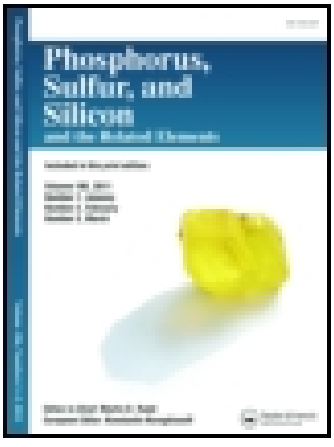

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ELEMENTAL SELENIUM REACTIONS WITH 4-ETHYLPYRIDINE

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ELEMENTAL SELENIUM REACTIONS WITH 4-ETHYLPYRIDINE

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A reaction of elemental selenium with 4-ethylpyridine has been studied. The process was run in sealed ampuls, within 205 – 240 °C, under nitrogen. The reaction products were indentified by GC-MS and ^{1}H NMR. The following products have been identified: (4-pyridyl)hydroxymethyl ketone, (4-pyridyl)methyl ketone, (4-pyridyl)-hydroselenomethyl ketone, 2,3-di(4-pyridyl)butane, 1,3-di(4-pyridyl)butane, 1-(4-pyridyl)-1-[2-(4-ethyl)pyridyl]-ethane, 1-(4-pyridyl)-1-[2-(4-ethenyl)pyridyl]ethane.

Keywords: Selenium; 4-ethylpyridine; gas chromatography; mass spectrometry; proton magnetic resonance

INTRODUCTION

The present work is a continuation of our research on reaction of elemental sulfur[1-3] and selenium[4,5] with heterocyclic aromatic amines. The results of investigation of the reactions of selenium with 2-, 3-, and 4-picoline have shown that the element is markedly less reactive than sulfur. This notwithstanding, a number of compounds have been obtained including products containing selenium. Our further attempt has been a closer examination of the interaction of selenium with isomeric ethylpyridines. Here are the results of investigation of the reaction of selenium with 4-ethylpyridine.

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RESULTS

Preliminary experiments have shown that selenium begins to react with 4-ethylpyridine at a temperature well above the boiling point of the latter, i.e. 164 °C. Also the reaction time was very long. Further, it was observed that the amine underwent facile oxidation with atmospheric oxygen in the presence of selenium. Hence, further experiments were conducted in a sealed ampul under nitrogen. Under these conditions the process could be run at 250 °C. Initially, the red modification of elemental selenium was used which was obtained by reduction of selenium dioxide with hydroxylamine.[6] However, it turned out that this modification was quickly converted to the grey one under experimental conditions and further experiments were conducted with the latter only.

In each ampul, 0.05 g of selenium and 2 ml of 4-ethylpyridine were placed. After cooling the reaction mixture, an excess of reactants was removed and the products were identified by thin-layer chromatography and gas chromatography coupled with a mass spectrometer (GC-MS). Attempts have been made to isolate the main products by liquid chromatography. The yields of the products at various temperatures and reaction times are presented in Table I.

TABLE I Conditions and the products of the reaction of elemental selenium with 4-ethylpyridine

Sample No.	*Number of ampuls*	*T [°C]*	*Reaction time [h]*	*Loss of selenium [%]*	*Product yield [g]*
1	4	205	50	4	0.032
2	6	220	122	5	0.084
3	10	235	72	6	0.187
4	10	235	126	11	0.223
5	10	240	75	8	0.198

In order to determine molecular weights of the products, their mass spectra were taken using the electron impact (EI) and field desorption (FD) techniques. Some of the isolated products were examined by ^1H

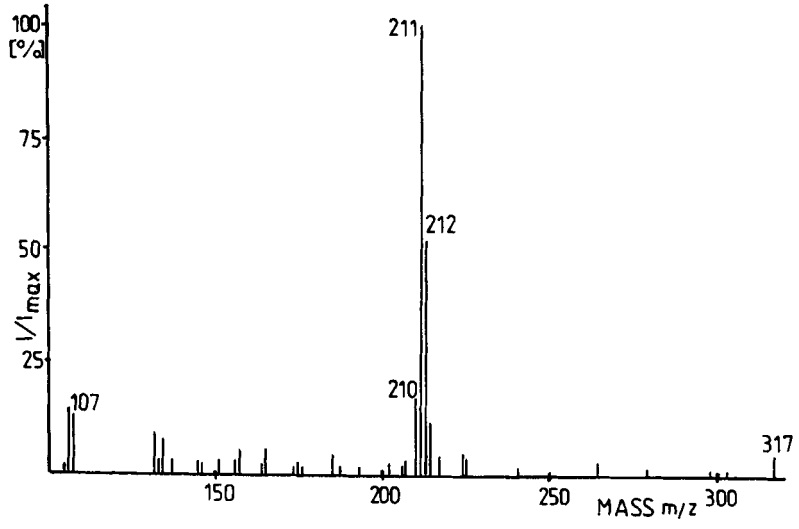


FIGURE 1 The FD mass spectrum of a mixture of reaction products of 4-ethylpyridine with selenium (20 mA)

NMR. The mass spectra of a crude mixture recorded by the FD technique after removal of unreacted reactants are shown in Figure 1. The most intense peaks appear at m/z 211 and 212 and are due to condensation products of the two 4-ethylpyridine molecules. The remaining peaks are weak. Some of these are fragment ions, and a part, e.g. those at m/z 202 and 303 are due to background ions. The peak at m/z 317 is likely to be due to a condensation product of three ethylpyridine molecules. A GC chromatogram of the mixture of products is shown in Figure 2. All the identified products, including those detected on the basis of the mass spectra and the ^{1}H NMR spectra, are summarized in Table II and presented in Scheme 1. The mass spectra of particular compounds giving peaks in the chromatogram (Figure 2) and their fragmantation pathways are presented in subsequent Figures.

TABLE II Identified products of the reaction of selenium with 4-ethylpyridine

Molecular weight (measured)	*Molecular formula*	*Compound**
137	$C_7H_7NO_2$	(4-pyridyl) hydroxymethyl ketone **1**[a]
121	C_7H_7NO	methyl (4-pyridyl) ketone **2**[a]
201	C_7H_8NOSe	(4-pyridyl) hydroselenomethyl ketone **3**[a]
212	$C_{14}H_{16}N_2$	2,3-di(4-pyridyl) butane **4**[a]
212	$C_{14}H_{16}N_2$	1,3-di(4-pyridyl) butane **5**[a,b]
212	$C_{14}H_{16}N_2$	1-(4-pyridyl)-1-[2-(4-ethyl)pyridyl] ethane **6**[b]
	$C_{14}H_{14}N_2$	1-(4-pyridyl)-1-[2-(4-ethenyl)pyridyl] ethane **7**[b]

*Product numbering corresponds to the numbers in the reaction schemes. [a]Structure determined by mass spectrometry. [b]Structure determined by ^1H NMR spectroscopy.

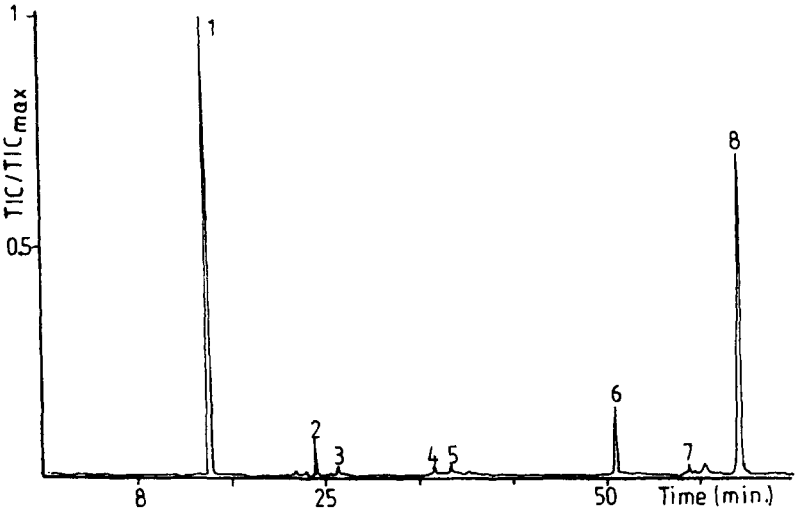
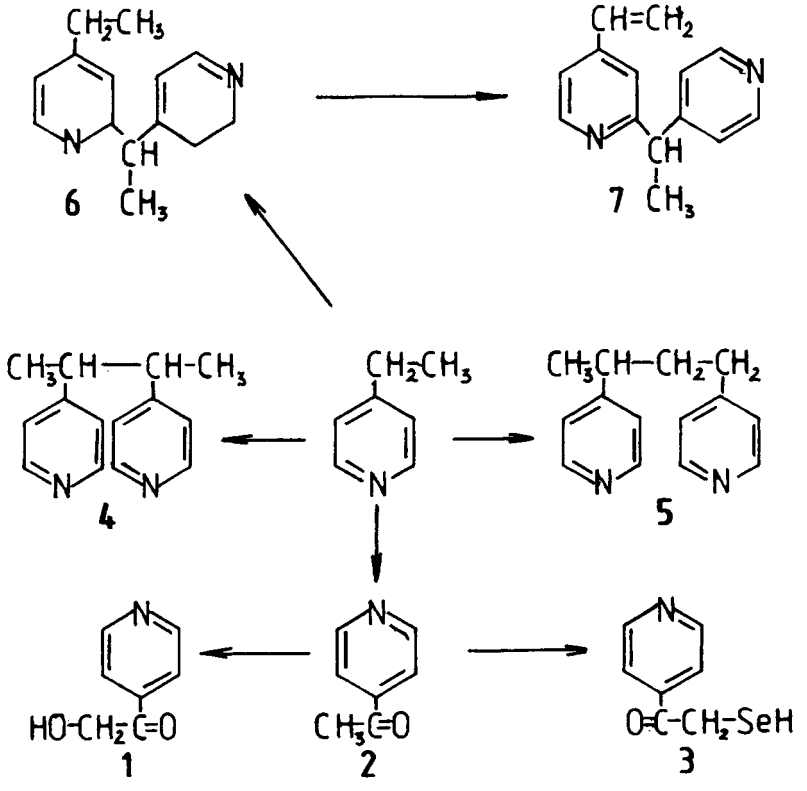


FIGURE 2 Gas chromatogram of the reaction products of 4-ethylpyridine with selenium. Peak 1 – 4-ethylpyridine, peak 2 – compound **1**, peak 3 – compound **2**, peak 4 compound **3**, peak 5 – unidentified organoselenium compound, peak 6-compound **4**, peak 7 – unidentified compound with molecular mass 212, peak 8 – compound **5**. Capillary column DB-DXN, L = 50 m, 80 °C, 4°C/min



SCHEME 1 Reaction pathways of elemental selenium with 4-ethylpyridine

DISCUSSION

Peak 1 in the chromatogram is due to a compound of molecular weight 107 (Figure 3), i.e. 4-ethylpyridine. Its presence shows that removal of residual amine is very difficult even after repeated vacuum evaporations at elevated temperature (80 °C).

Peak 2 in the chromatogram can be assigned to a compound of molecular weight 137. A small difference between molecular weights of this compound and 4-ethylpyridine (137 – 107 = 30) reveals that the former must have been formed by dehydrogenation followed by inclusion of two oxygen atoms. Molecular weight of 137 corresponds to the formula $C_7H_7NO_2$.

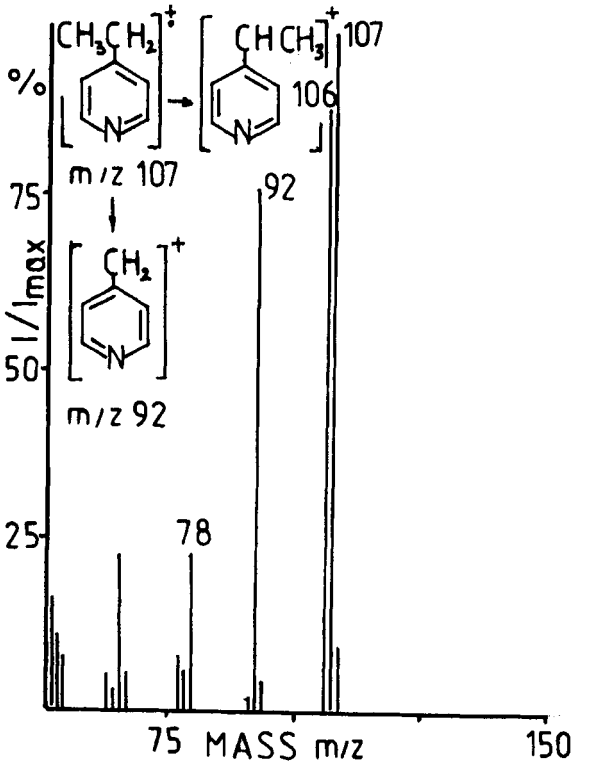


FIGURE 3 Mass spectrum and fragmentation pathways of 4-ethylpyridine

This would represent either (4-pyridyl)acetic acid or a dehydrogenation product of 2-(4-pyridyl)-1,2-ethanediol, i.e. (4-pyridyl) hydroxymethyl ketone or an isomeric aldehyde. Examination of the mass spectrum (Figure 4) rules out the first-named compound, because the acid cannot undergo fragmentation (M − 31) leading to an intense peak at m/z 106. Also the aldehyde is unlikely, as it would have been oxidized. Consequently, peak 2 in the chromatogram can be assigned to the hydroxy ketone **1**. Its fragmentation pathway closely resembles that of aromatic ketones.[7]

A small peak 3 can also be assigned to a compound formed by dehydrogenation and subsequent oxidation of 4-ethylpyridine. Its molecular peak at m/z 121 corresponds to C_7H_7NO and its mass spectrum (Figure 5),

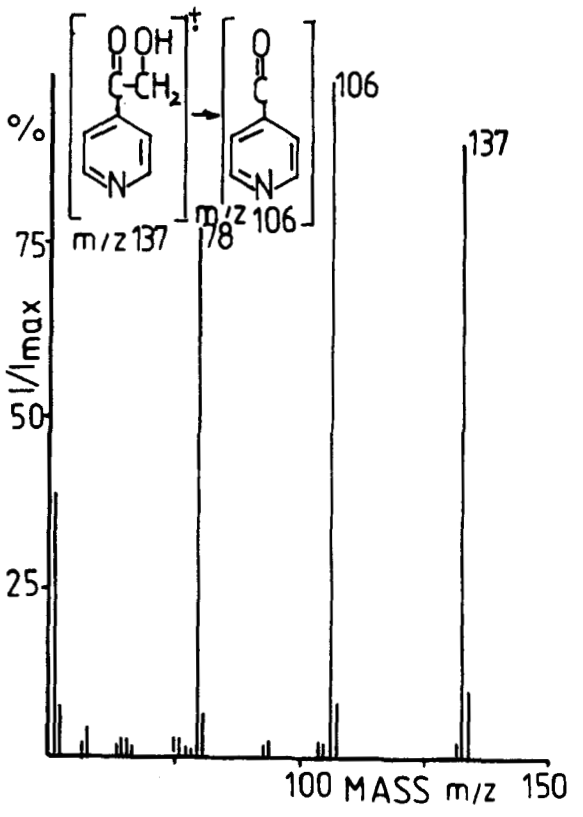


FIGURE 4 Mass spectrum and fragmentation pathways of product **1**

except for the molecular ion, is identical to that of ketone **1**. Product **2** can thus be identified as methyl (4-pyridyl) ketone. Compounds **1** and **2**, similar to the further mentioned hydroselenoketone **3**, result from the reactions of 4-ethylpyridine with oxygen. At this point it must be emphasized that the presence of selenium enhances the reactivity of the amine with trace amounts of oxygen. Anhydrous ethylpyridine heated under identical conditions in the absence of selenium remained unchanged.

Two small peaks 4 and 5 can be referred to selenium-containing compounds as evidenced by a group of peaks in their mass spectra (Figures 6 and 7) differing by two m/z units due to isotopic ions of masses 197 – 201. Among six natural selenium isotopes, the most abundant ones are just ^{80}Se

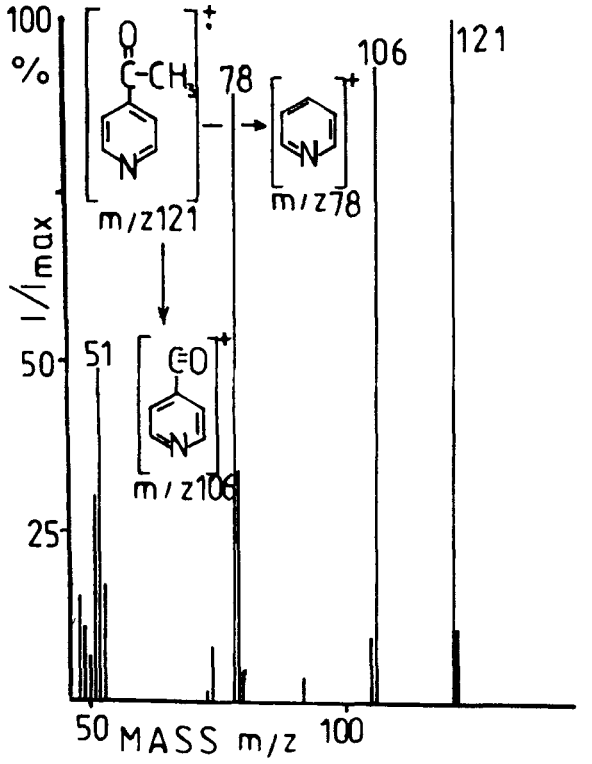


FIGURE 5 Mass spectrum and fragmentation pathways of product **2**

and ^{78}Se. Consequently, any selenium-containing ion produces a group of peaks in the mass spectrum. The molecular ion at m/z 201 corresponds either to PyC(O)CH_2SeH or Py(Se)CH_2OH. Intense fragment ions at m/z 121 (PyC(O)CH_3) and 106 (PyCO) show that peak 4 is due to (4-pyridyl) hydroselenomethyl ketone **3**, a selenium analogue of hydroxy ketone **1**.

Bearing in mind the structure of the reactants, it can be predicted that there is only one isomer of compound **3**, namely the selenone PyC(Se)CH_2OH. Unfortunately, the mass spectrum (Figure 7) contradicts this structure, as its fragmentation pathway should closely resemble that of aromatic ketones producing an intense fragment ion at m/z 170 (PyCSe). Since this is not the case, it can be stated that the ion at m/z 201 is a con-

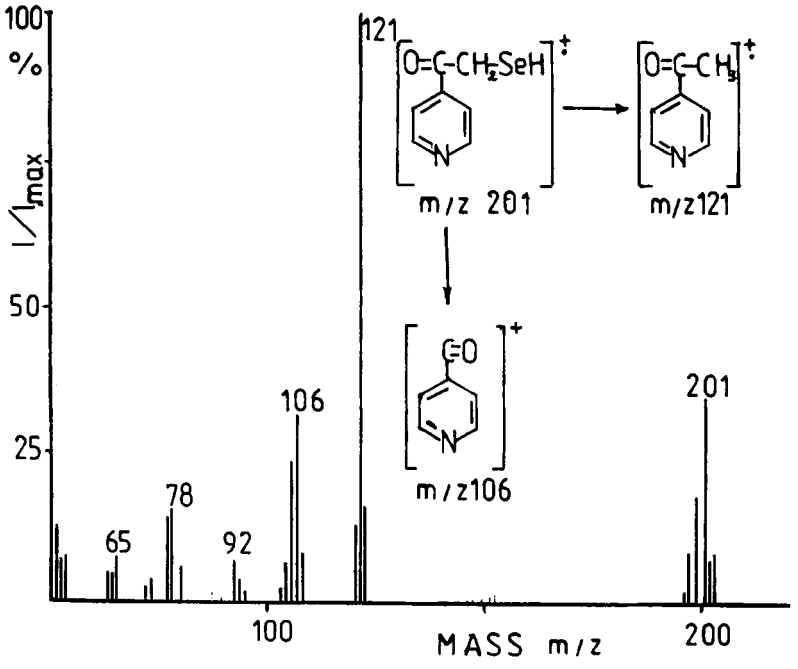


FIGURE 6 Mass spectrum and fragmentation pathways of product **3**

stituent of the fragment ion, while the molecular ion does not appear at all in the spectrum. Hence,it is difficult to unambiguously establish the structure of this organoselenium compound. The next three peaks in the chromatogram, i.e. 6, 7 and 8, the last being the most intense, belong to a product of molecular mass 212 formed by condensation of two ethylpyridine molecules. There are as many as five options (A through E) for this condensation as presented in Scheme 2. In the mass spectrum (Figure 8) of a compound giving rise to peak 6, apart from the fragment ion at m/z 211 (M – H), there are other ions at m/z 196 (M – H – CH_3), 134 (M – Py) and 106 (M – CH_2Py), while the molecular ion is missing. The appearance of the m/z 211 (M – H) peak as the base one suggests that there is at least one tertiary carbon atom adjacent to the pyridine ring in the molecule. Again, emergence of the m/z 181 ion reveals the presence of two methyl groups. These findings allow the product to assign structure C. Ultimately, product **4** can be identified as 2,3-di(4-pyridyl)methane. The next mass spectrum

(Figure 9) of peak 7 in the chromatogram is rather simple. The tree major components are the molecular ion at m/z 212, fragment (base) ion at m/z 106 ($M - C_2H_4Py$) and m/z 78 (Py). This simple spectrum is rather useless for establishing the structure of the compound.

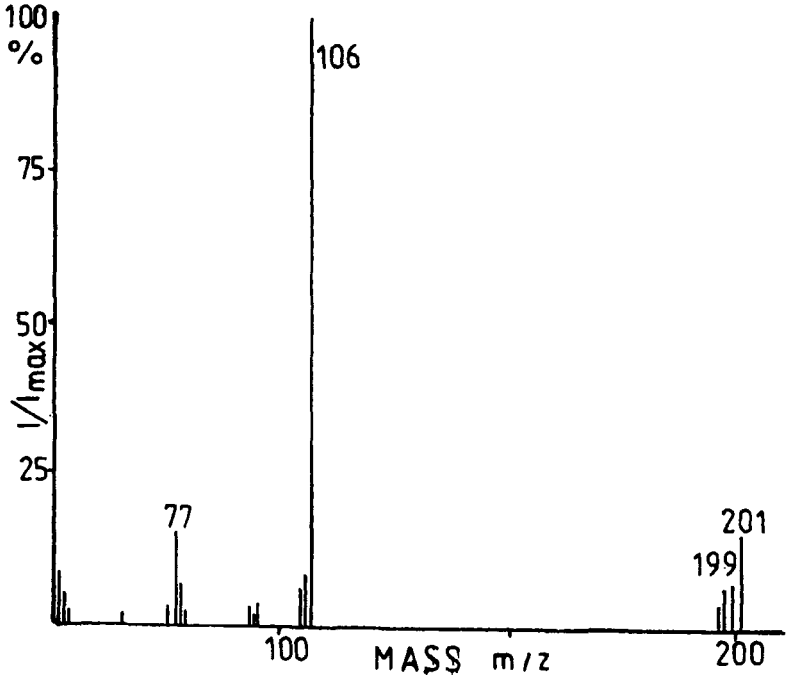
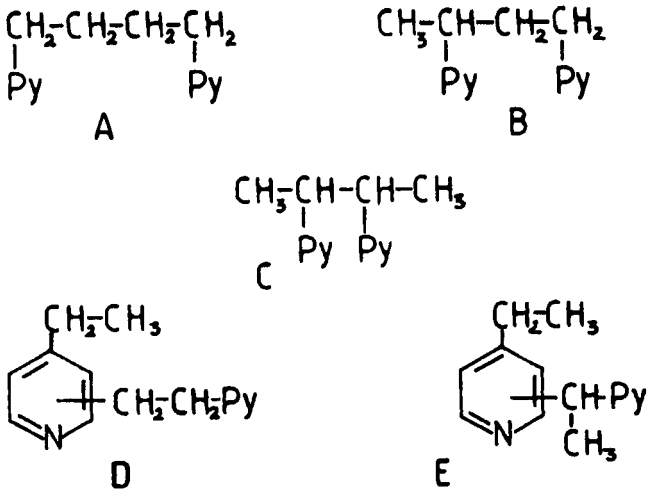


FIGURE 7 Mass spectrum of an unidentified organoselenium compound

Peak 8 in the chromatogram belongs to the main, volatile under the GC conditions, product of reaction of 4-ethylpyridine with selenium. Its mass spectrum (Figure 10) exhibits four intense peaks at m/z 212, 120, 106 and 93 assignable to the molecular ion, $M - PyCH_2$, $M\text{-}PyCHCH_3$ and $PyCH_3$, respectively. On this basis compound **5** can be identified as 1,3-di(4-pyridyl)butane. It was isolated by liquid chromatography and its structure was confirmed by ^1H NMR. Main features of the spectrum are presented in Table III and the structure of the compound is shown in Scheme 3.

In the ^1H NMR spectrum of compound **5** there are signals of the methyl protons (H – 1, $\delta = 1.31$ ppm) split into a doublet owing to coupling



SCHEME 2 Plausible structures of compounds of the general formula $C_{14}H_{16}N_2$(MW 212)

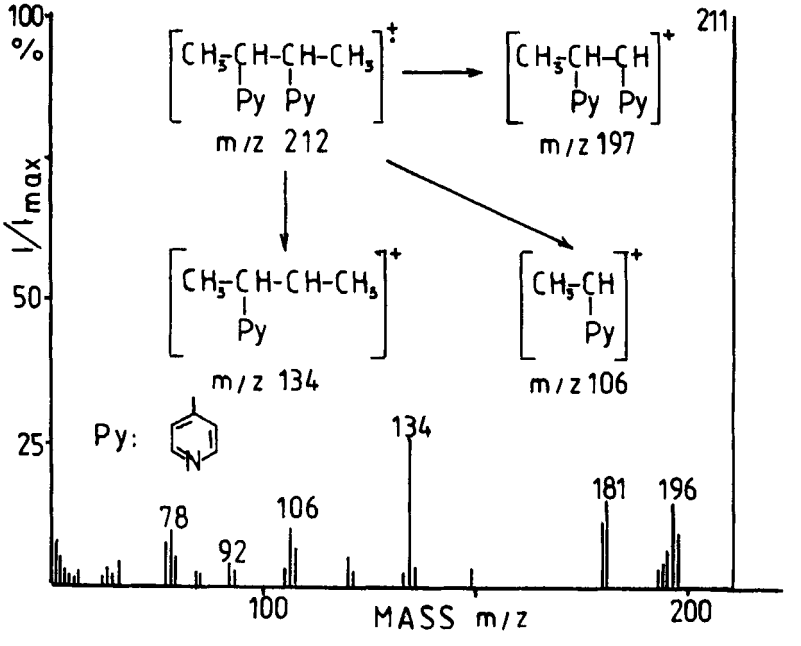


FIGURE 8 Mass spectrum and fragmentation pathways of product **4**

(J = 7.5 Hz) with the CH protons (H-2), a multiplet of the CH_2 group (H-3, δ = 1.96 ppm) and a peak arising from protons of two groups, CH (H-2) and CH_2 (H-4) residing in the same environment (pyridine ring).

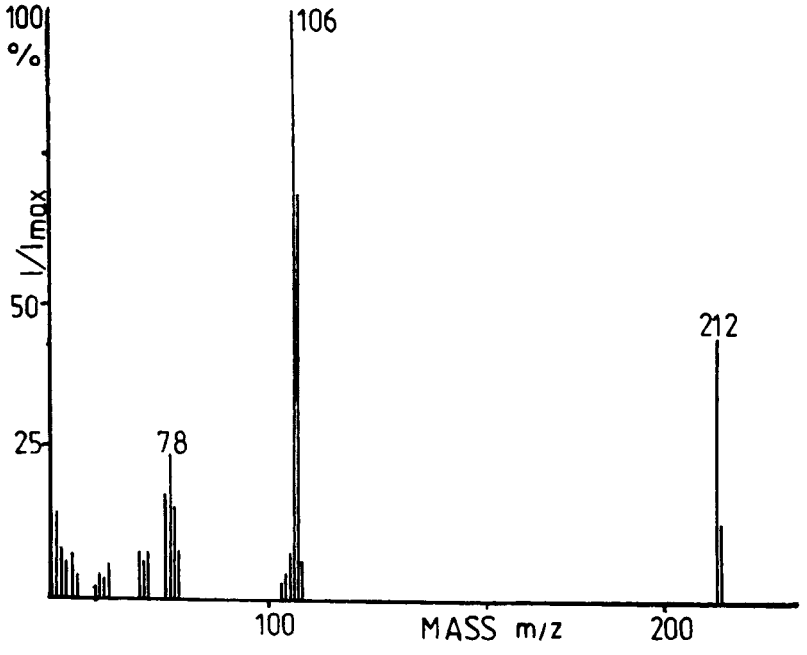


FIGURE 9 Mass spectrum of unidentified compound of molecular mass 212

A peak at δ = 7.21 ppm is due to coupling of the H-5 and H-6 protons of the ring with the H-7 ones adjacent to the nitrogen atom. The last peak emerges at low fields (δ = 8.52 ppm) and is due to H-7 protons adjacent to the nitrogen atoms.

In the gas chromatogram there are also peaks of other products whose identity could not be unambiguously determined on the basis of the mass spectra.

Apart from gas chromatography, also the liquid chromatography technique was used for separation of the reaction products. Similar to product **5**, also other compounds were isolated whose structures could not be determined on the basis of their mass spectra only. It was possible to establish their structure by examination of their ^1H NMR spectra. The chemical

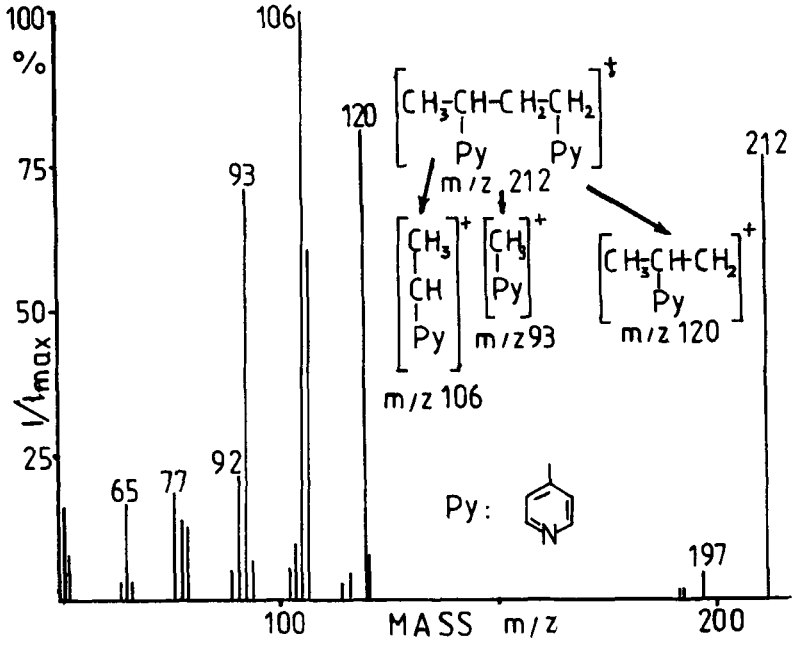
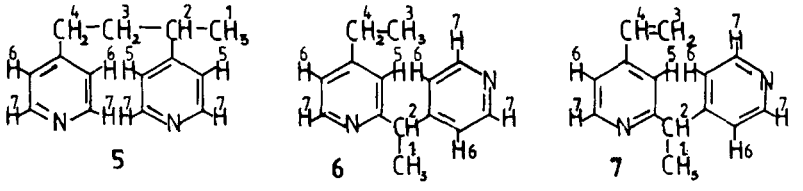


FIGURE 10 Mass spectrum and fragmentation pathways of product **5**

shifts, coupling constants and integration areas in the spectra of products **6** and **7** are presented in Table IV, whereas their structures in Scheme 3. It is concluded that compound **6** results from alkylation of the ring of another ethylpyridine molecule. The presence of only three H-7 protons in the aromatic ring reveals that position 2 is that at which substitution took place.



SCHEME 3 Structure of products **5**, **6** and **7**

TABLE III Chemical shifts (δ, ppm), coupling constants (J, Hz) and integration areas of protons in the ^{1}H NMR spectrum of product **5**

Protons	δ	*Multiplicity*	*Integration*
H-1	1.31	d	3
H-3	1.96	m	2
H-2, H-4	2.70	m	3
H-5	7.21	t* (1,2,1)	2
H-6	7.21	t* (1,2,1)	2
H-7	8.52	s*	4
$J_{1,2}$	7.5	$J_{3,4}$	7.5
$J_{2,3}$	5	$J_{5,7}$	5.5
$J_{2,4}$	9	$J_{6,7}$	5.5

* Bands consisting of a larger number of peaks which underwent overlapping and amplification to give the presented structure.

TABLE IV Chemical shifts (δ, ppm), coupling constants (J, Hz) and integration areas of protons in the ^{1}H NMR spectra of products **6** and **7**

	Compound 6			*Compound 7*			
Protons	δ	*Multiplicity*	*Integration*	δ	*Multiplicity*		*Integration*
H-1	1.35	d	3	1.35	d		3
H-3	2.0	m	3	1.98	m		2
H-2,H-4	2.7	m	3	2.70	m		2
H-5	7.4	s	1	7.48	s		1
H-6	7.3	t*(1,2,1)	3	7.30	t*(1,2,1)		3
H-7	8.6	m	3	8.62	m		3
$J_{1,2}$	7.5	$J_{3,4}$	6	$J_{1,2}$	7.5	$J_{3,4}$	9
$J_{2,4}$	7	$J_{6,7}$	5.5	$J_{2,4}$	6	$J_{6,7}$	5.5

*Band consisting of a larger number of peaks which underwent overlapping and amplification to give the presented structure.

The ^{1}H NMR spectrum of the next product (**7**, Table IV) resembles closely that of compound 6. This suggests the similar structure of both compounds. However, the signal ratio 3 : 2 : 2 : 1 : 3 : 3 of the latter show that product **7** is an unsaturated species. It is interesting to note that the spot of the compound on TLC chromatogram undergoes unfading colouration when irradiated with UV, before spraying with a reagent. The reaction

pathways of 4-ethylpyridine in the presence of selenium are shown in Scheme 1. The process requires very high temperatures to proceed and the degree of conversion of selenium is small (cf. Table I). Similar to the reaction of 4-picoline[4] with selenium, the condensation process may entrain both the side chain and to be the outcome of substitution of a hydrogen atom in another molecule of the amine. This article presents only low-molecular-weight products of the reaction of 4-ethylpyridine with selenium. However, it should be added that apart from these products, large quantities of complex mixtures are formed consisting of high-molecular-weight components, nonvolatile under GC conditions and difficultly resolvable by liquid chromatography.

EXPERIMENTAL

Sample preparation

In 5-ml ampuls, 0.05 g of the grey modification of selenium and 2 ml of 4-ethylpyridine were placed. The contents of the ampuls was flushed for 3 min with nitrogen, sealed and maintained within 205 – 240 °C. At about 200 °C the contents of the ampuls turned red-braun. After cooling, the colour turned pale-brown. After termination of the reaction, the ampuls were cooled, unreacted selenium was filtered off and washed successively with toluene and methanol. The filtrates were combined and evaporated in vacuo at 80 °C to give a badly smelling brownish oil. Particulars referring to the reaction conditions and the results are shown in Table I.

Mass spectrometry (GC-MS)

The GC-MS spectra were taken on a Micromass 16F, VG (Micromass Ltd.) mass spectrometer linked to a Pye Unicam 104 gas chromatograph and a PDR 8A computer. A 50-m long DB-DXN capillary column was used.

Mass spectrometry (FD)

The mass spectra were taken on a Varian MAT 711 mass spectrometer equipped with anEI – FD combined source. The wire current was 20 mA.

A mixture of products was analyzed after removing unreacted selenium and 4-ethylpyridine.

Liquid chromatography

The mixtures were separated in columns packed with a MN Kieselgel 60 (below 0.08 mm; 200 mesh ASTM) supplied by MN Macherey Nagel & Co.

Nuclear magnetic resonance

The ^1H NMR spectra were taken on a 100 MHz Tesla BS Model 567A spectrometer in $CDCl_3$ and CH_3OD using TMS as internal reference.

Thin-layer chromatography (TLC)

The chromatograms were developed on DC-Plastikfolien (E. Merck) coated with silica gel 60F254 in ethyl acetate – methanol and chloroform – methanol solvent systems of variable composition. Spots were located either in the UV light or by spraying with iodine vapours.

Acknowledgements
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