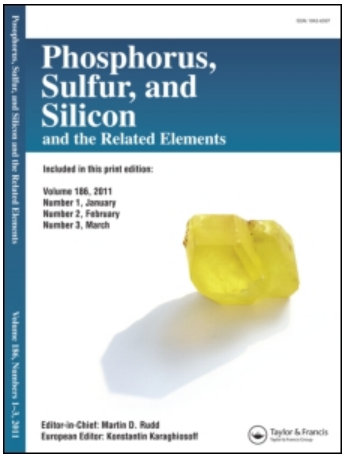

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ELEMENTAL SELENIUM REACTIONS WITH 4-PICOLINE

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A study of the reaction of the elemental selenium with 4-picoline is reported. The process was carried out at the boiling point of the 4-picoline under argon. After removing unreacted solids, the reactions products were identified by means of GC and GC-MS. The following products have been identified: 1,2-di(4-pyridyl)-ethane, 1,2-(4-pyridyl)-ethene, 4-methyl-2-(4-pyridyl)methylpyridine, 4-[2-(4-methyl)-pyridyl)]-2-(4-pyridyl)methylpyridine, 1-[2-(4-methyl)pyridyl]-1,2-di(4-pyridyl)-ethane, 1-[3-(4-methyl)-pyridyl]-1,2-di(4-pyridyl)-ethane, 1-hydroseleno-1,2-di(4-pyridyl)-ethane and 1-hydroperseleno-1,2-di-(4-pyridyl)-ethane.

Key words: Selenium; 4-picoline; mass spectrometry-gas chromatography.

INTRODUCTION

In the late 20's one of the methods leading to elucidation of the structure of complex naturally-occurring compounds was dehydrogenation. Elemental sulfur was frequently used for this purpose. In many reactions, however, sulfur turned out to be too reactive affording complex mixtures of products. In such cases the method proved useless. This prompted Diels and co-workers to replace sulfur by selenium in these reactions. Encouraging results were obtained with cholesterol.[1] With sulfur, cholesterol gave a complex, partially charred mixture of compounds. Diel's dehydrogenations of other organic compounds[2] with selenium gave less complicated mixtures and the yields of the main products were improved. Studies on the use of selenium in dehydrogenation reactions and on elucidation of their mechanisms have also been carried out by other authors.[3,4]

Another use of elemental selenium was as catalyst for isomerization of oleinic acid into its trans modification, elaidic acid. This reaction was first described by Bertram[5] and studied in more detail by Fitzpatrick and Orchin[6] who demonstrated that selenium formed a π-complex with oleinic acid.

Our previous article[7] dealt with products of the reaction of elemental sulfur with 4-picoline. The literature survey shows that there are differences in the reactivity of sulfur and selenium with organic compounds. The purpose of this work was to detect these differences in the reaction with 4-picoline.

RESULTS

First of all, the excess of reactants was removed from the mixture of products left after the reaction of 4-picoline with selenium. Molecular weights of the products

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were measured by taking their field-desorption (FD) and electron-impact (EI) mass spectra. The high-resolution measurement of the m/z ratios allowed the molecular formulas to be established. The mixture of products was also analyzed by gas chromatography coupled with mass spectrometry (GC-MS). A gas chromatogram is shown in Figure 1 and the results of analyses are summarized in Table I.

The mass spectra together with fragmentation pathways are presented in successive Figures and the structures of compounds and a reaction scheme in Scheme 1.

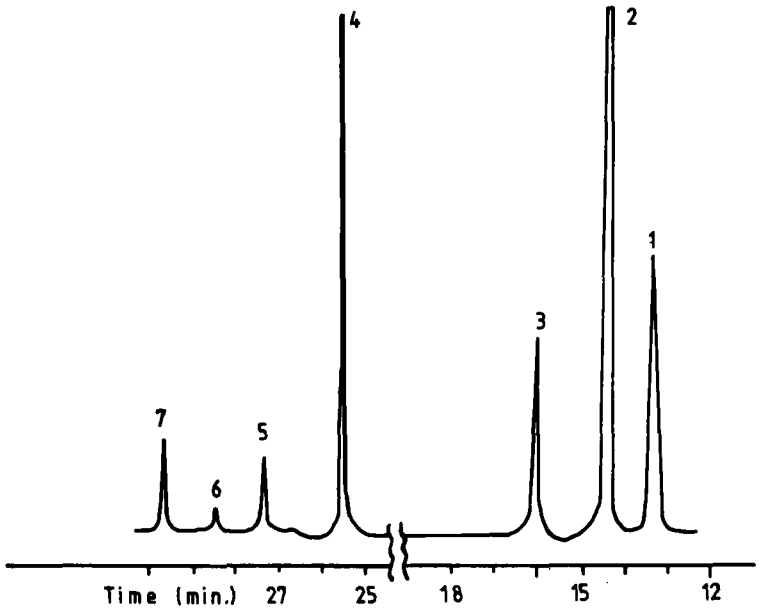


FIGURE 1 GC analysis of products of the reaction of 4-picoline with selenium. Capillary column Dexsil 300, initial temp. 85°C, 4°/min.

TABLE I

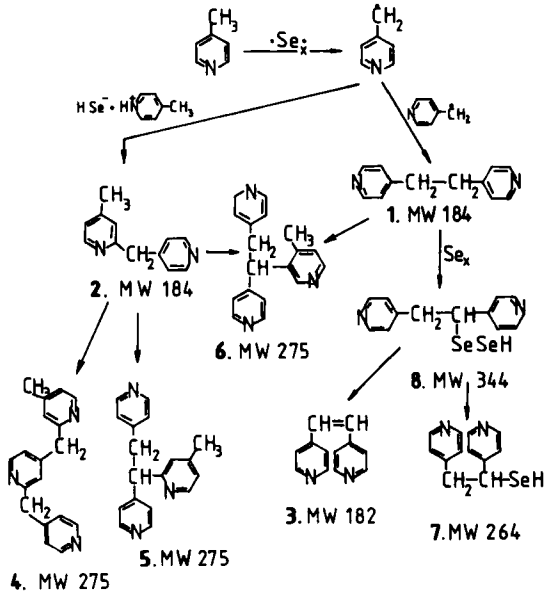
High-resolution mass spectra of products of the reaction of selenium with 4-picoline (48 hours, refluction at the boiling point)

Precise mass (measured)	Elemental composition	Compound
182.0852	$C_{12}H_{10}N_2$	1,2-di(4-pyridyl)-ethene, **3***
184.1001	$C_{12}H_{12}N_2$	1,2-di(4-pyridyl)-ethane, **1**
		4-methyl-2-(4-pyridyl)methylpyridine, **2**
275.1421	$C_{18}H_{17}N_3$	4-[2-(4-methylpyridyl)]-2-(4-pyridyl)methylpyridine, **4**
		1-[2-(4-methyl)pyridyl]-1,2-di(4-pyridyl)-ethane, **5**
		1-[3-(4-methyl)pyridyl]-1,2-di(4-pyridyl)-ethane, **6**
264.0159	$C_{12}H_{12}N_2Se$	1-hydroseleno-1,2-di(4-pyridyl)-ethane, **7**
343.9321	$C_{12}H_{12}N_2Se_2$	1-hydroperseleno-1,2-di(4-pyridyl)-ethane, **8**

*The numbering of the compounds in Table I and in figures is consistent with the numbering defined in the Scheme 1.

DISCUSSION

Figure 1 shows a gas chromatogram of the reaction products. The spectra of compounds appearing as peaks 1 and 2 in the chromatogram are presented in Figures 2 and 3. In both cases the molecular ion appears at m/z 184 (accurate mass 184.1001) corresponding to molecular formula $C_{12}H_{12}N_2$ of a condensation product of two 4-picoline molecules. This process may afford 1,2-dipyridylethane and two products of hydrogen substitution in the pyridine ring. The mass spectrum in Figure 2 is



Scheme 1. Reaction of 4-picoline with elemental selenium.

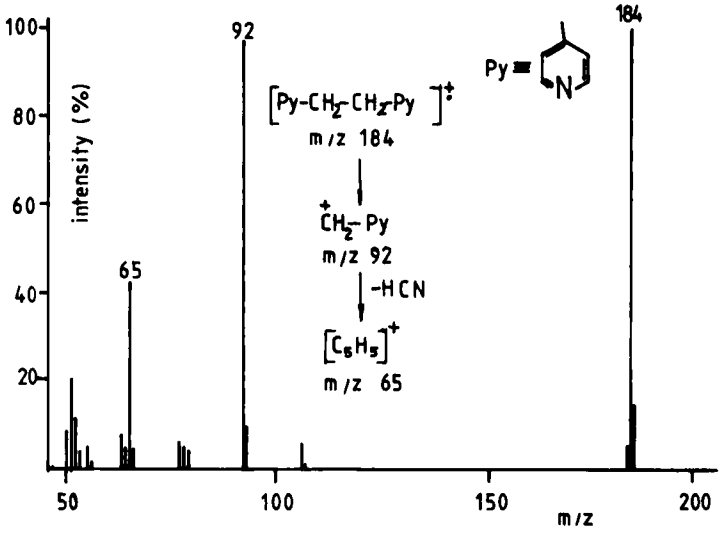


FIGURE 2 Mass spectrum and fragmentation pathways of compound 1.

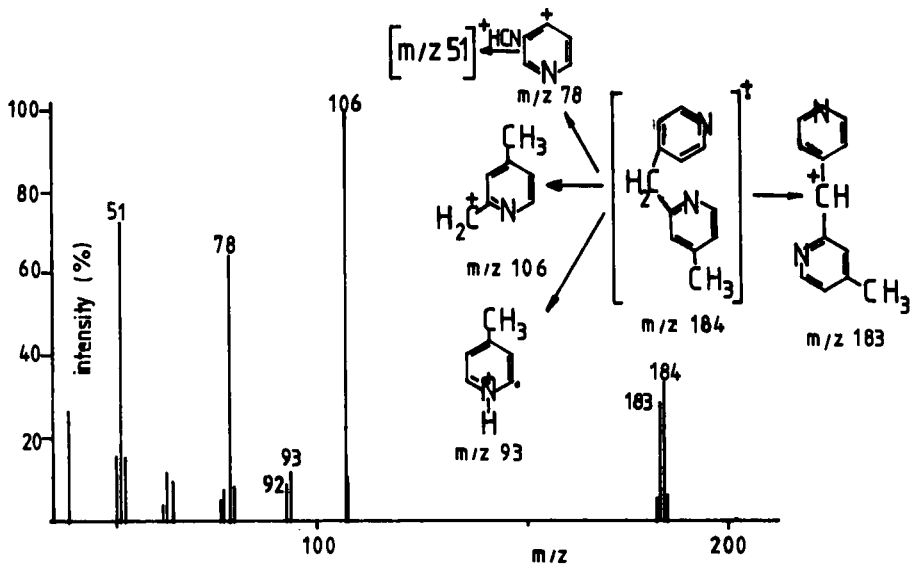


FIGURE 3 Mass spectrum and fragmentation pathways of compound **2**.

identical with that of 1,2-di(4-pyridyl)-ethane.[7,8] Consequently, the compound is formed in the reaction of 4-picoline with both sulfur[7] and selenium.

Inspection of the mass spectrum (Figure 3) supports the finding that the reaction of 4-picoline with selenium gives alkylation products of the ring which were not detected in analogous reaction with sulfur.There is a very intense peak at m/z 106 (M-78) in this spectrum, which is very weak in the spectrum of dipyridylethane **1**. It is worth noting that this ion appears also in the fragmentation pattern of ethylmethylpyridines (M-15)[8] and of methylpropylpyridine (M-29).[17] It was also detected in the mass spectrum of analogous product **2** resulting from the reaction of 2-picoline with sulfur.[9] Bearing in mind the reactants employed, the molecular mass of the product and two strong peaks at m/z 106 (M-78) and 183 (M-1) in the mass spectrum, peak 2 (Figure 1) can be assigned to 4-methyl-2-(4-pyridyl)methylpyridine **2**. Taking into account its chemical structure one should expect occurrence in the mass spectrum fragmentation ion at m/z 169 (M-15). Such ion is present in the spectrum of the above mentioned product which is forming in the reaction of the 2-picoline with sulfur.[9] Its appearance would unambiguously confirm the suggested structure. This notwithstanding, its absence does not necessarily eliminate the structure, as the fragmentation pathways of the reactants themselves, i.e., 2-picoline and 4-picoline, are different. The intensity of the (M-15) peak of the former (18%) is much larger than that of the latter (3%).[8,10]

As mentioned above, the substitution of a hydrogen atom in the ring of 4-picoline may afford two products with molecular weights of 184. However, a comparison of the 2-H and 3-H during homolytic methylation of the ring[11] shows that position 2 is much more prone to the attack of a radical.

Peak 3 in the chromatogram corresponds to a compound with molecular mass 182.0838 ($C_{12}H_{10}N_2$). Its mass spectrum (Figure 4) is identical with that of 1,2-di(4-

pyridyl)-ethene.[7,8] Consequently, **3** is formed by dehydrogenation of 1,2-di(4-pyridyl)-ethane.

Peak 4 in the chromatogram corresponds to a compound with molecular mass 275.1421 ($C_{18}H_{17}N_3$). This molecular formula fits to a range of structures presented in Figure 5. Product A can result from the reaction of 4-picoline with **1**, whereas products B and C can be derived both from reactions with dipyridylethane and its isomers, products of substitution of hydrogen in the pyridine ring, for instance **2**. These compounds are also the sole starting reagents in the synthesis of products D and E.

1,2,3-tri(4-pyridyl)-propane (A) was obtained in the reaction of 4-picoline with elemental sulfur.[7] A comparison of its mass spectrum[7] with the mass spectrum of products of the reaction with selenium (Figure 6) shows that it is not formed in this reaction. This is indicated by missing peak at m/z 183, and low intensities of

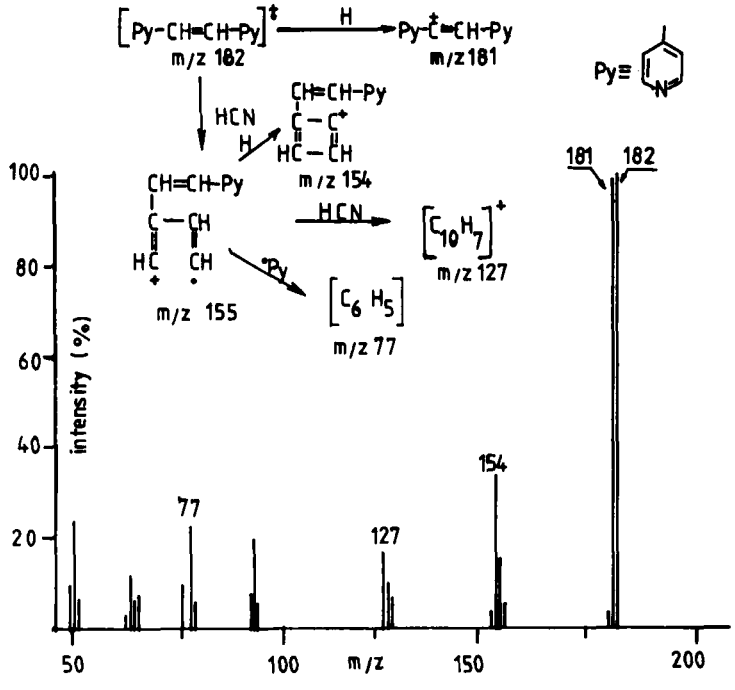


FIGURE 4 Mass spectrum and fragmentation pathways of compound **3**.

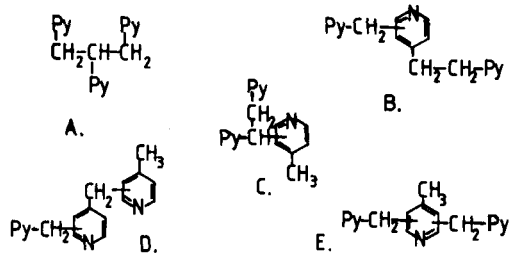


FIGURE 5 The possible structures of compounds of molecular formula $C_{18}H_{17}N_3$ (MW 275).

peaks of the molecular ion (m/z 275; 5%) and the fragment ion (m/z 197; 10%). Respective intensities in the spectrum of tripyridylpropane were 16 and 85%.[7] The analyzed spectrum exhibits three very strong peaks of the fragment ions at m/z 182, 181 and 106. Of structures B, C, D and E in Figure 5, only compound D can be assigned to the peak at m/z 106(M-169). However, the structure of compound D rules out the possibility of formation of an ion with m/z 182. This leads to conclusion that peak 4 in the gas chromatogram can be assigned to a mixture of products of molecular weight 275. The formation of this ion (m/z 182) must be realized by elimination of the picoline molecule with concurrent hydrogen transfer. This finding eliminates structures E and B.

At this point it is worthwhile to discuss the structure of a compound producing the small peak 6 in the chromatogram. Its mass spectrum is shown in Figure 7. Similarly as with compounds producing peak 4 in the chromatogram, its molecular ion appears at m/z 275. There are also peaks at m/z 182 and 181, whereas no peak appears at m/z 106. This suggests that peak 4 can be assigned to one of the isomers of C. Inspection of the sensitivity of 2-H and 3-H in the pyridine ring[11] to methylation in radical reactions leads to the conclusion that the small peak 6 can be due to 1-[3-(4-methyl)pyridyl]-1,2-di(4-pyridyl)-ethane **6**, whereas peak 4 to products **4** and **5**.

The mass spectrum and fragmentation pathways of a product corresponding to peak 5 in the chromatogram are shown in Figure 8. The peak of molecular ion appears at m/z 264. Its accurate mass is 264.0159 ($C_{12}H_{12}H_2Se$). The presence of selenium in the molecule is confirmed by isotopic ion M-2 whose intensity is about one half that of the molecular peak. Natural abundance of ^{78}Se and ^{80}Se are about 23% and 50% respectively. The mass spectrum resembles that of product **1** (Figure 2). The differences are: molecular peak at m/z 264, 70% of intensity of the m/z 183 ion (M-SeH) as well as the occurrence of peaks at m/z 172 (M-$PyCH_2$) and 157 (M-Se-HCN). The presence of the fragment ions at m/z 183 and 184, i.e., fragmentation with concurrent elimination of either the Se atom or the ·SeH radical shows that the compound is a hydrogen selenide **7** rather than selenide.

Also the next product (peak 7 in the chromatogram) whose mass spectrum and

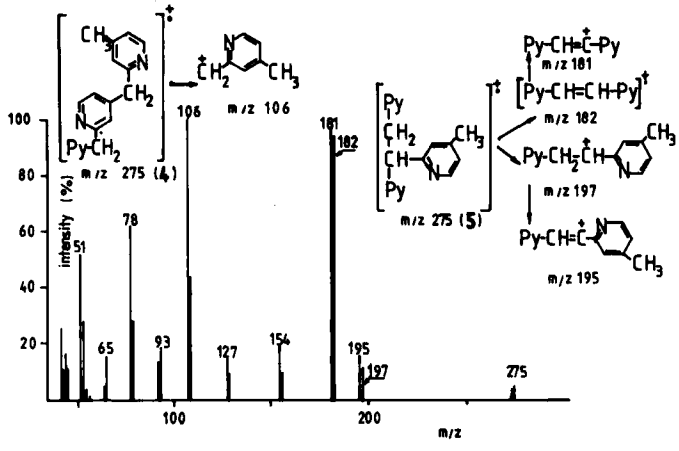


FIGURE 6 Mass spectrum and fragmentation pathways of the mixture of compounds **4** and **5**.

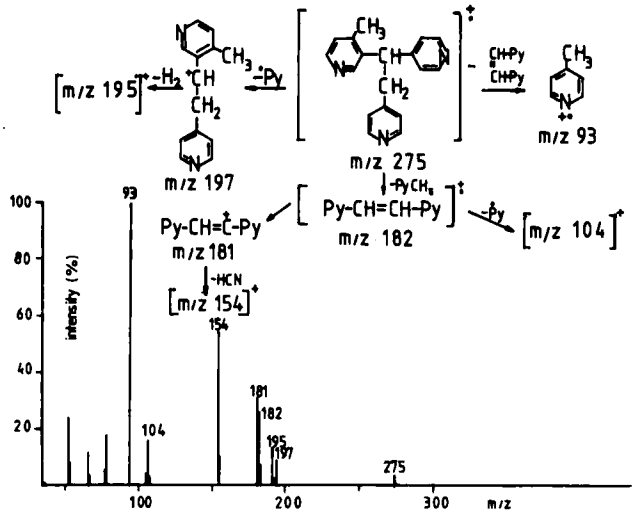


FIGURE 7 Mass spectrum and fragmentation pathways of compound **6**.

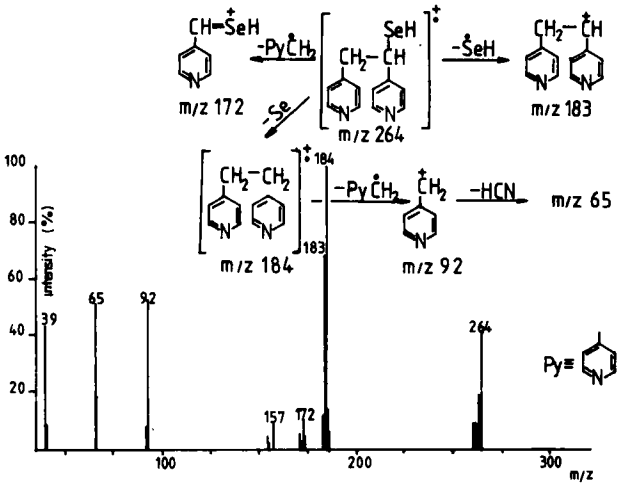


FIGURE 8 Mass spectrum and fragmentation pathways of compound **7**.

fragmentation pathways are shown in Figure 9, is an organoselenium compound. Its accurate molecular mass is 343.9321 corresponding to the formula $C_{12}H_{12}N_2Se$. A compound of such composition might be formed either by attaching two selenium atoms to products **1** or **2**, or by recombination of two $PyCH_2Se\cdot$ radicals. Similar to **7**, the product undergoes fragmentation to produce ion with m/z 184 ($M\text{-}Se_2$). The peak at m/z 106 is missing. This indicated that **8** is formed following incorporation of Se_2 into the molecule of 1,2-di(4-pyridyl)-ethane.

The presence of compounds **7** and **8** among the reaction products supports the hypothesis of Fitzpatrick and Orchin[6] that during the reaction of selenium with compounds containing allylic or benzylic hydrogen atoms, a stable "sigma complex" is formed of tentative hydroperselenide structure. The authors stated that the reaction resembles that of autooxidation of organic compounds. The same mech-

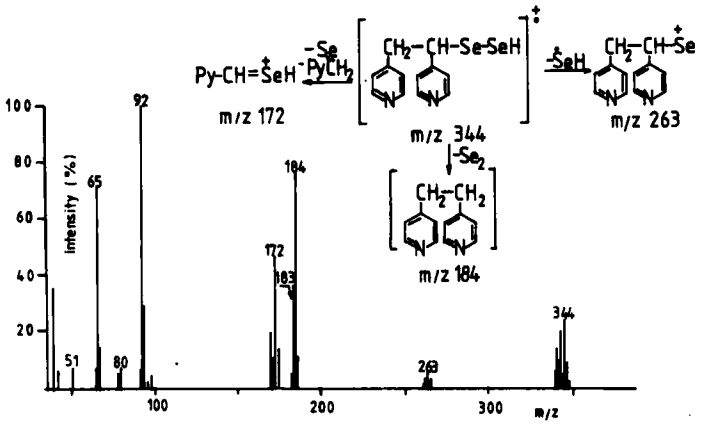


FIGURE 9 Mass spectrum and fragmentation pathways of compound **8**.

anism of the reaction of selenium with hydrocarbons during dehydrogenation has been accepted by House and Orchin.[3] They confirm the formation of hydroperselenide as an intermediate during dehydrogenation of a natural alcohol-guaiol and of related compounds. At elevated temperature the intermediate decomposed to give guaiazulene. The reaction was accompanied by evolution of hydrogen selenide. According to these authors, the kinetics of evolution of that gas supports the formation of the intermediate during dehydrogenation. In all reactions studied by them, the rate of evolution of hydrogen selenide initially increased, attained a maximum, and then fell off. If the hydrogen selenide were formed in direct reaction of selenium with the hydrocarbon, the maximum would have occurred at the start of the reaction.

In another article dealing with the use of selenium to dehydrogenation of organic compounds, Silverwood and Orchin[4] investigated, amongst others, 1,2,3,4,-tetrahydroquinoline. The results showed that the dehydrogenation of the base occurred at lower temperature than that of 3,4-dihydro-1,5,8-trimethylnaphthalene. Similar observations refer to the reaction of picolines with sulfur[7,9] and of 4-picoline with selenium. All reactions were conducted at the boiling points of the picolines i.e., at about 140°C, whereas the reaction with toluene[13] required about 300°C. Pryor[14] has found that both the nucleophilic and electrophilic reagents, as well as radicals, facilitate the breakdown of S_8 rings. The chain structures formed dissociate into radicals much more readily. The finding that the reaction of selenium with 4-picoline proceeds at relatively low temperature reveals that the amine acts as an activator of this element.

The reaction is obviously of a consecutive-parallel radical type. Its course is outlined in Scheme 1. The main products are compounds **2**, **4** and **5**, which were not found among the reaction products of 4-picoline with sulfur.[7]

The difference in the course of the reactions with selenium and sulfur can be attributed to strong protonation of the amine by formed hydrogen selenide. The effect of protonation on the direction of radical reactions involving pyridine derivatives, was noted earlier. Nababsing and Bass[11] have found that benzyl radicals failed to react with pyridine in the absence of acid. Also dibenzylmercury and picolines failed to afford ring-substituted products in the absence of acid. Under

these conditions, toluene, dibenzyl and the corresponding phenethylpyridines were formed. Another example is the reaction of toluene and isomeric xylenes with 2-vinylpyridine.[15] No ring substituted compounds were found among the products of thermally induced (250–350°C) reactions involving these reactants.

Quite another course took the reactions in acid medium. Reactions of picolines with dibenzylmercury in the presence of acetic acid[11] gave appropriate ring-substituted products. With 4-picoline, 2-benzyl-4-methylpyridine was obtained in 34.8% yield. Consequently, protonation of the nitrogen atom enhanced markedly the reactivity of the ring in reactions of homolytic substitution. A comparison of the acidity constants of hydrogen selenide (pK_1 3.48) and hydrogen sulfide (pK_1 6.61)[16] explains the presence of compounds **2**, **4** and **5** in the reaction products with selenium on one hand, and their absence in the reaction products with sulfur, on the other.

EXPERIMENTAL

The reaction of selenium with 4-picoline. To 7.9 g of red selenium powder (0.1 mole), 20 ccm (0.2 mole) of 4-picoline was added and the mixture was maintained at reflux for 48 h under argon. It was then cooled, the excess of selenium (75% was recovered) was filtered off and the filtrate was evaporated to dryness at room temperature, under vacuum. A dense, dark brown oil was obtained which was further investigated.

Mass spectrometry. The mass spectra were taken on the mass spectrometer Varian MAT 711 furnished with the combined source EI, FI and FD. High-resolution spectra for R = 10 000 were recorded by means of the peak-matching or with the use of the computer Varian MAT SS-100 MS with PFK as an internal standard. GC-MS measurements were carried out with VG Micromass 7070 E mass spectrometer coupled with a Dani 3800 gas chromatograph. A fused silica capillary column with SE-30 liquid phase was used. The mass spectra were recorded at 70 eV.

Gas chromatography. Separation were carried out with Varian Aerograph model 1400 gas chromatograph adapted for work with capillary columns. The columns were coated with Dexsil 300 or SE 30 liquid phase. Helium was used as a carrier gas. The column was coupled with an inlet system with the splitting ratio equal to 1:30. The end of the column was joined to a detector in the make-up system, with an additional gas flow of 25 cm^3min^{-1}. The sensitivity employed equalled to 2×10^{-12} AmV^{-1}.

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