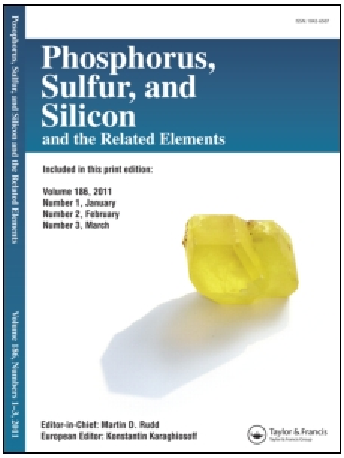

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REACTIONS OF ELEMENTAL SELENIUM WITH 2-ETHYLPYRIDINE

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REACTIONS OF ELEMENTAL SELENIUM WITH 2-ETHYLPYRIDINE

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Reactions of elemental selenium with 2-ethylpyridine in the presence and absence of KOH have been studied. The reactions were conducted under nitrogen in sealed ampoules, at 200°C. After removing unreacted substrates, the following products were identified by GC-MS: methyl 2-pyridyl ketone ***1****, 2,3-di-(2-pyridyl)butane* ***2****, 1-(2-pyridyl)-2-[3-(2-ethyl)pyridyl]ethane* ***3****, 1-(2-pyridyl)-[6-(2-ethyl)pyridyl]ethane* ***4****, 1-(2-pyridyl)-1-[5-(2-ethyl)pyridyl]ethane* ***5****, 1-(2-pyridyl)-1-[6-(2-ethyl)pyridyl]ethane* ***6****, 1-(2-pyridyl)-1-[4-(2-ethyl)pyridyl]ethane* ***7****, and 1-(2-pyridyl)-1-[3-(2-ethyl)pyridyl]ethane* ***8****. Among the products two organoselenium compounds ($C_{14}H_{16}N_2Se_2$) were also detected whose structure could not be established.*

Keywords: 2-Ethylpyridine; gas chromatography; mass spectrometry; selenium

Reactions of elemental sulfur and selenium with organic compounds constitute one of the alleys leading to new chemical compounds. This work is a continuation of our investigations into the reactions of sulfur[1–3] and selenium[4–6] with aromatic heterocyclic bases—isomeric picolines and 4-ethypyridine. Our previous experience has shown that selenium is markedly less reactive towards the amines than sulfur. Nonetheless, a variety of new compounds have been obtained using this element. This paper presents the results of the reactions of selenium with 2-ethylpyridine.

RESULTS AND DISCUSSION

Preliminary investigations have shown that 2-ethylpyridine, similar to 4-ethylpyridine,[6] undergoes smooth oxidation with air oxygen in the

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TABLE I Conditional of Carrying Out Reactions of Elemental Selenium with 2-Ethylpyridine

			Quantity			
No. of ampoule	Duration of reaction [h]	Temperature [°C]	KOH [mg]	Se [mg]	Loss of Se [%]	Yield [mg]
8	50	200	2	50	~7	28,1
9	50	200	—	50	~7	32,6

presence of selenium. For this reason all reactions were carried out in sealed ampoules under nitrogen. To attain higher yields, elevated temperatures (ca. 200°C) and extended reaction times were necessary.

Some reactions were carried out in the presence of KOH to learn whether the presence of the nucleophile can contribute to activation of selenium as was frequently the case with elemental sulfur.

Each ampoule contained 0.05 g of powdered gray modification of selenium, 2 mL of 2-ethylpyridine and, optionally, 2 mg of KOH. The excess of the reactants was removed after termination of the reaction. The residues were analyzed by TLC and GC coupled with mass spectrometer which served as a detector.

Both the conditions of carrying out experiments and the yields of the products are shown in Table I.

A comparison of the TLC and GC chromatograms of the products obtained in the presence and absence of KOH as well as of respective yields shows that KOH has no effect on the rate and direction of the reaction.

One of the mass spectra (taken by using FAB technique) of the reaction mixtures is presented in Figure 1. Prominent peaks emerging at m/z 211 and 214 are assigned to condensation products of two 2-ethylpyridine molecules. No structural assignments could be made to relatively intense peaks at m/z 389–392 as the gas chromatogram did not display peaks of species with m/z higher than 380. Perhaps these are fragment ions of products of higher molecular masses.

A gas chromatogram of the reaction products is shown Figure 2. The peaks of identified compounds have been marked in it and compounds are collected in Table II.

Chromatographic analysis of the reaction products revealed the presence of a variety of compounds. Potassium hydroxide did not affect the yield of the reaction. Both the mass of the products and the fraction of the selenium reacted are comparable in runs with and without KOH (Table I). Also the reaction pathways are alike yielding identical products. The structures of eight of these were established based on their mass spectra.

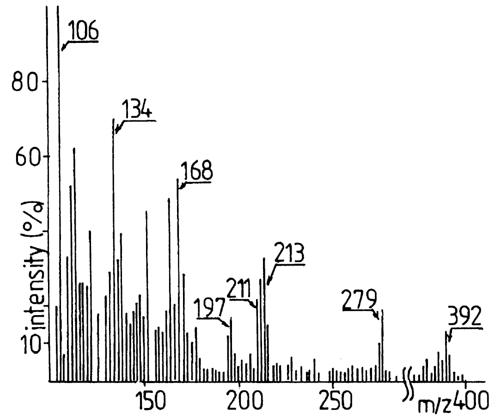
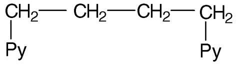


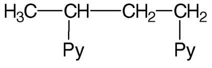
FIGURE 1 The mass spectra of the reaction mixtures.

Main peaks in the mass spectrum (Figure 1) at m/z 211–214 are assigned to condensation products of two 2-ethylpyridine molecules. The molecules mass of the product is 212, and the ions at m/z 213 and 214 are formed by attachment of hydrogen atoms split from glycerol used as a matrix in the FAB technique.

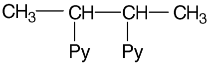
There may be five types of the condensation products of two 2-ethylpyridine molecules as illustrated by formulas A through E.


$\underset{\mathrm{Py}}{\mathrm{CH_2}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Py}}{\mathrm{CH_2}}$

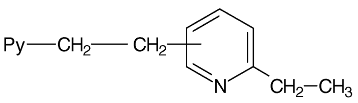
A


$\mathrm{H_3C}-\underset{\mathrm{Py}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Py}}{\mathrm{CH_2}}$

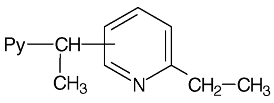
B


$\mathrm{CH_3}-\underset{\mathrm{Py}}{\mathrm{CH}}-\underset{\mathrm{Py}}{\mathrm{CH}}-\mathrm{CH_3}$

C



D



E

Products A, B, and C are formed by reactions involving the ethyl substitution of the amine, whereas compounds D and E emerge by substitution of the hydrogen atom in the ring of another 2-ethylpypidine molecule.

The ions at m/z 279 and 392 (Figure 1) cannot be assigned to molecular ions of condensation products of a greater number of 2-ethylpyridine molecules as their molecular masses condensation products. These are thus either fragment ions or background ions similar to those of m/z lower than 212.

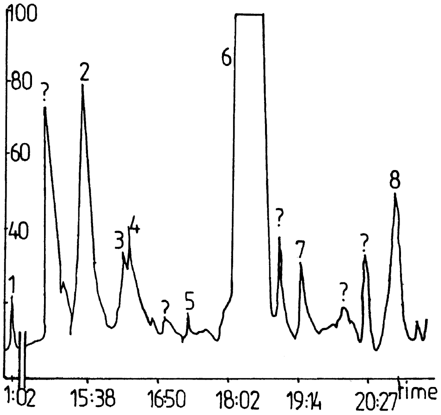


FIGURE 2 A gas chromatogram of the reaction products.

A very small peak 1 in the chromatogram (Figure 2) can be assigned to compound C_7H_7NO of molecular mass 121. Its mass spectrum together with fragmentation pathways is shown in Figure 3.

A small difference between molecular masses of this compound and the reactant (121 and 107 respectively) suggests that it might be formed by attachment of an oxygen atom with simultaneous dehydrogenation. This would thus be either a ketone (Py(O)CH_3) or aldehyde (PyCH_2CHO). However, under the reaction conditions the latter compound would have been unstable. For this reason peak 1 was assigned to methyl (2-pyridyl)ketone **1**. The presence of the oxidized 2-ethylpyridine among the reaction products call for the necessity of a more efficient flushing of the reaction mixtures with the inert gas.

TABLE II Identified Products of the Reaction of Selenium with 2-Ethylpyridine

Molecular mass	Elemental composition	Compound
121	C_7H_7NO	Methyl(2-pyridyl)ketone **1**
212	$C_{14}H_{16}N_2$	2,3-di(2-pyridyl)butane **2**
212	$C_{14}H_{16}N_2$	1-(2-pyridyl)-2-[3-(2-ethyl)pyridyl]ethane **3**
212	$C_{14}H_{16}N_2$	1-(2-pyridyl)-2-[6-(2-ethyl)pyridyl]ethane **4**
212	$C_{14}H_{16}N_2$	1-(2-pyridyl)-1-[5-(2-ethyl)pyridyl]ethane **5**
212	$C_{14}H_{16}N_2$	1-(2-pyridyl)-1-[6-(2-ethyl)pyridyl]ethane **6**
212	$C_{14}H_{16}N_2$	1-(2-pyridyl)-1-[4-(2-ethyl)pyridyl]ethane **7**
212	$C_{14}H_{16}N_2$	1-(2-pyridyl)-1-[3-(2-ethyl)pyridyl]ethane **8**
372	$C_{14}H_{16}N_2Se_2$	Indefinite structure **9**
372	$C_{14}H_{16}N_2Se_2$	Indefinite structure **10**

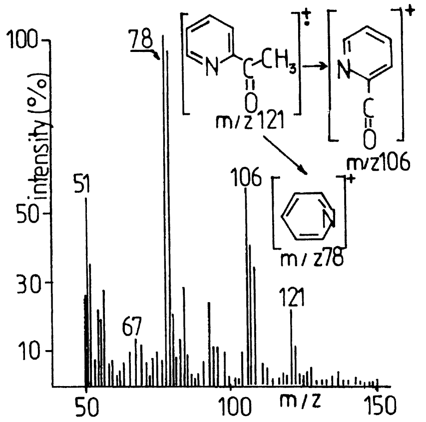


FIGURE 3 The mass spectrum together with fragmentation pathways of peak 1.

Mass spectrum of the peak 2 in the chromatogram (Figure 4) is characterized by higher intensities of the ions at m/z 211 (M—H), 197 (M—CH_3) and 134 (M—Py) than that of the molecular ion at m/z 212. This suggests the presence of at least one tertiary carbon atom in the molecule adjacent to the pyridyl ring. Again, the fragment ion at m/z 181 reveals the presence of two methyl groups. On this basis, either structure C or E can be assigned to the compound. However, with structure E, fragment ions of M—C_2H_4 or C_2H_5 should be expected and these are missing. Thus structure C corresponding to 2,3-di(2-pyridyl)butane **2** seems to be the most probable one.

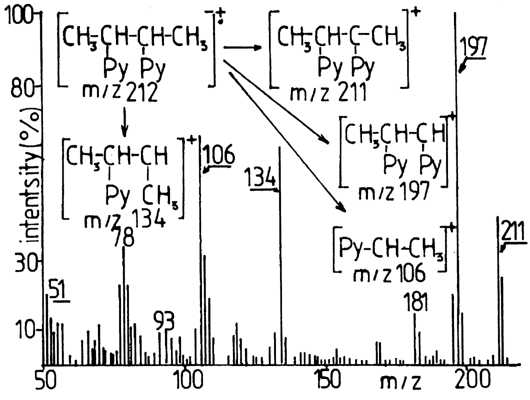


FIGURE 4 The mass spectrum together with fragmentation pathways of the peak 2.

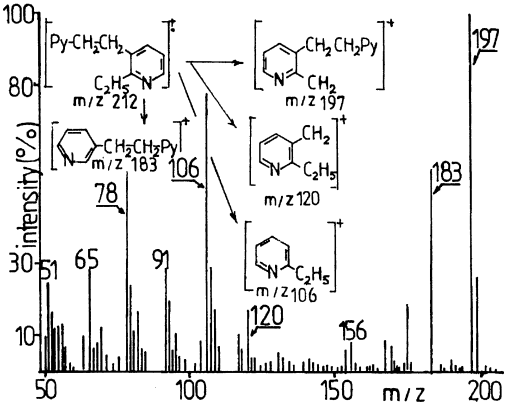


FIGURE 5 The mass spectrum together with fragmentation pathways of the peak 3.

The next two mass spectra (Figures 5 and 6) belong to products producing overlapping peaks 3 and 4 in the chromatogram. Both spectra are almost identical with missing molecular ions and those at m/z 211 (M—H), with intense peaks at m/z 197, 183, and 106. The lack of the M—H ion suggests the lack of a tertiary carbon atom, and this in turn leads to conclusion that the chromatographic peaks are due to isomer D. The fragment ion at m/z 197 is due to the preferred at β position to the ring splitting of the alkyl substituent (M—CH_3), whereas ions at m/z 183 and 106 emerge as a consequence of splitting the bond linking the substituent with the ring. It can thus be concluded that the compounds

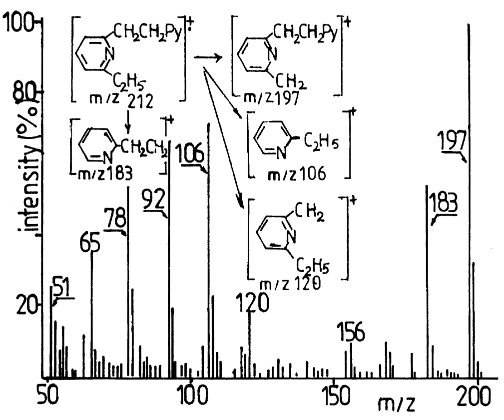


FIGURE 6 The mass spectrum together with fragmentation pathways of the peak 4.

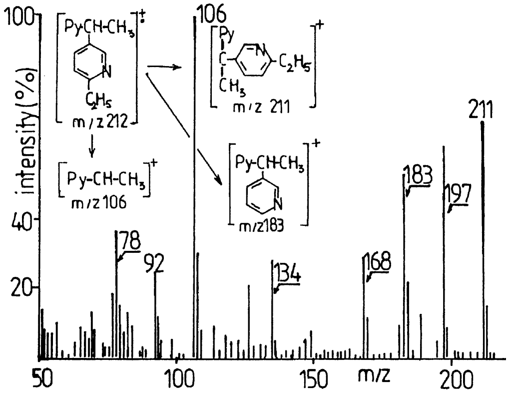


FIGURE 7 The mass spectrum together with fragmentation pathways of the peak 5.

differ in the substitution positions of hydrogen in the pyridine ring and can be identified as 1-(2-pyridyl)-2-[x-(2-ethyl)pyridyl]ethanes. Bearing in mind the ring reactivity in radical alkylations[7] of alkylpyridines, the preferred substitution sites in the ring are 6 and 3. Unfortunately, the mass spectra do not allow to assign peaks 3 and 4 in the chromatogram to either of the isomers.

A small peak 5 in the chromatogram is also due to a condensation product of two 2-ethylpyridine molecules. Its mass spectrum (Figure 7) resembles those of compounds **3** and **4** and differs only in the presence of the fragment ion at m/z 211 (M—H).

The lack of the molecular ion together with the presence of the [M—H] ion suggests that there is a tertiary carbon atom in the molecule. On the other hand, fragment ions at m/z 197 and 183 reveal the presence of the methyl and ethyl groups. Based on these findings, peak 5 in the chromatogram can be assigned structure E. Beforehand it was found that the mass spectra of the product giving much more intense peaks 6, 7, and 8 in the chromatogram were almost identical and structure E had been assigned to them as well. However, as peak 5 is the least intense among them, it should be assigned to a substitution product of the hydrogen atom at the least reactive site of the pyridine ring,[7] i.e., at position 5.Consequently, the compound is 1-(2-pyridyl)-1-[5 -(2-ethyl)pyridyl] ethane **5**.

The unusually intense peak 6 in the chromatogram is due the main reaction product. Its mass spectrum (the left-hand slope of the peak in Figure 8) together with the fragmentation pathways is identical with the mass spectrum of compound **5**. On the basis of a relationship between reactivity of the pyridine ring[7] and the content of the compound

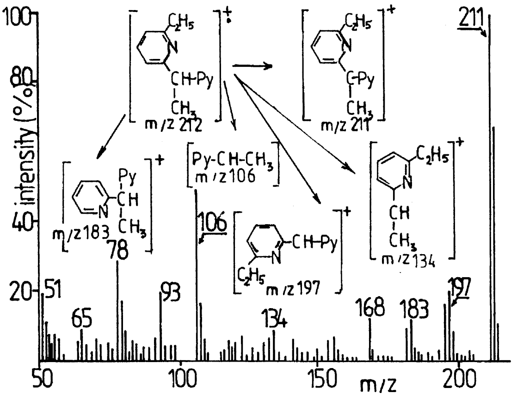


FIGURE 8 The mass spectrum together with fragmentation pathways of the peak 6.

in the reaction mixture, it can be identified as 1-(2-pyridyl)-1-[6-(2-ethyl)pyridyl]ethane **6**.

Another peak in the chromatogram (7) is also due to the alkylation product of the pyridine ring having structure E. Its mass spectrum together with fragmentation pathways is shown in Figure 9. Bearing in mind intensity of the peak relative to those of 5, 7, 8, and 6, the compound was identified as 1-(2-pyridyl)-1-[4-(2-ethyl)pyridyl] ethane **7**.

The mass spectrum of the compound producing an intense peak 8 together with its fragmentation pathways is shown in Figure 10. Its characteristic features are the molecular peak at m/z 212, intense

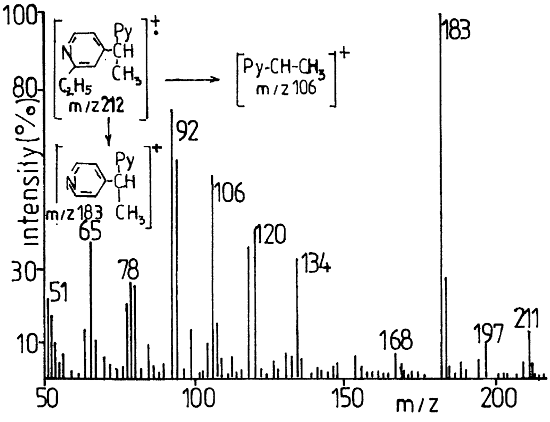


FIGURE 9 The mass spectrum together with fragmentation pathways of the peak 7.

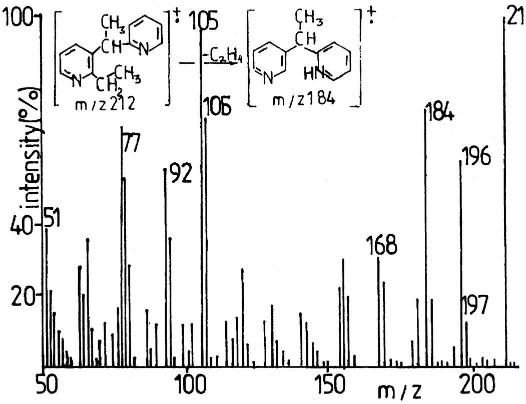


FIGURE 10 The mass spectrum together with fragmentation pathways of the peak 8.

fragment ions at m/z 196 (M—H—CH_3), 184 (M—C_2H_4), 169, and 105. The peak at m/z 184 reveals an ethyl substituent in the pyridine ring, thus suggesting either structure D arising by alkylation of the ring by the C_β atom of another 2-ethylpyridine molecule or structure E arising by alkylation with the C_α atom of the molecule. The fragment ion at m/z 169 formed as a result of secondary fragmentation of the radical ion with m/z 184 (M—C_2H_4—CH_3) reveals the presence of another methyl group in the molecule.

Consequently, the compound has structure E similar to the previously discussed compounds **5**, **6**, and **7**. Elimination of the neutral C_2H_4 molecule is indicative of the ease of transfer of the hydrogen atom from the leaving group into the nitrogen atom of another pyridine ring. Owing to steric reasons, the process is most probable in a molecule with substituents at positions 2 and 3 of the ring. Accordingly, the compound can be identified as 1-(2-pyridyl)-1-[3-(2-ethyl)pyridyl]ethane **8**. A further proof in favor of this conclusion is provided by comparison of the area of peak 8 with those of 5, 6, and 7 of structure E. The same conclusion can be drawn bearing in mind reactivities of particular position of the pyridine ring.[7]

In order to find products occurring at lower concentrations in the reaction mixture, additional GC-MS analyses were accomplished by increasing the injection volume from 0.2 to 1 μL. In this way compounds **9** and **10** with molecular masses 372 could be detected. Their spectra are presented in Figures 11 and 12.

Over the range of the mass of the molecular ion two sets of peaks occur which differ by two m/z units of isotopic ions. This indicates the

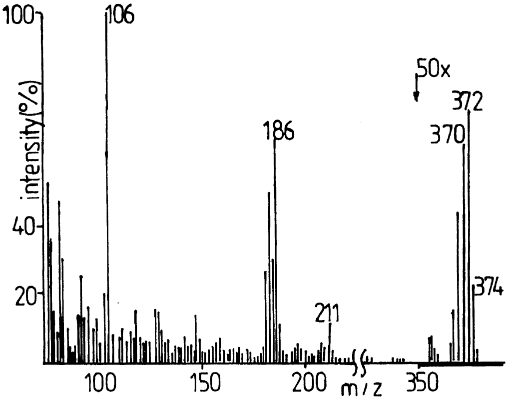


FIGURE 11 The spectrum of compound **9**.

presence of selenium atoms in their molecules whose ^{78}Se and ^{80}Se isotopes are responsible for this spectral pattern. Molecular mass of 372 corresponds to molecular formula $C_{14}H_{16}N_2Se_2$which might be formed by insertion of two selenium atoms into a molecule of the aforementioned compounds of molecular masses 212.

In the spectrum of compound **9** (Figure 11) emerge ions at m/z 211 (M—HSe_2) and 106 (PyC_2H_4) as well as a group of ions at m/z 186. However, solely on this basis the structure of organoselenium compound **9** and **10** cannot unambiguously be established. In the latter case, the mass spectrum (Figure 12) with missing fragment ions characteristic of the condensation products of two molecules of 2-ethylpyridine (m/z 211, 197, 134, 120) suggest only that compound **10** may be diselenide,

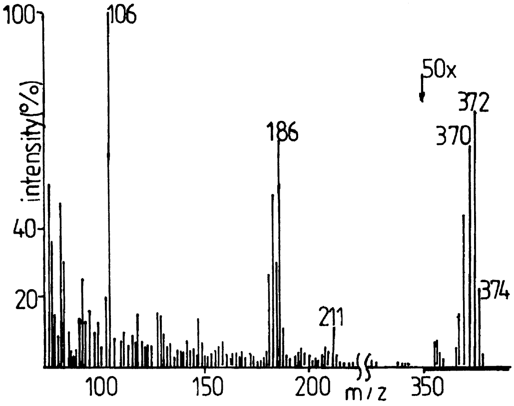
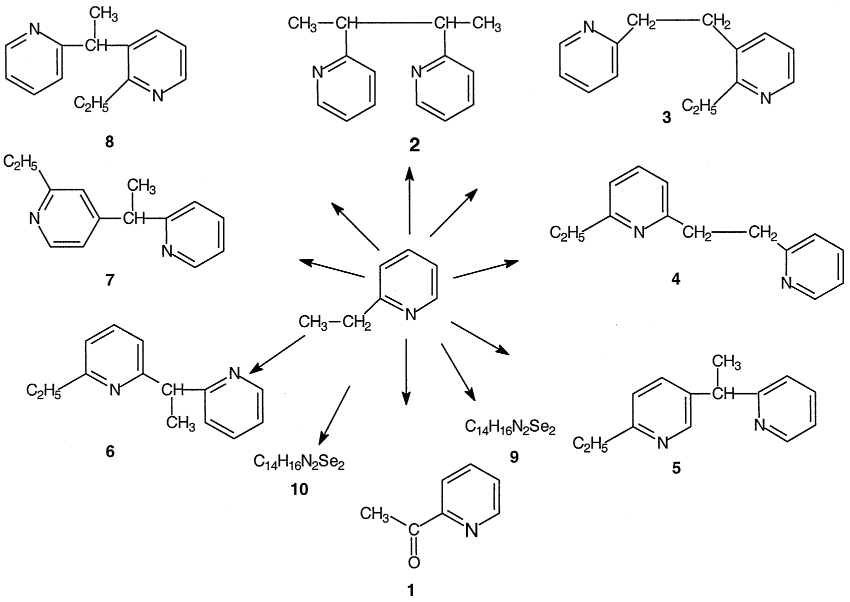


FIGURE 12 The spectrum of compound **10**.

$\mathrm{PyCH_2CH_2SeSeCH_2CH_2Py}$. All identified products are shown in Table II and Scheme 1.



SCHEME 1

CONCLUSION

The reaction of elemental selenium with 2-ethylpyridine, carried out under oxygen-free conditions at about 200°C affords a variety of compounds among which condensation products of two molecules of pyridine were identified. They may have resulted from a reaction wherein either the ethyl substituent of the amine or a hydrogen atom of the pyridine ring had been involved. It is concluded that the reaction of 2-ethyl with selenium requires more drastic conditions (elevated temperature) than analogous one with sulfur. Among the reaction products, two Se-containing compounds were also detected. Apart from the identified reaction products, also compounds of higher molecular masses were formed which could not be identified by GC-MS due to their low volatility under gas chromatography conditions.

EXPERIMENTAL

Sample Preparation

In 5-mL ampoules, 0.05 g of the grey modification of selenium was placed followed by 2 mL of 2-ethylpyridine and, optionally, 2 mg of KOH. After a three-minute flushing of the ampoule with nitrogen, it was sealed and maintained at ca 200°C during 50 h. After this time, the contents of the ampoule was cooled, the unreacted selenium was filtered off and washed successively with chloroform, toluene, and methanol. The combined filtrates were then evaporated under vacuum at temperatures at up to 80°C to leave a brown oil of unpleasant smell.

Thin-Layer Chromatography (TLC)

The chromatograms were developed on DC Plastikfolien coated with silica gel (Kieselgel 60F254, Merck) in the following solvent systems of variable composition: methyl acetate-methanol, chloroform-methanol and toluene-methanol. The chromatograms were observed in the LW light, and spots were localized by spraying with iodine vapors.

Mass Spectrometry

The mass spectra were recordered using a FAB technique on an 8-ky Varian Matt 711 spectrometer. The GC-MS analyses were run on a Micromass 16F (VG Micromass, Ltd.) mass spectrometer coupled with a Pye Unicarn Model 104 gas chromatograph and a PDP 8A computer. A 20-m long RTX-1 capillary column was used.

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