obtained in the reaction of 2-picoline with sulfur.[1] In the mass spectrà of products giving peaks 5 and 7 (Figures 6 and 7) remarkable is an abundant fragment ion at m/z 169 resulting from ejection of the CH_3PyCH_2 radical. This process is likely to involve compounds of structure D (Figure 10) for which the reactants are the aforementioned "nonlinear" isomer with molecular mass of 184. Consequently, these products can be identified as compounds **6** and **7**, differing in the location of substituents in the ring. In the mass spectrum (Figure 8) of a product giving peak 6 in the chromatogram, there is an abundant molecular ion at m/z 275 followed by fragment ions at m/z 260 (M—CH_3), 197 (M—Py) and 182 (M—$PyCH_3$) and ions at m/z 154 and 104 characteristic of the dipyridylethane fragmentation pathway. These evidence is satisfactory for identification of this compound as one of the isomers with structure C (Figure 10). A product of similar, but

TABLE III

Products of the reaction of selenium with 3-picoline

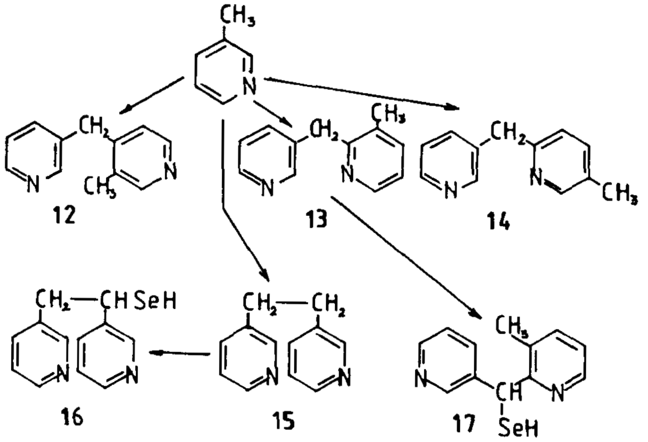
Molecular mass (measured)	Elemental composition	Compound
184	$C_{12}H_{12}N_2$	3-methyl-4-(3pyridyl)methylpyridine, **12** 2-methyl-6-(3-pyridyl)methylpyridine, **13** 3-methyl-2-(3-pyridyl)methylpyridine, **14** 1,2-di(3-pyridyl)ethane, **15**
264	$C_{12}H_{12}N_2Se$	1,2-di(3-pyridyl)-1-hydroselenoethane, **16** 3-methyl-2-(3-pyridyl)hydroselenomethylpyridine, **17**



SCHEME I Reaction of 2-picoline with elemental selenium.

differing only in abundances of the fragment ions, spectrum was obtained in the reaction of 2-picoline with sulfur.[1] The differences in abundances of particular fragment ions show them to be isomers C differing in the positions of substitution in the ring.

It has long been known that acidification of the reaction medium during radical



SCHEME II Reaction of 3-picoline with elemental selenium.

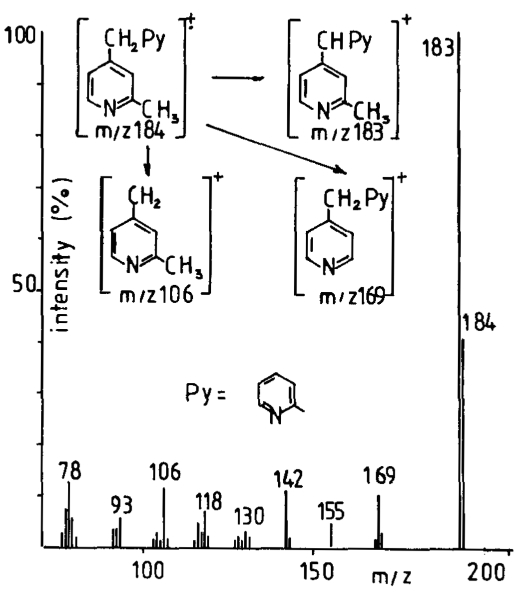


FIGURE 3 Mass spectrum and fragmentation pathways of compound **2**.

methylation of picolines affects the sensitivity of particular positions of the ring to substitution.[5] In the absence of acid, the yields of products substituted at positions 6, 3 and 4 are respectively 43, 37 and 11.4%. In the presence of acid, the respective yields are 80, 1.3 and 6.18%. As the hydrogen selenide formed during the reaction is a much stronger acid than hydrogen sulfide [pK_1 (H_2Se) = 3.48; pK_1 (H_2S) = 6.61],[6] it can be speculated that the reaction with sulfur afforded a product substituted at position 3 or 4, whereas with selenium, a 6-substituted product (**8**) was formed.

In the mass spectrum (Figure 9) of a product giving peak 9 in the chromatogram, the molecular ion is missing and the abundances of the fragment ions, with the exception of that at m/z 93, are small. The ions at m/z 183 and 181 reveal the presence of a dipyridylethane derivative, i.e. a compound of structure B or C (Figure

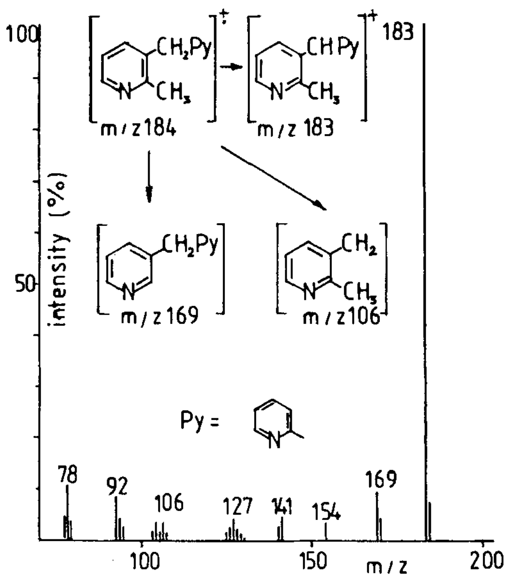


FIGURE 4 Mass spectrum and fragmentation pathways of compound 3.

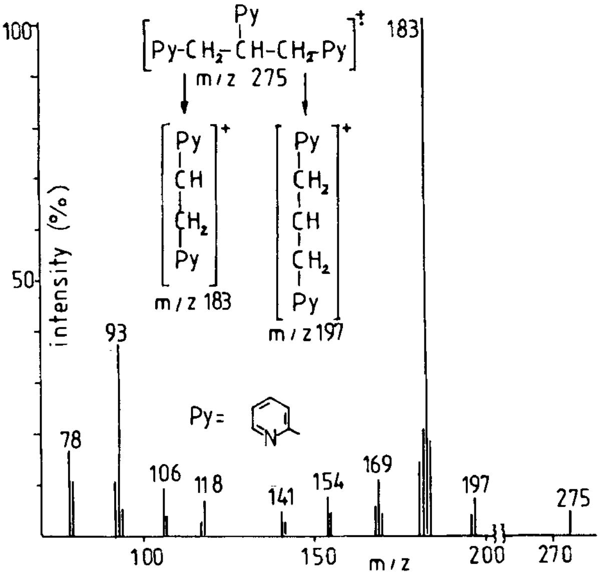


FIGURE 5 Mass spectrum and fragmentation pathways of compound 5.

10). Again, the fragment ion at m/z 168 reveals a methyl substituent in the molecule (M—PyCH$_2$—CH$_3$) thus ruling out structure B. As the reactivity of position 2 of 2-picoline in its reaction with selenium is higher than that of position 3, the compound was assigned structure **9**. Thus, in the reaction with sulfur, 1,2-di(2-pyridyl)-1-[3-(2-methyl)pyridyl]ethane was formed.

Peak 8 in the chromatogram is assigned to compound with M = 182, i.e. **4**, being

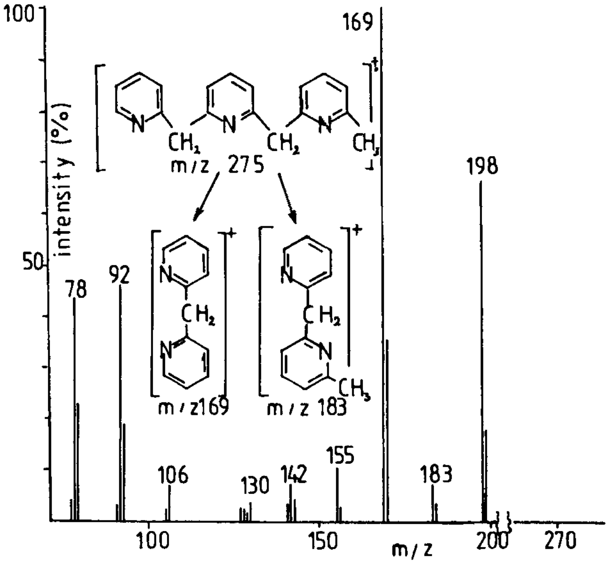


FIGURE 6 Mass spectrum and fragmentation pathways of compound 6.

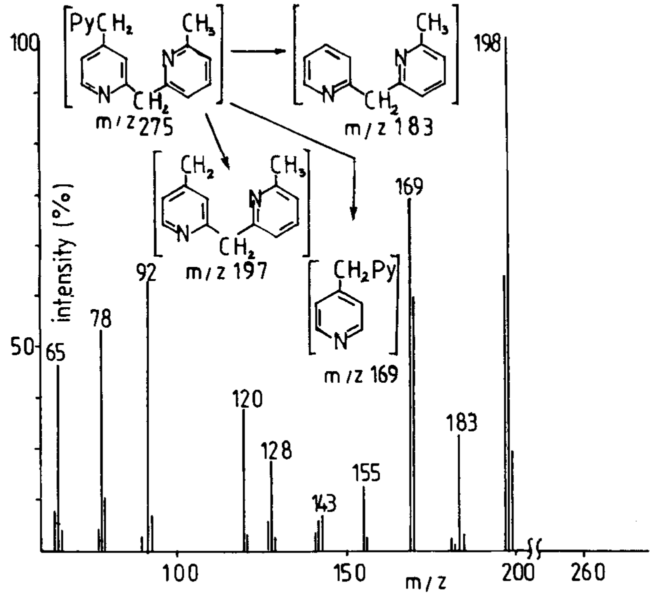


FIGURE 7 Mass spectrum and fragmentation pathways of compound 7.

a dehydrogenation product of dipyridylethane which was not detected in this reaction. Its mass spectrum (Figure 11) is identical with that of dipyridylethene obtained from the reaction of 2-picoline with sulfur.[1]

Peak 10 in the chromatogram is assigned to compound with M = 273 ($C_{18}H_{15}N_3$). It is either a dehydrogenated condensation product of 3 molecules of picoline, an unsaturated derivative of compounds with structures A, B or C (Figure 10) or a

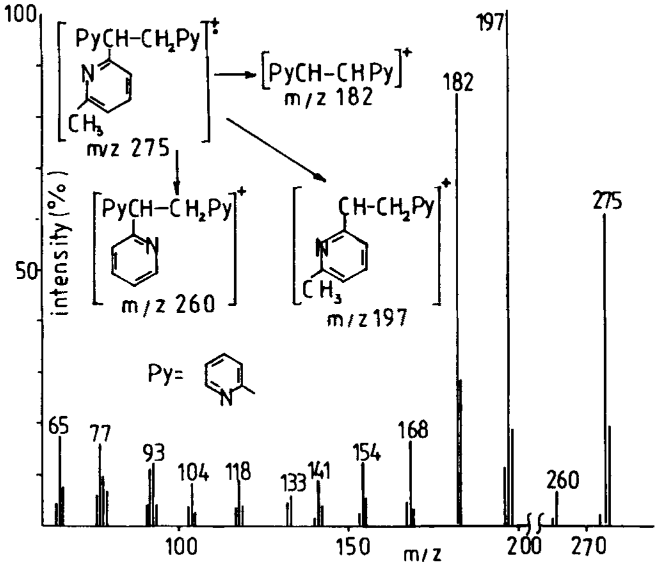


FIGURE 8 Mass spectrum and fragmentation pathways of compound **8**.

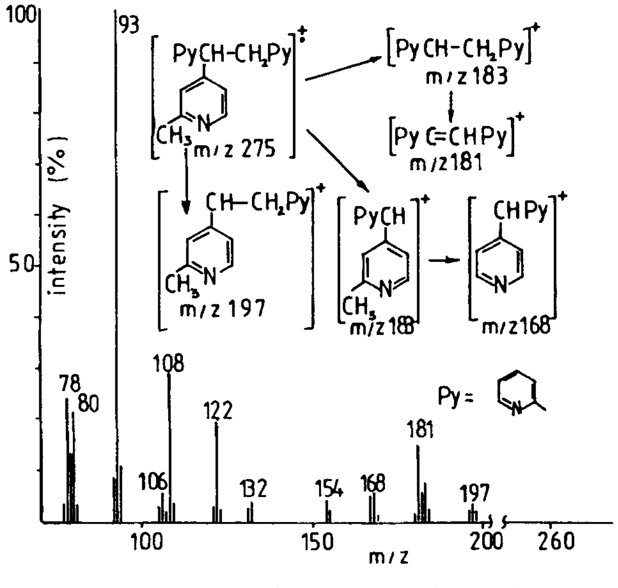


FIGURE 9 Mass spectrum and fragmentation pathways of compound **9**.

cyclic tripyridylpropane derivative likely to be formed via intramolecular hydrogen substitution in the pyridine ring. The mass spectrum (Figure 12) displays a molecular ion at m/z 273 and a fragment ion at m/z 258 (M—CH_3). The latter indicates that the compound's structure is C. This conclusion has further been supported by close similarity of its mass spectrum over the region of lower m/z values to that of **8** (Figure 8). Consequently, based on the likeness of the mass spectra and on the

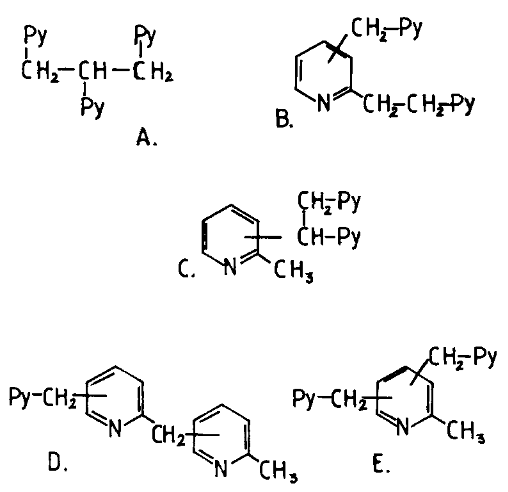


FIGURE 10 The possible structures of compounds of molecular formule $C_{18}H_{17}N_3$ (MW 275).

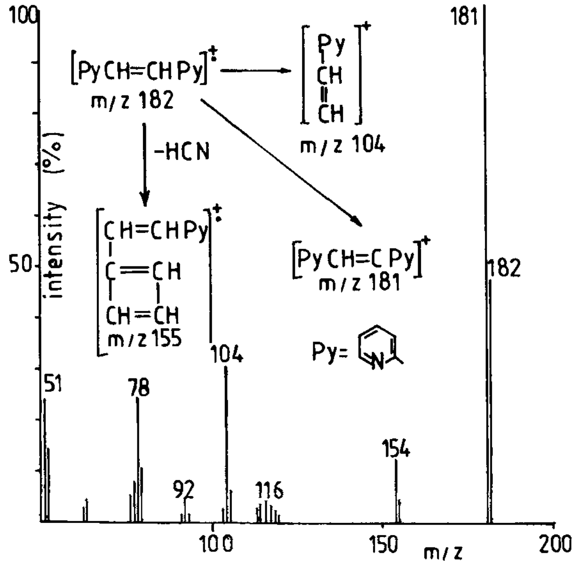


FIGURE 11 Mass spectrum and fragmentation pathways of compound **4**.

finding that the yield of **8** is higher than that of **9** peak 10 can be assigned to the ethane derivative **10**.

Peak 11 in the chromatogram is due to a compound with M = 344 corresponding to a molecule assembled from two picoline molecules and two selenium atoms. A group of ions (Figure 13) at m/z 399–345 supports the hypothesis that the compound is a diselenide, as the two most abundant isotopes of selenium ($^{80}Se/^{78}Se = 2:1$) give rise to different masses of the molecular ion. The spectrum exhibits fragment ions M—SeH and M—SeSeH as well as a fragment ion at m/z 169. The last-named is characteristic of a "nonlinear" condensation product of two picoline molecules, e.g. **4**, formed in the highest yield. Accordingly, the selenide was assigned formula **11**.

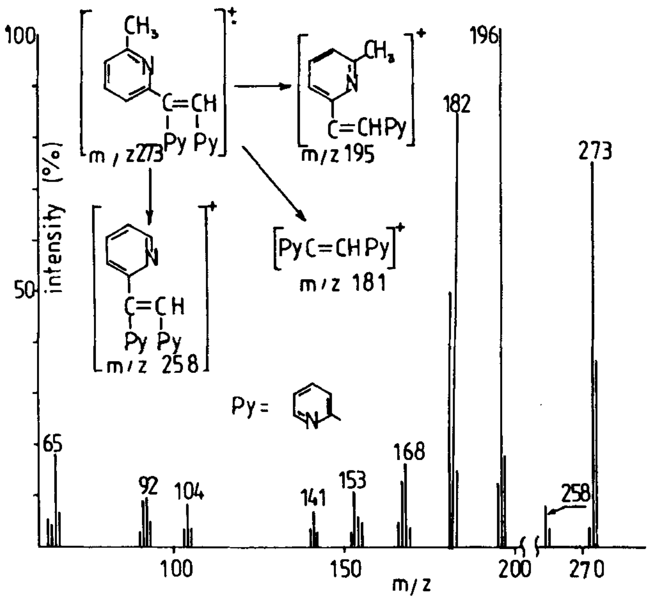


FIGURE 12 Mass spectrum and fragmentation pathways of compound **10**.

There are also peaks of other products in the gas chromatogram, but their mass spectra do not allow to elucidate unambiguously their structures.

3-Picoline

Figure 14 shows a gas chromatogram of the reaction products of 3-picoline whereas successive figures show their mass spectra and fragmentation pathways. The spectra of peaks 1, 2, 4, and 3 (Figures 15, 16, 17 and 18) are due to a product of M = 184 ($C_{12}H_{12}N_2$). In the first three spectra, fragment ions at m/z 169 (M—CH_3) appear. These are the substitution products of hydrogen in the pyridine ring. It is worth noting that in the mass spectrum of peaks 1 and 2 (Figures 16 and 17), two sets of the fragment ions appear, at m/z 184, 169, 106 and 92 and at m/z 190, 175 and 161. Inspection of abundance of these two sets of ions at various positions of a peak 1 in the chromatogram shows that they are due to different compounds. Obviously, only the first set refers to the products of the reaction considered. On the basis of the mass spectra, the structure of compounds with M = 184 cannot be elucidated. It is known, however, that the most reactive position during radical methylation of 3-picoline is position 2[5] (55% yield of the isomer), followed by position 4 (20%) and 6 (19%). On this basis, structure **13**, has been assigned to the most abundant peak 4 in the chromatogram; peaks 1 and 2 have been assigned to compounds **12** and **14** respectively. Peak 3 is also attributed to compound with M = 184 but in its mass spectrum (Figure 18), the ion at m/z 169 (M—CH_3) is missing, a very abundant being the ion at m/z 92. Such a fragmentation pathway can be attributed to cleavage of the β bond relative to the alkylpyridine ring and shows that it is the mass spectrum of dipyridylethane **15**. This compound was also obtained in the reaction of 3-picoline with sulfur.[2]

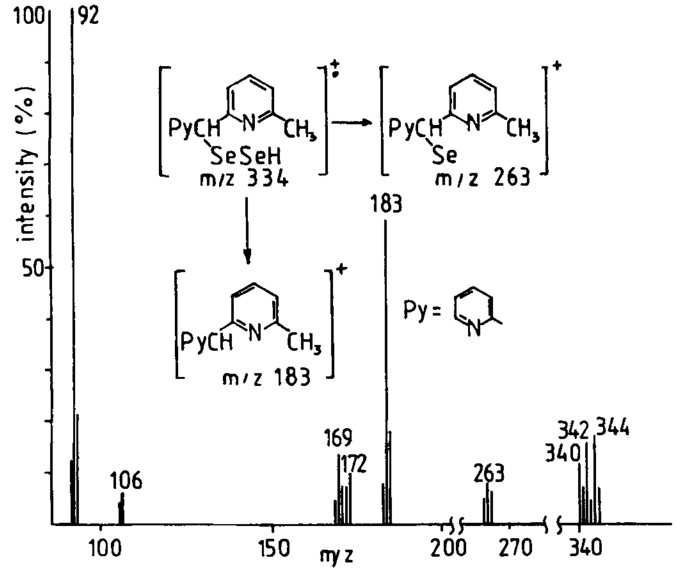


FIGURE 13 Mass spectrum and fragmentation pathways of compound **11**.

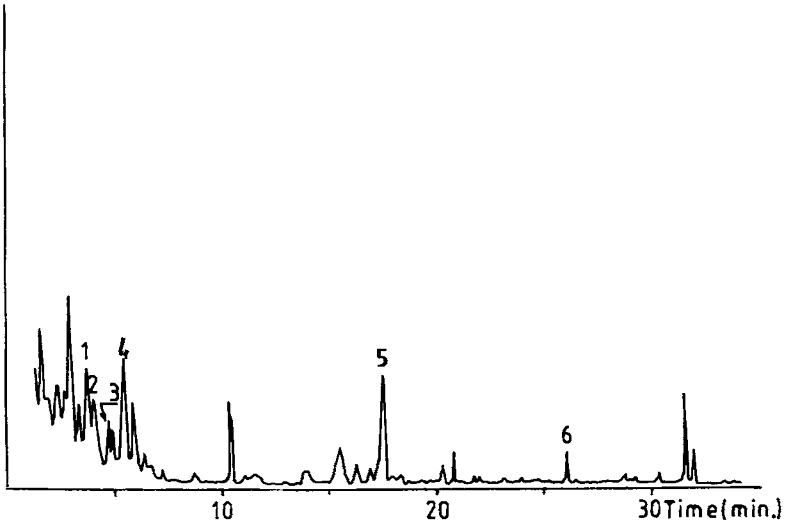


FIGURE 14 GC analysis of products of the reaction of 3-picoline with selenium, 1 μl. Initial temperature 100°C, 4°/min.

The next two peaks in the chromatogram, 5 and 6, are due to compounds with M = 264 ($C_{12}H_{12}N_2Se$). They are the selenization products of the previously reported isomers, $C_{12}H_{12}N_2$. The spectrum of peak 5 together with the fragmentation pathway of the products are shown in Figure 19. It exhibits a molecular ion, two fragment ions at m/z 182 (M—H_2Se) and 171 (M—$PyCH_3$) as well as a very intense peak at m/z 92 ($PyCH_2^+$). These ions allow to identify the compound a a derivative of dipyridylethane **16**.

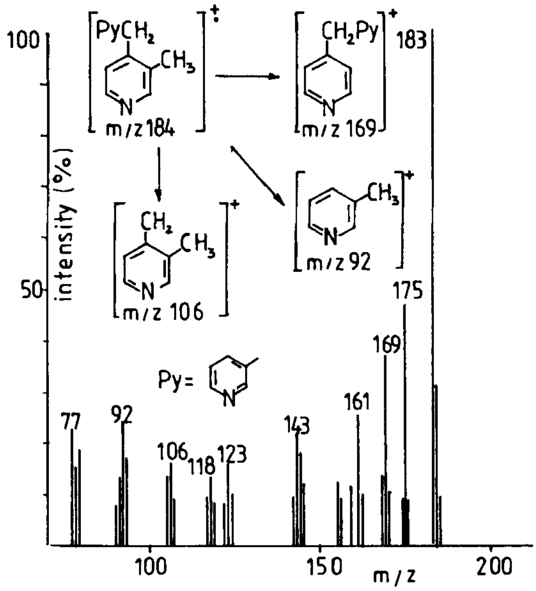


FIGURE 15 Mass spectrum and fragmentation pathways of compound 12.

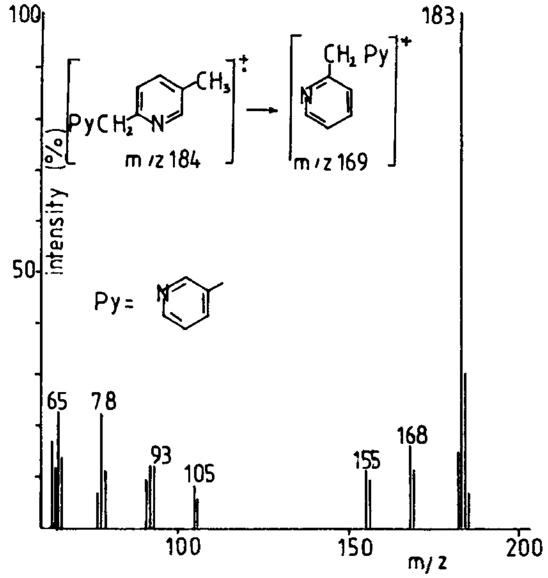


FIGURE 16 Mass spectrum and fragmentation pathways of compound 14.

The spectrum of peak 6 is slightly different (Figure 20). There is also a slightly more abundant molecular peak at m/z 264. By ejection of the pyridine molecule, an abundant ion at m/z 185 is produced, whereas elimination of the picoline molecule affords the ion at m/z 171 derived from the selenium analog of 3-pyridylcarbinol. These data suggest that the compound was formed by selenization of either of the

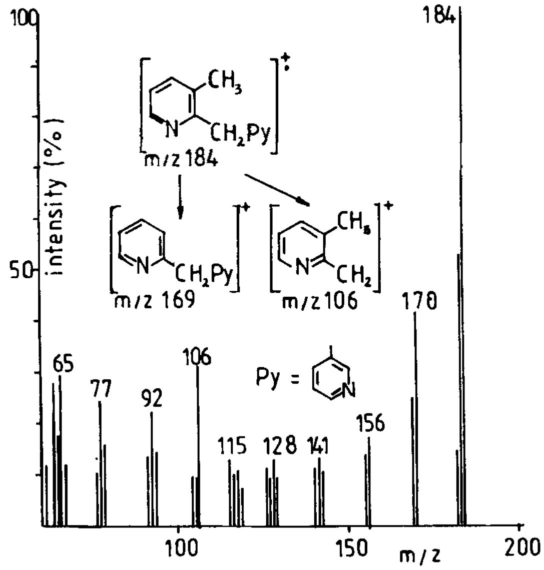


FIGURE 17 Mass spectrum and fragmentation pathways of compound **13**.

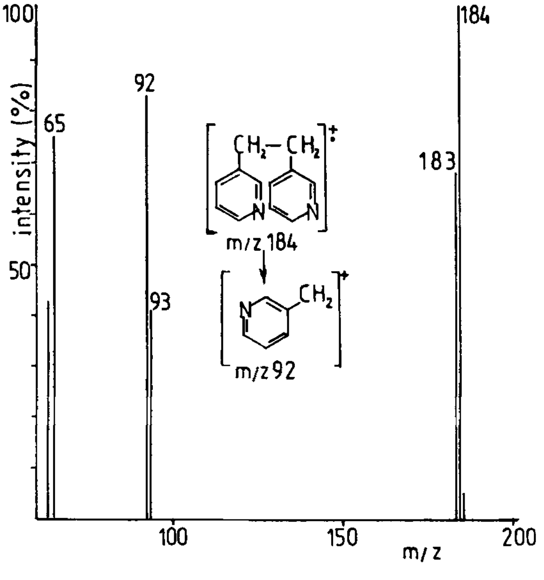


FIGURE 18 Mass spectrum and fragmentation pathways of compound **15**.

isomers **12**, **13**, or **14**. Bearing in mind the highest yield of isomer **13**, it is concluded that the compound was the selenide **17**.

Elucidation of the structures of the products obtained in the reactions of both amines allowed to suggest the reactions pathways shown in Schemes I and II. These reactions, similar to the previously studied ones with sulfur[1-3] are consecutive-parallel radical processes. They require, however, much higher temperatures and the extent of transformation of selenium is markedly lower than that of sulfur.

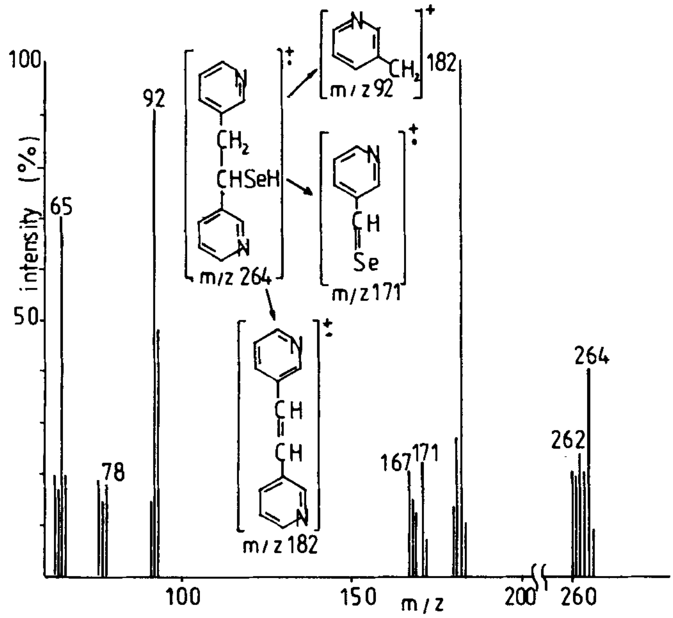


FIGURE 19 Mass spectrum and fragmentation pathways of compound **16**.

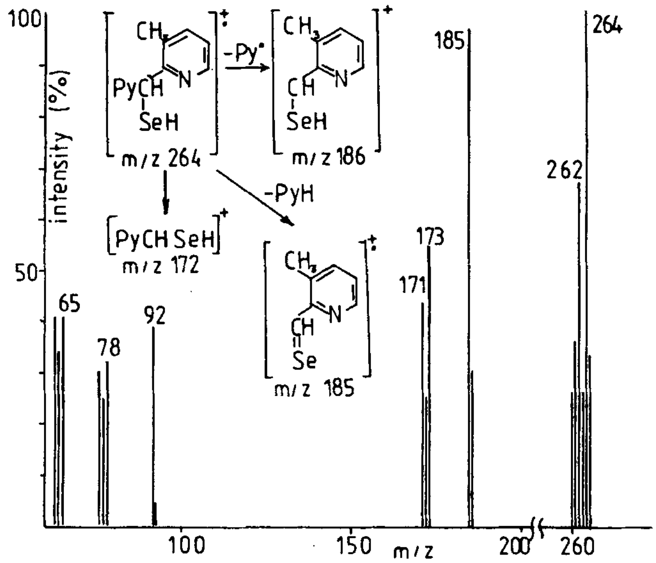


FIGURE 20 Mass spectrum and fragmentation pathways of compound **17**.

There are distinct differences between the reactions of 2-picoline with selenium and sulfur. In the latter case, the reaction entraining the side chain of the picoline molecule is preferred, leading to dipyridylethane and tripyridylpropane. Reactions of hydrogen substitution of another molecule do not proceed at all. On the other hand, with selenium, the other direction leading to "nonlinear" isomers, $C_{12}H_{12}N_2$ and

$C_{18}H_{17}N_3$, is clearly preferred. With sulfur, cyclization of tripyridylpropane takes place to give new polycyclic compounds, whereas with selenium, these products are missing.

The finding that the reaction with selenium affords a variety of products of the methylation of the ring can also be explained in terms of the influence of hydrogen selenide. Bonnier and Court[7] have shown that the protonation enhance distinctly the reactivity of the ring in picolines. As mentioned previously, hydrogen selenide is a much stronger acid than hydrogen sulfide, thus affecting the course of the reaction distinctly. The lack of the cyclization products of the propane derivative can be interpreted as being due to a low yield of its formation.

Also 3-picoline reacts much more reluctantly with selenium than does sulfur. No more complex compounds were found among the reaction products (Scheme II), whereas with sulfur, a variety of polycyclic compounds could be detected which were missing with selenium. Condensation products of two 3-picoline molecules could only be identified. A number of products, as in the case of the reaction of 2-picoline, remained, however, unidentified because their mass spectra could not be interpreted due to the absence of molecular ions and characteristic fragment ions at higher m/z values.

EXPERIMENTAL

Preparation of the Red Modification of Selenium

A 6.3 M solution of $NH_2OH \cdot HCl$ (30.5 g of the hydrochloride in 70 mL of water) was neutralized with a 25% ammonia solution and added slowly to a 1 M SeO_2 solution (8 g SeO_2 in 73 mL of water). The mixture was left for 24 hrs, filtered and washed to give 5.6 g of elemental selenium (98% yield).

The Reaction of Selenium with 2-picoline

A. Reaction under atmospheric pressure: To 5.6 g (0.07 mole) of Se, 54 mL of 2-picoline was added and the mixture was gently refluxed (ca. 130°C) in an oil bath under argon. The argon leaving the condenser was passed through a washing bottle filled with a saturated lead(II) acetate solution. After 48 h the unreacted selenium was filtered off and washed successively with toluene, chloroform and methanol. The recovery was 99.9%. All filtrates were combined and evaporated *in vacuo* at ambient temperature to afford 18 mg of a dark-brown oil.

B. Reaction in sealed ampuls: In 5-mL ampuls were placed 0.07 g Se and 3 mL of the amine, the mixture was saturated with argon and the ampuls were sealed. The reaction was carried out at 220–250°C for 72 h. The unreacted Se was then filtered off, washed successively with toluene, chloroform and methanol. The extracts were combined and evaporated *in vacuo* at ambient temperature to give a brown oil. Illustrative examples of these experiments are shown in Table I.

Reactions of Selenium with 3-picoline

The reactions were carried out in the same manner as those with 2-picoline. Under atmospheric pressure the recovery of selenium was 98%. In ampuls, the extent of the transformation of selenium was 12.05%. Seventy mg of selenium and 3 mL of 3-picoline gave 12 mg of products.

Mass Spectrometry

The GC-MS spectra were taken on a Micromass 16F, VG Micromass Ltd. mass spectrometer coupled with a Pye Unicam Model 104 gas chromatograph and a PDP 81 computer. The EI mass spectra were recorded at 70 eV. A DB-1 capillary column was used for separations.

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