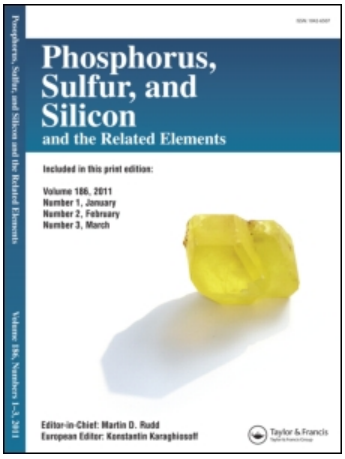

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Edward Gleich[a]; Zygmunt Warnke[a]; Walter Schwarting[b]
[a] Institute of Chemistry, University of Gdańsk, Gdańsk, Poland [b] Universität Oldenburg, Fachbereich Chemie, Oldenburg, BRD

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ELEMENTAL SULFUR REACTIONS WITH 3-PICOLINE

EDWARD GLEICH, ZYGMUNT WARNKE* and WALTER SCHWARTING[a]

Institute of Chemistry, University of Gdańsk, ul. Sobieskiego 18, 80-952 Gdańsk, Poland, [a]Universität Oldenburg, Fachbereich Chemie, D-2900 Oldenburg, BRD

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A study of the reaction of the elemental sulfur with 3-picoline is reported. The process was carried out at the boiling point of the 3-picoline under argon. After removing unreacted solids, the reaction products were identified by means of LC, GC and GC-MS. The following products have been identified: 1,2-di-(3-pyridyl)-ethane, Z-1,2-di(3-pyridyl)-ethene, E-1,2-di(pyridyl)-ethene, 6-(3-pyridyl)-thieno[2,3-b]pyridine, 4,5-di(3-pyridyl)-4H-cyclopenta[c]pyridine, 4,5-di(3-pyridyl)-6H-cyclopenta[c]pyridine, 6,7-di(3-pyridyl)-7H-cyclopenta[b]pyridine, 6,7-di(3-pyridyl)-5H-cyclopenta[b]pyridine, tetra(3-pyridyl)-cyclobutene, 6,7,8-tri(3-pyridyl)-thiepino[3,2-c]pyridine, 6,7,8-tri(3-pyridyl)-thiepino[2,3-b]pyridine and tetra(3-pyridyl)-thiophene.

Key words: sulfur; sulfuration; 3-picoline; mass spectrometry-gas chromatography.

INTRODUCTION

This study is a continuation of our investigations into the products of reactions of picolines with elemental sulfur and selenium. In the previous reports, products of the reaction of sulfur with 2-picoline[1] and 4-picoline[2] and of selenium with 4-picoline[3] were described. As far as we are aware, reactions of sulfur with 3-picoline have not been studied so far. In this connection, the purpose of this study was to conduct the reaction under the same conditions as those of 2-picoline and 4-picoline in order to find differences and similarities in the behavior of the picoline isomers in respect to sulfur. By using thin layer chromatography, gas chromatography and mass spectrometry, a variety of products were detected including those containing sulfur.

RESULTS

Fractions A and B, described in the experimental section, were analyzed by TLC, gas chromatography and mass spectrometry.

Fraction B is a mixture of products sparingly soluble in alkohols. Attempts to separate its constituents by TLC in various developing systems failed, as only one streak from the start to the front of the chromatograms was obtained. In the mass spectrum of this fraction, taken by the FD technique, components with MW lower

*Author to whom all correspondence should be sent.

than 900 a.u. were missing, this indicating that 3-picoline forms high molecular weight compounds in the reaction with sulfur.

Again, the constituents of fraction A were readily soluble in alkohols, chlorinated hydrocarbons and aromatic hydrocarbons. Chromatograms (TLC) of this mixture are quite similar to those of fraction B but distinct spots are discernible on the

TABLE I

Low- and high-resolution mass spectra of products of the reaction of sulfur with 3-picoline (48 hours, refluction at the boiling point)

Precise mass measured	Elemental composition	Compound
182.0851	$C_{12}H_{10}N_2$	Z-1,2-di(3-pyridyl)-ethene (**3**),* E-1,2-di(3-pyridyl)-ethene (**2**).
184.1005	$C_{12}H_{12}N_2$	1,2-di(3-pyridyl)-ethane (**1**).
212.0398	$C_{12}H_8N_2S$	6-(3-pyridyl)-thieno[2,3-b]pyridine (**4**).
271.1068	$C_{18}H_{13}N_3$	4,5-di(3-pyridyl)-4H-cyclopenta[c]pyridine (**5**), 4,5-di(3-pyridyl)-6H-cyclopenta[c]pyridine (**6**), 6,7-di(3-pyridyl)-7H-cyclopenta[b]pyridine (**7**), 6,7-di(3-pyridyl)-5H-cyclopenta[b]pyridine (**8**).
362.1491	$C_{24}H_{18}N_4$	tetra(3-pyridyl)-cyclobutene (**9**).
392.1110	$C_{24}H_{16}N_4S$	6,7,8-tri(3-pyridyl)-thiepino[3,2-c]pyridine (**10**), 6,7,8-tri(3-pyridyl)-thiepino[2,3-b]pyridine (**11**), tetra (3-pyridyl-)-thiophene (**12**).

*The numbering of the compounds in tables and in figures is consistent with the numbering in the reaction scheme, Scheme II.

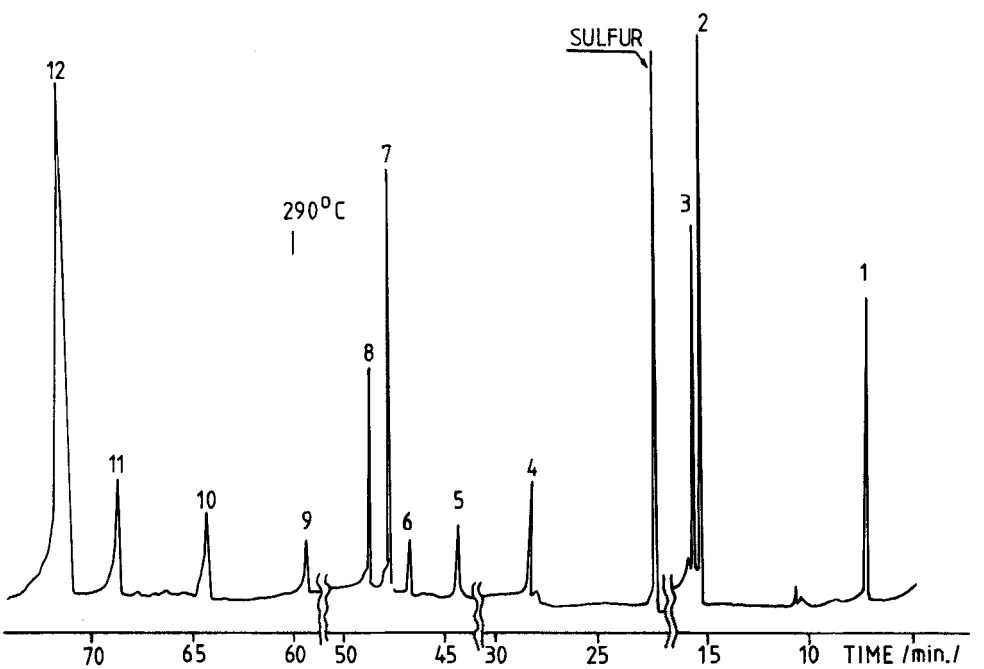


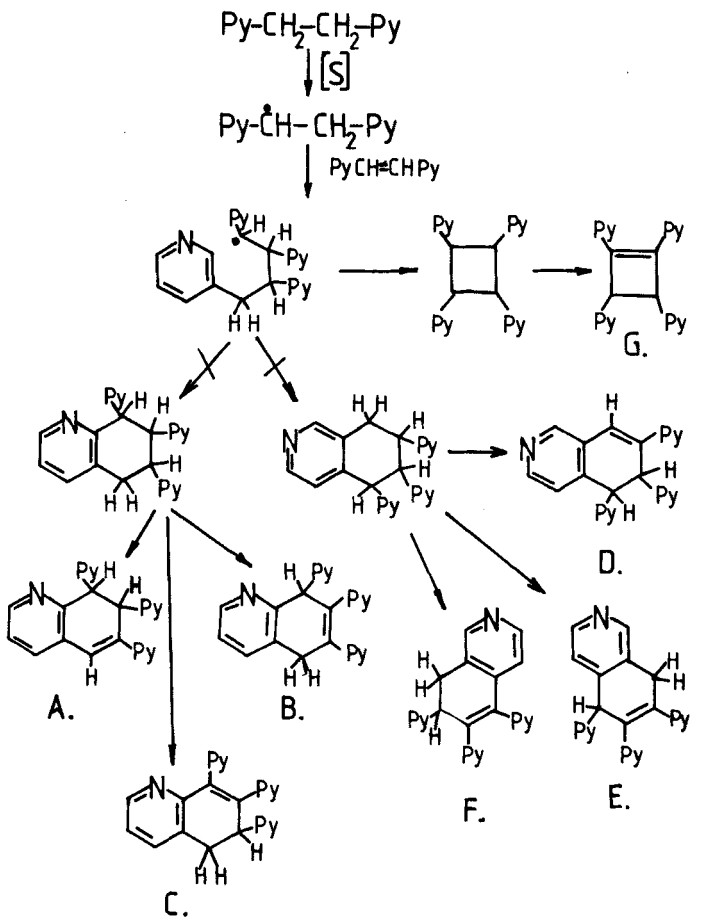
FIGURE 1 GC analysis of products of the reaction of 3-picoline with sulfur. Capillary column SE 52, initial temp. 50°C, 4°/min, 290°C-isotherm.

streak. It can thus be concluded that the fraction consist of low molecular weight compounds which produce the spots and the compounds with MW higher than 900 a.u.

Molecular weights of the compounds were determined by mass spectrometry using FD and EI techniques. High resolution measurements of the m/z ratios were done, as well, which enabled the molecular formulas to be established (Table I). Table I lists also names of the compounds identified by means of the mass spectra obtained by the GC-MS technique. A gas chromatogram of the volatile components of fraction A is shown in Figure 1 and their mass spectra and suggested fragmentation pathways are shown in successive Figures.

After completion of the reaction, 58% of sulfur was recovered, thus its consumption for the formation of organosulfur compounds and hydrogen sulfide was smaller than in reaction of 2-picoline (20% recovery of sulfur)[1] and 4-picoline[2] (25% recovery) conducted under the same conditions.

Products of the reactions of all isomeric picolines comprised dipyridylethane formed by recombination of the pyridylmethyl radicals, and its dehydrogenation

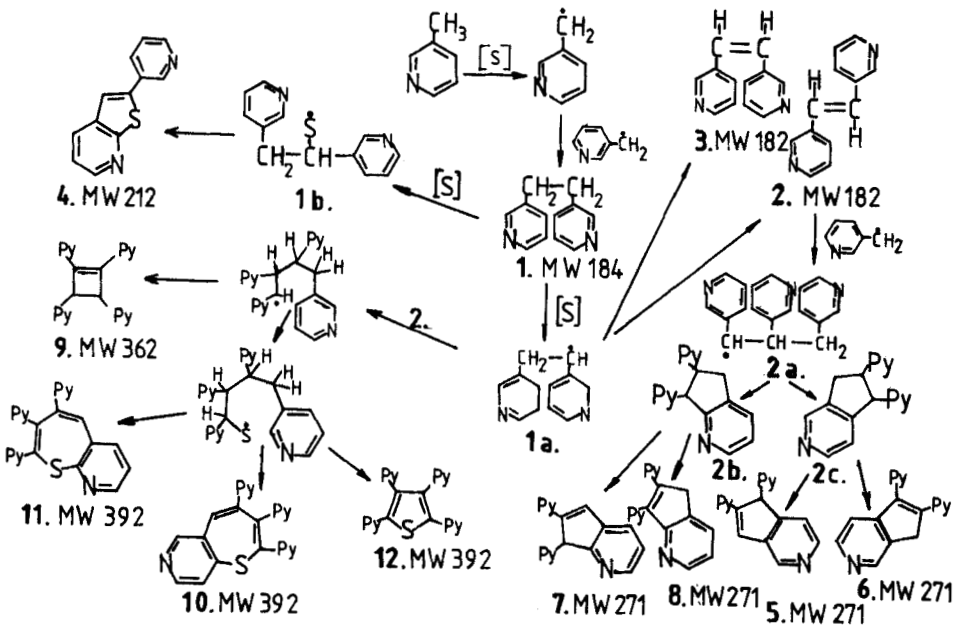


SCHEME I. The possible structures of compounds of molecular formula $C_{24}H_{18}N_4$ (MW 362).

product, dipyridylethene. Dipyridylethane isomers, arising from pyridylmethylation of the ring of another picoline molecule were detected exclusively among the products of the reaction of 2-picoline.[1] Apart from the ethane derivative, it afforded isomeric 2-methyl-x-[(2-pyridyl)-methyl]pyridines.

Reactivity of the pyridine ring of the reaction products of 3-picoline, in contrast to those of 4-picoline, increased in processes of homolytic substitution as shown by the presence of compounds **6**, **7**, **8** and **9**. These isomers of the general formula $C_{18}H_{13}N_3$ arise from intramolecular cyclization and dehydrogenation of the tripyridylpropyl radical (Scheme II). Analogous isomers were also formed in the reaction of 2-picoline, whereas with 4-picoline the cyclization did not take place and the process was terminated as soon as tripyridylpropane and tripyridylpropene were formed.

Thiols, sulfides and disulfides were missing among the reaction products of 3-picoline and 4-picoline. With 2-picoline, however, isomeric thiols of the formula $C_{12}H_{12}N_2S$, as well as a sulfide, $(C_{18}H_{11}N_3)_2S$, and disulfide, $(C_{18}H_{11}N_3)_2S_2$, derived from the products of the general formula $C_{18}H_{13}N_3$, were found. Again, 2-picoline failed to produce tetrapyridylthiophene, which was the ultimate product of the transformations of 3-picoline and 4-picoline. Together with this compound (**12**), its isomers **10** and **11** were formed during the transformations of 3-picoline. Their presence provides further evidence for higher reactivity of the transformation products of 3-picoline in processes of homolytic substitution in the pyridine ring as compared with the 4-picoline counterparts. The latter failed to afford such products with sulfur.



SCHEME II. Reaction of 3-picoline with elemental sulfur.

DISCUSSION

Chromatographic analysis of fraction A showed that the reaction of elemental sulfur with 3-picoline gave a variety of products. The structure of twelve of them was established from the mass spectra.

Peak 1 in the chromatogram (Figure 1) is due to a compound with MW of 184.1005 ($C_{12}H_{12}N_2$). It is condensation product of two 3-picoline molecules. The reaction under consideration can produce either 1,2 dipyridylethane or products of substitution of the hydrogen atom in one 3-picoline molecule by the pyridylmethyl radical of the other. The main peaks of the product (Figure 2) are those of the molecular ion (m/z 184) and a fragment ion (m/z 92). However, the two peaks do not allow to unequivocally establish the molecular structure. In the spectrum, an ion at m/z 106, characteristic of dialkylpyridines,[4] is missing. It appears in the spectra of 2-methyl-[(2-pyridyl) methyl]-pyridines.[1]

This allows to unequivocally assign peak 1 of the chromatogram to 1,2-(3-pyridyl)-ethane **1**. The relatively low intensity of this peak is due to high volatility of compound **1**. It was found that a large fraction of this compound distilled together with picoline during workup of the reaction mixture.

Peaks 2 and 3 in the chromatogram can be assigned to isomers with MW of 182.0851 ($C_{12}H_{10}N_2$). Bearing in mind that the starting reagent is 3-picoline, the formula fits to E and Z isomers of 1,2-di(3-pyridyl) ethene **2** and **3** respectively arising by dehydrogenation of **1**. Both the patterns and peak abundances of the fragment ions of the isomers are identical. One of the spectra, quite resembling that of 1,2-di(4-pyridyl)-ethene,[2] is shown in Figure 3.

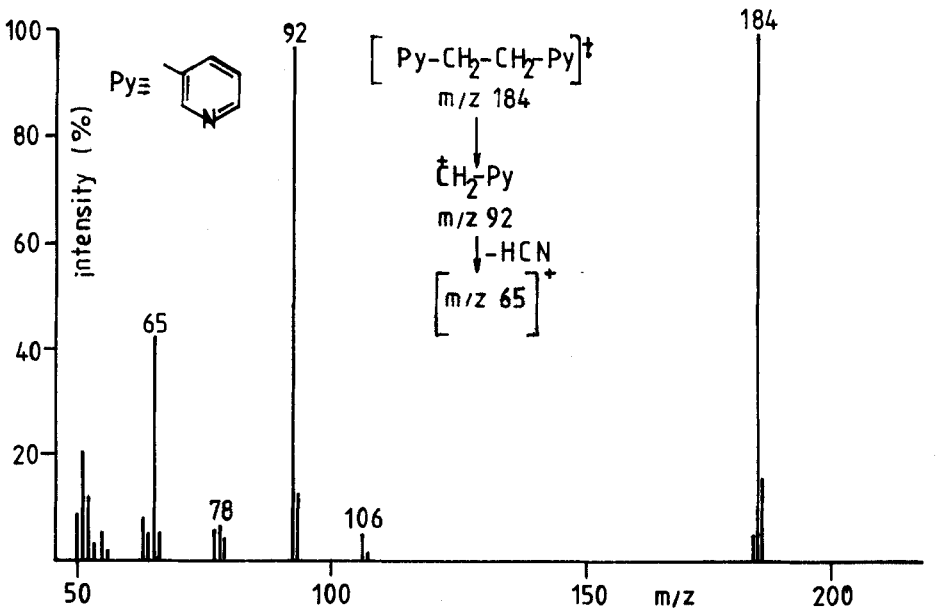


FIGURE 2 Mass spectrum and fragmentation pathways of compound **1**.

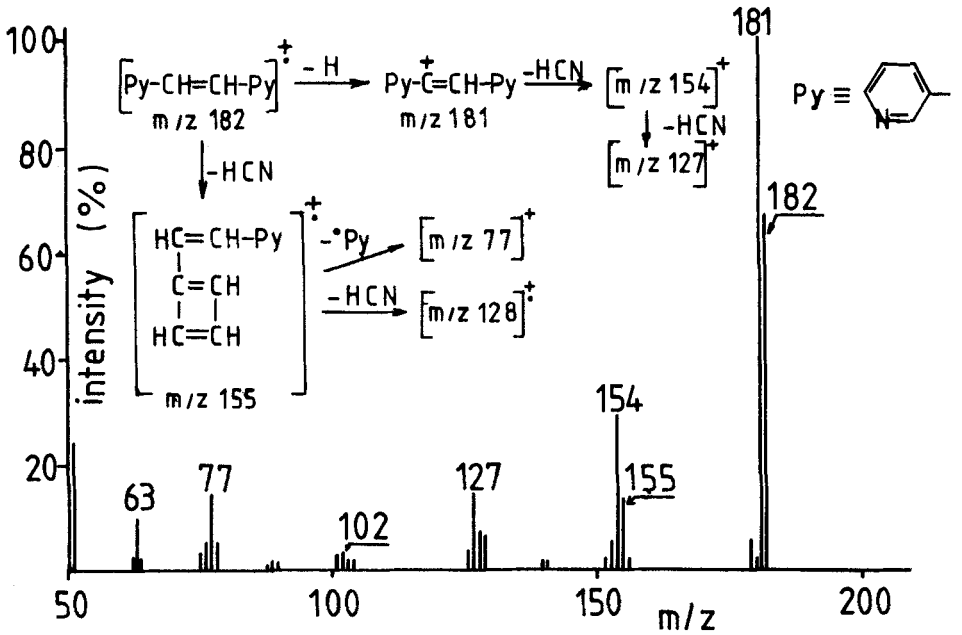


FIGURE 3 Mass spectrum and fragmentation pathways of compound **2**.

Both the mass spectrum and the fragmentation pathways of compound producing peak 4 in the chromatogram are shown in Figure 4. Its accurate MW is 212.0398 ($C_{12}H_8N_2S$) and indicates that it is formed by dehydrogenation of the condensation product of two picoline molecules with sulfur. The spectrum exhibits a fragmentation ion at m/z 122 (Py—C≡S) characteristic of α-substituted thiophenes.[5] Pyridyl is a substituent in this case. A thiophene derivative with MW of 212 may result from the reaction of dipyridylethane **1** with sulfur. Thioradical **1b** (Scheme II), formed during the first stage, undergoes cyclization followed by dehydrogenation to afford 6-(3-pyridyl)-thieno[2,3-b]pyridine **4**. The remaining fragment ions, especially those at m/z 211 (M—H) and m/z 134 (M—Py'), resulting from the abstraction of substituents from the molecular ion, support that structure. An isomeric compound was detected among the reaction products of sulfur with 4-picoline,[2] as well as, with toluene.[7]

Peaks 5, 6, 7 and 8 in the chromatogram can be assigned to compounds with MW of 271.1068 ($C_{18}H_{13}N_3$), which may arise by intramolecular cyclization of the tripyridylpropyl radical **2a** followed by dehydrogenation of the compound formed (Scheme II). With the 1,2,3-tri(3-pyridyl)-propyl radical, there are two directions of cyclization feasible: substitution either at position 2 or 4 of the pyridine ring. Dehydrogenation of compounds **2b** and **2c** leads to two pairs of isomers, **5**, **6** and **7**, **8**. It has been well established that the 3-picoline ring undergoes homolytic methylation and benzylation to give a variety of products.[6] The reactivity of position 2 in these reactions has been found to be 2–3 times that of position 4.[6] This holds both for acid and neutral solutions. The presence of four isomeric products with MW 271 shows that the cyclization proceeds in both directions, but more intense

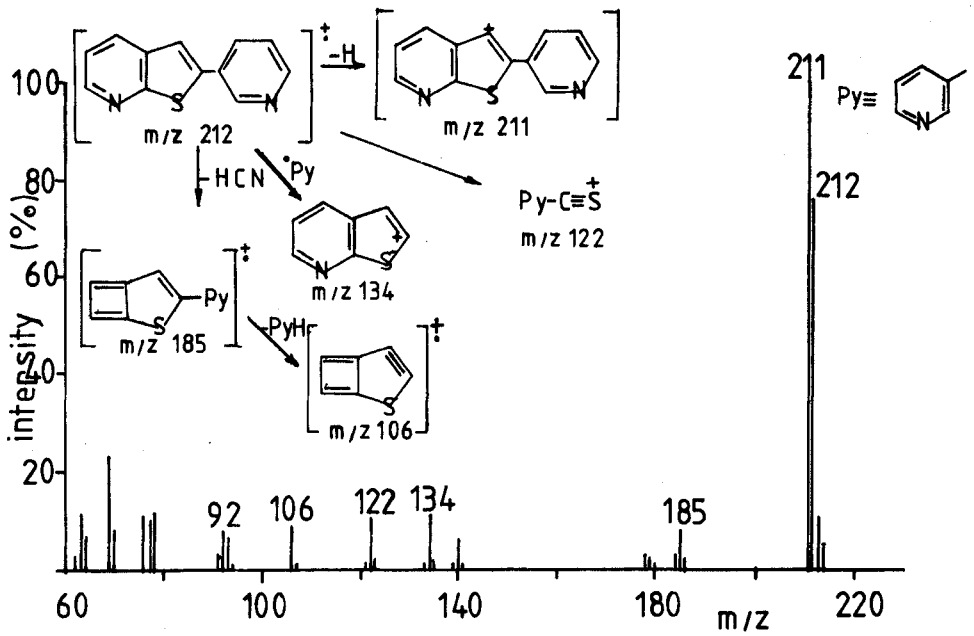


FIGURE 4 Mass spectrum and fragmentation pathways of compound **4**.

peaks 7 and 8 in the chromatogram can be assigned to compounds **7** and **8**, whereas the remaining two to compounds **5** and **6**.

There are two kinds of carbon in saturated 5-membered rings of intermediates **2b** and **2c** which differ in dehydrogenation capacity by sulfur. Apparently the carbon atoms attached to pyridyl substituents are less prone to interaction with sulfur on steric grounds. Consequently, the smaller peak 6 in the chromatogram can be assigned to compound **6** and peak 5 to compound **5**. A similar picture is observed with the pair of isomers **7** and **8**. Peak 7 was assigned to a more readily formed compound **7**. The mass spectra of compounds with MW 271 are shown in Figures 5–8 together with their fragmentation patterns. They support the conclusions drawn from the foregoing considerations. Of particular value is comparison of the intensity of the fragment ions (M-1) with that of the molecular ions. Compounds **7** and **5** should more readily undergo fragmentation than respectively **8** and **6** to give more stable tertiary cations. Hence, the abundance of the m/z 270 peak is larger. In the mass spectra of products **7** and **8** the main fragment ions occur at m/z 270 (M—H), 243 (M—H—HCN), and 192 (M—H—Py). In the spectra of **5** and **6** also an ion at m/z 181 (Py—$\overset{+}{C}$H=C—Py) appeared. As has been mentioned above, the two last-named reaction products resulted from cyclization at position 4 of the pyridine ring.

Peak 9 in the chromatogram can be assigned to compound with MW of 362.1491 ($C_{24}H_{18}N_4$). It should be formed by condensation of four picoline molecules. There are three pathways leading to that product: (i) The first involving substitution of the hydrogen atom in compound with MW 271, for instance **8**, for the $PyCH_2$ radical. Two such products are known to be formed in the reaction of sulfur with 2-picoline.[1] The $PyCH_2$ substituent should emerge in the mass spectrum as the M-

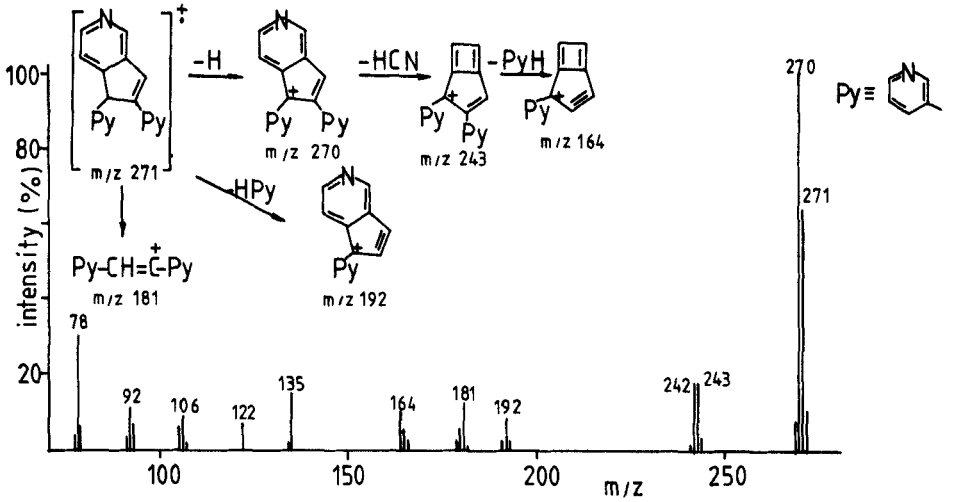


FIGURE 5 Mass spectrum and fragmentation pathways of compound **5**.

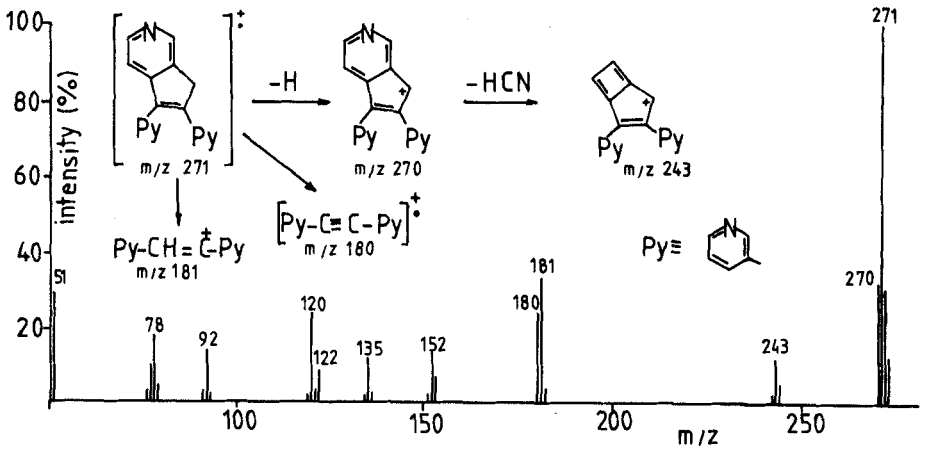


FIGURE 6 Mass spectrum and fragmentation pathways of compound **6**.

92 fragment ion. The 2-picoline counterparts undergo such fragmentation and the abundances of the m/z 270 ions are ca 70% and 100% in the first and second instance respectively. In the mass spectrum of the compound under consideration (Figure 9) the ion is missing and this allows to rule out this reaction pathway.

(ii) The second pathway leading to product with MW 362 consists in disproportionation of a radical-adduct resulting from reaction of radical **1a** with dipyridylethene (**2** or **3**) followed by its dehydrogenation by sulfur. Tetra(3-pyridyl)-1,3-butadiene formed in this way should produce an intense peak of the fragment ion at m/z 181 (Py—CH=C—Py). This is, however, missing in the mass spectrum (Figure 9).

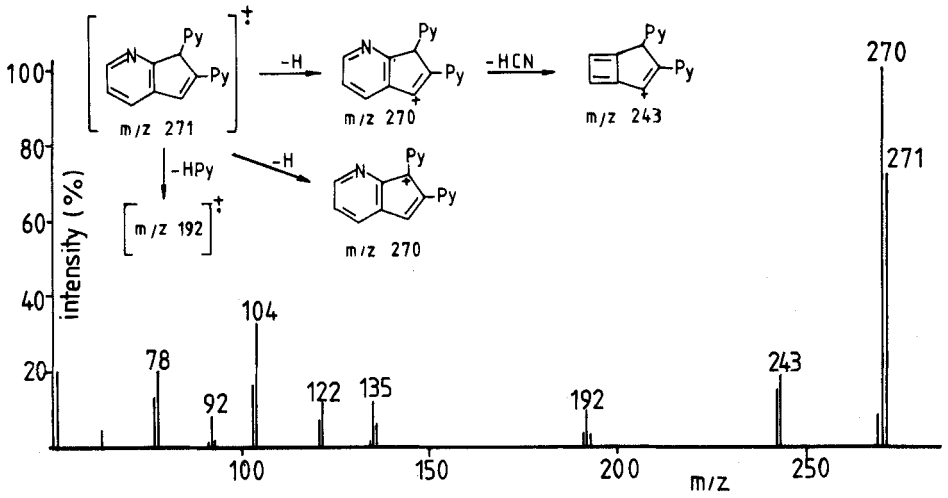


FIGURE 7 Mass spectrum and fragmentation pathways of compound **7**.

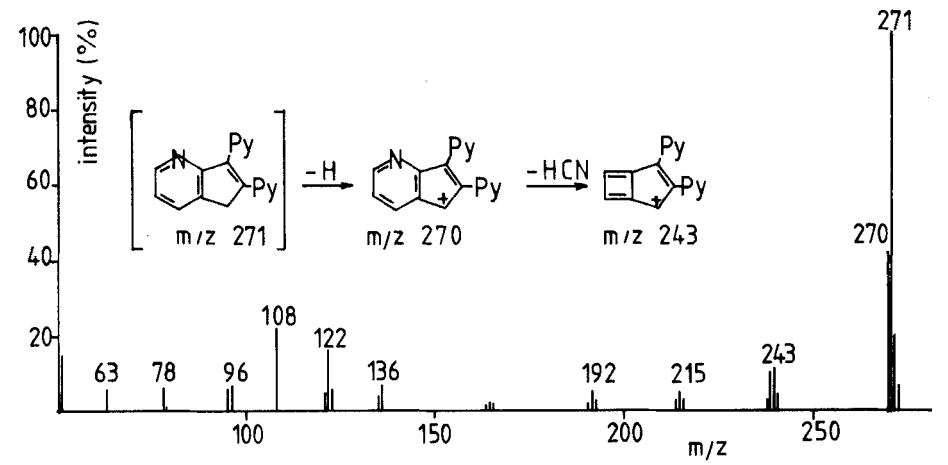


FIGURE 8 Mass spectrum and fragmentation pathways of compound **8**.

(iii) The third pathway leading to compound with MW 362 is presented in Scheme 1. As seen, the tetrapyridylbutyl radical undergoes cyclization. The intramolecular substitution of the hydrogen atom can afford three compounds: two after the attack on position 2 or 4 of the pyridine ring and the third after the attack on the fourth carbon of the hydrocarbon chain. These intermediates can be dehydrogenated by sulfur to give three quinoline derivatives (A–C), three isoquinoline derivatives (D–F), and tetra(3-pyridyl)-cyclobutene (G). The mass spectrum of the product is shown in Figure 9. The molecular ion at m/z 362 is the base ion. It is worth noting that the products of transformation of 2-picoline[1] gave considerably smaller peaks of that ion (50 and 5%). Further, there are peaks of the fragment ions at m/z 361 (M—H), 334 (M—H—HCN), 283 (M—Py—H) and 180. The last-named

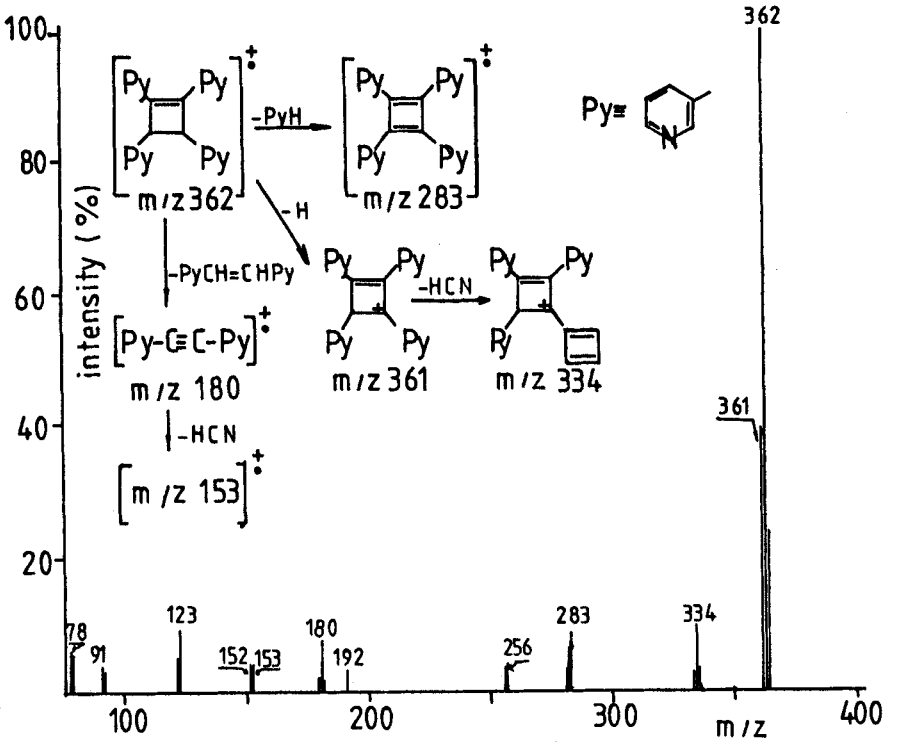


FIGURE 9 Mass spectrum and fragmentation pathways of compound **9**.

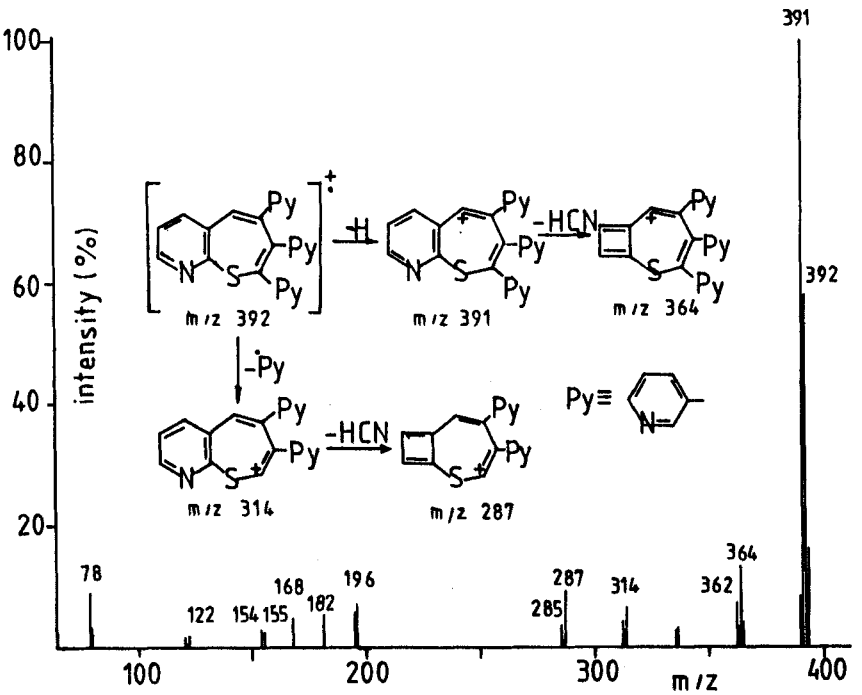


FIGURE 10 Mass spectrum and fragmentation pathways of compound **11**.

peak seems crucial for structure elucidation, because it might be formed via fragmentation accompanied by elimination of the Py—CH=CH—Py molecule. Inspection of the possibility of such fragmentation pathway of compounds A–G (Scheme I) reveals that only compounds A, D and G are capable of undergoing this type of fragmentation. It is likely that peak 9 in the chromatogram is due to tetra(3-pyridyl)-butene **9**. This conclusion is supported by the fact that processes of radical substitution occur much more readily in the side chain rather than in the aromatic ring. It is confirmed by the much enhanced contribution of **12** rather than of **10** and **11** whose structures will be discussed later. On the other hand, it seems likely that dehydrogenation of tetrahydroquinoline and tetrahydroizoquinoline should yield several products with MW 362. Detection of only one of them supports our conclusion that **9** is the reaction product.

Peaks 10, 11 and 12 in the chromatogram are due to compounds of MW 392. Their accurate mass of 392.1110 fits to molecular formula $C_{24}H_{16}N_4S$. These are condensation products of four picoline molecules with sulfur, which subsequently underwent cyclization and dehydrogenation of the cyclic products formed (Scheme II). The tetrapyridylbutyl radical, which is also an intermediate in synthesis of **9**, reacts with sulfur to give a tetrapyridylbutylsulfanyl radical that may undergo cyclization via intramolecular substitution. This homolytic process is likely to involve position 2 or 4 of the pyridine ring to produce a 7-membered ring containing sulfur. Alternatively, the attack can be exerted on the most remote carbon atom of the hydrocarbon chain to afford a 5-membered ring. Dehydrogenation of these compounds gives **10**, **11** and **12** whose mass spectra are shown in Figures 10 and 11.

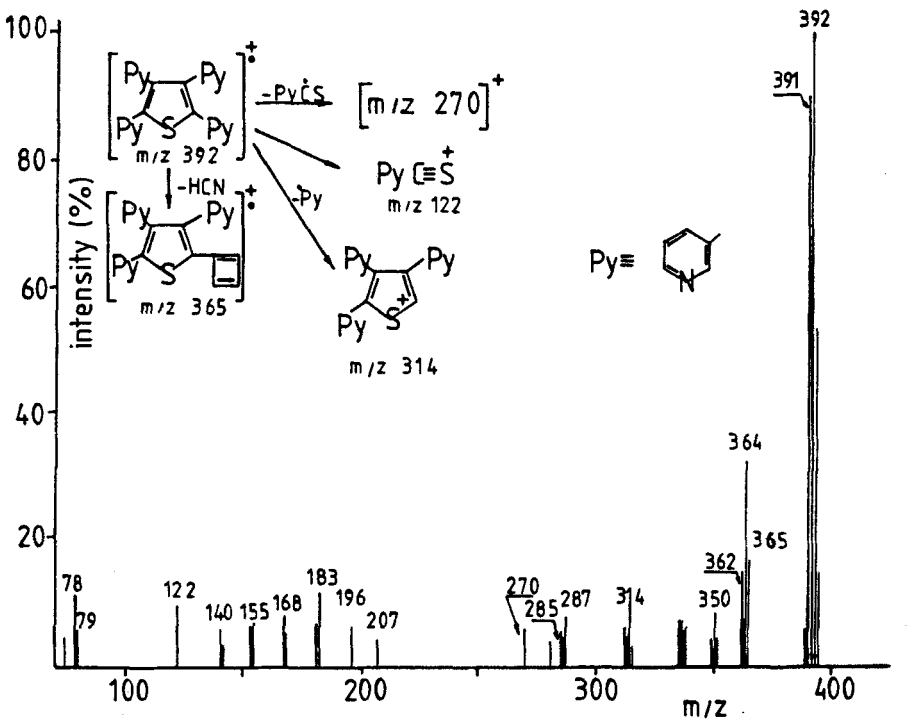


FIGURE 11 Mass spectrum and fragmentation pathways of compound **12**.

As the spectra of compounds 10 and 11 are identical regarding their composition and abundances of the fragment ions, only one of them is presented in Figure 10. The spectrum is characterized by a very abundant fragment ion M—H (100%), the abundance of the remaining ions is small. The most intense peaks occur at m/z 364 (M—H—HCN), 314 (M—Py) and 287 (M—Py—HCN).

The last peak in the chromatogram (peak no. 12) is also due to the isomer with MW 392. Its mass spectrum is shown in Figure 11. The base ion is the molecular ion at m/z 392. Apart from the fragment ions at m/z 364, 314 and 287, appearing in the spectra of its isomers, also peaks at m/z 270 (M—PyCS) and m/z 122 (Py—C≡S) are observed which were likewise recorded in the spectrum of tetra(4-pyridyl)-thiophene.[2] The fragmentation pattern of that compound closely resembles that of the considered isomer and the differences are seen in peak intensities only. Consequently, the most intense peak 12 in the chromatogram can be assigned to tetra(3-pyridyl)-thiophene.

EXPERIMENTAL

The reaction of sulfur with 3-picoline. To 16 g of elemental sulfur, 100 cm^3 (1 mol) of 3-picoline was added and the mixture was refluxed for 48 h under argon. This inert gas ensured oxygen-free atmosphere during the reaction and eliminated hydrogen sulfide. After cooling the mixture, the excess of sulfur (8 g) was filtered off and the filtrate was evaporated in vacuo at room temperature to leave a dense, dark-red oil. A mixture of ethanol-benzene (5:1) was added. A part of the oil dissolved (fraction A). The brown, solid residue (1.5 g) contain much sulfur along with the reaction products. The residue was moistened with ca 1 cm^3 of 50% sulfuric acid and transfered to 300 cm^3 of distilled water. Filtration of the mixture gave 1.3 g of pure sulfur. The filtrate was neutralized with sodium carbonate and extracted first with benzene and then with chloroform. Evaporation of the combined extracts in vacuo at room temperature gave 0.15 g of dark-brown powder (fraction B) which was sparingly soluble in methanol and ethanol, more soluble in benzene and freely soluble in chloroform. As much 9.3 (58%) of sulfur was recovered.

Thin Layer Chromatography (TLC). Particular steps of workup of the reaction mixture were monitored by TLC on DC Plastikfolien Kieselgel 60, Merck. The developing systems used were chloroform-methanol and benzene-methanol of variable composition (from 50:1 to 1:50) depending on needs. The substances were detected on the chromatograms visually in the UV light or by using iodine vapors as the detection reagent.

Gas Chromatography. Separation were carried out with Varian Aerograph model 1400 gas chromatograph adapted for work with capillary columns. The columns were coated with SE 52 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 $cm^3\ min^{-1}$. The sensitivity employed equalled to $2 \times 10^{-12}\ AmV^{-1}$.

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. The m/z ration was measured using the FD technique over the a.u. range 100–900. GC-MS measurements were carried out with Finnigen-MAT 212-SS-300 mass spectrometer coupled with Varian 3700 gas chromatograph. A fused silica capillary column with OV-101 liquid phase was used.

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