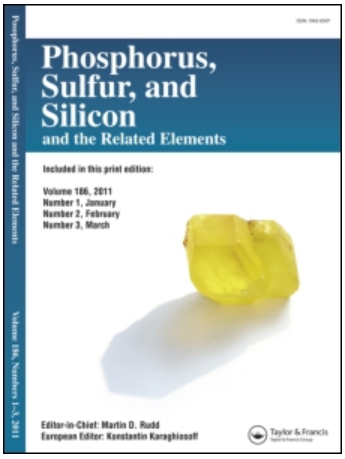

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ELEMENTAL SULFUR REACTIONS WITH 2-PICOLINE

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A study of the reaction of the elemental sulfur with 2-picoline is reported. The process was carried out at the boiling point of the 2-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 by mass spectrometry: 1,2-di/2-pyridyl/-ethane, 1,2-di/2-pyridyl/-ethene, 2-methyl-x-[/2-pyridyl/methyl]pyridines, 2-mercapto-methyl-[x/2-pyridyl/methyl]-pyridines, 1-mercapto-1,2-di/2-pyridyl/-ethane, 5,6-di/2-pyridyl/-5H-cyclopenta-[b]pyridine, 5,6-di/2-pyridyl/-7H-cyclopenta[b]pyridine, 1,2,3-tri/2-pyridyl/-propane, 1,2-di/2-pyridyl/-1-[x-/2-methyl/-pyridyl]-ethane, 5,6-di/2-pyridyl/-7-[/2-pyridyl/methyl]-7H-cyclopenta[b]pyridine, 5,6-di/2-pyridyl/-5-[/2-pyridyl/-methyl]-5H-cyclopenta-[b]pyridine, di{7-[5,6-di/2-pyridyl/-7H-cyclopenta[b]pyridyl]} sulfide and di{7-[5,6-di/2-pyridyl/-7H-cyclopenta[b]pyridyl]} disulfide.

INTRODUCTION

This study is a continuation of our investigations into the products of reaction of elemental sulfur with substituted pyridines. In the previous report,[1] products of the reaction with 4-picoline were described, whereas the present one deals with products of the reaction with 2–picoline.

Elemental sulfur has found wide-spread use in organic synthesis, for instance in the synthesis of bioactive derivatives of heterocyclic nitrogen-containing bases.[2] Further, it seems worthwhile to establish model chemical transformations involving sulfur under geochemical conditions of formation of solid fuels, petroleum and various deposits.[3,4,5]

The reaction of 2-picoline with sulfur has been little investigated so far. The reaction has been patented by Thayer[6] who found compounds of the general formulas $C_{12}H_{12}N_2$, $C_{18}H_{13}N_3$ and $C_{36}H_{24}N_6S_2$ among its products. Emmert and Groll[7] isolated the last-mentioned compound and suggested its structure.

In this article the formulas derived by these authors have been confirmed by using techniques of liquid chromatography, gas chromatography and mass spectrometry, but the structures of the compounds could not be accepted. A variety of other products have also been detected and identified.

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RESULTS

First of all, the excess of starting reagents was removed from an oily mixture resulting from the reaction of 2-picoline with sulfur. The residue was treated with *n*-hexane in which it was partially soluble. Both the undissolved residue and the hexane extract were examined by TLC. This showed both fractions to contain the same components but in different proportions.

In order to determine molecular weights of the products the field-desorption (FD) end electron impact (EI, 15 eV) mass spectra were recorded. The high-resolution m/z ratios were measured which enabled molecular formulas to be established (Table I).

These measurements confirmed the earlier-findings that both the hexane solution and the residue contained identical compounds, but the hexane fraction was richer in the high-molecular-weight components (MW 572, 604 and higher).

An attempt was subsequently made to separate the components by column chromatography on silica gel. The poorly soluble fraction could, however, not be separated in this way. From the hexane soluble fraction compounds **12** (MW 604) and **13** (MW 572) were isolated. The last one, however, was contaminated with low-molecular-weight compounds. The remaining components could not be separated into chromatographically homogeneous compounds.

The mixture of poorly soluble products in which contribution of high-molecular-weight compounds was lower, was analyzed by GC-MS. A chromatogram of this fraction is shown in Figure 1. Both the mass spectra and the suggested fragmentation pathways are shown in successive Figures, whereas the established structural formulas are presented in Scheme 2 and in Table I.

TABLE I

Low- and high-resolution mass spectra of products of the reaction of sulfur with 2-picoline (48 hours, refluction at the boiling point)

Precise mass (measured)	Elemental composition	Compound
182.0838	$C_{12}H_{10}N_2$	1,2-di(2-pyridyl)-ethene (**3**)*
184.0982	$C_{12}H_{12}N_2$	1,2-di(2-pyridyl)-ethane (**1**) 2-methyl-x-[/2-pyridyl/methyl]-pyridine** (**2**)
216.0752	$C_{12}H_{12}N_2S$	2-mercapto-methyl[x/2-pyridyl/methyl]-pyridine (**4**) 1-mercapto-1,2-di[2-pyridyl]-ethane (**5**)
271.1074	$C_{18}H_{13}N_3$	5,6-di[2-pyridyl]-5H-cyclopenta[b]-pyridine (**8**) 5,6-di[2-pyridyl]-7H-cyclopenta[b]-pyridine (**9**)
275.1395	$C_{18}H_{17}N_3$	1,2,3-tri[2-pyridyl]-propane (**6**) 1,2-di[2-pyridyl]-1-[x-/2-methyl/pyridyl]-ethane (**7**)
362.1498	$C_{24}H_{18}N_4$	5,6-di[2-pyridyl]-7-[/2-pyridyl/methyl]-7H-cyclopenta[b]pyridine (**11**) 5,6-di/2-pyridyl/-5-[2-pyridyl/-methyl]-5H-cyclopenta[b]pyridine (**10**)
572	$C_{36}H_{24}N_6S$	di{7-[5,6-di[2-pyridyl]-7H-cyclopenta[b]pyridyl]} sulfide (**13**)
604	$C_{36}H_{24}N_6S_2$	di{7-[5,6-di[2-pyridyl]-7H-cyclopenta[b]pyridyl]} disulfide (**12**)

* The numbering of the compounds in tables and in figures is consistent with the numbering defined in the reaction scheme, Scheme 2.

** x-Position of the substitution in the pyridine ring (3–6).

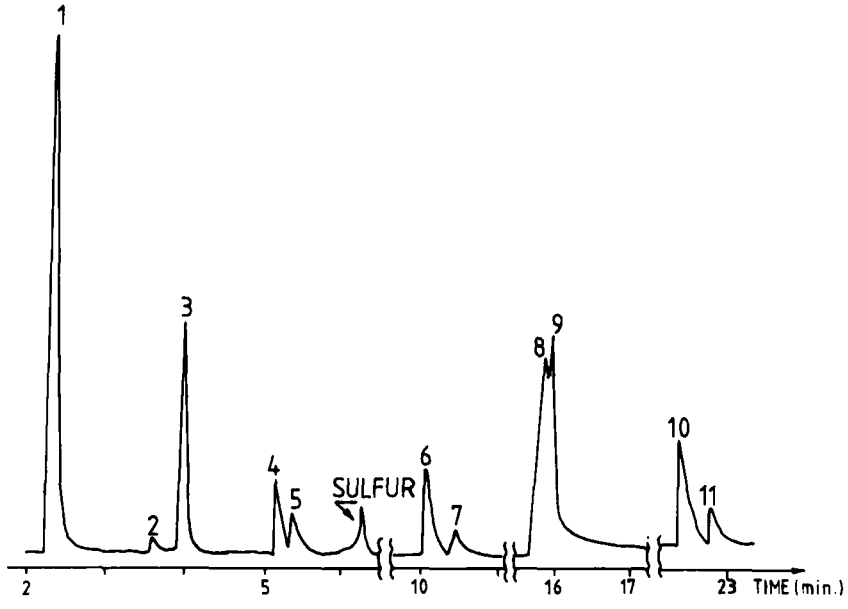


FIGURE 1 GC analysis of the residue undissolved in hexane. Capillary column OV-1. Initial temperature 150°C, 5°/min.

DISCUSSION

The mass spectrum of the main component of the poorly soluble mixture (peak 1, Figure 1) is shown in Figure 2. Regarding the fragment-ion composition and peak intensities, the spectrum is identical with that of the successive peak in the chromatogram. It is thus concluded that these are the peaks of isomers. Their

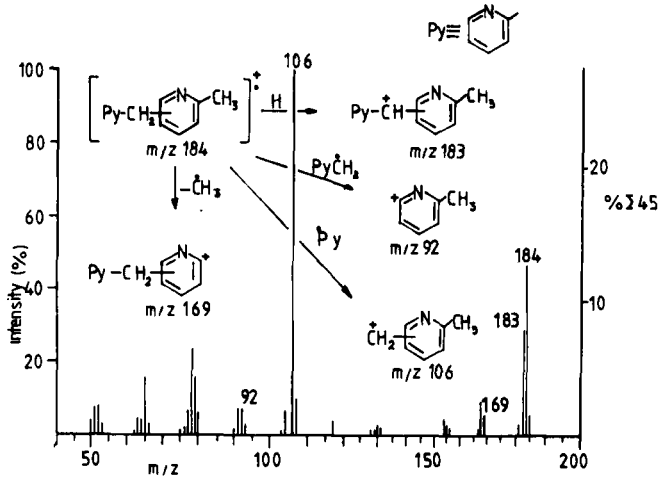


FIGURE 2 Mass spectrum and fragmentation pathways of compound **2**.

molecular ion at m/z 184 has the accurate mass of 184.0982 to which the molecular formula $C_{12}H_{12}N_2$ can be assigned. The isomers might have been formed by condensation of two 2-picoline molecules. This condensation might afford 1,2-di/2-pyridyl/ethane as well as four products of substitution of a hydrogen atom in the pyridine ring. The formation of such non-linear isomers in this reaction is supported by two fragment ions at m/z 183 (M-1), 169 (M-15) as well as a very strong peak at m/z 106 (M-78). It must be emphasized that these peaks are missing in the mass spectrum of 1,2-di/4-pyridyl/-ethane, the main product of reaction of 4-picoline with sulfur.[1] The peak at m/z 106 (M-15) occurs in the spectra of 3-ethyl-2-methyl-pyridine and of other ethylmethylpyridines.[8] These findings support the suggestion of nonlinear structure of the products. On the other hand, among the products, a linear isomer, whose analog is the main product of the reaction of 4-picoline with sulfur, should occur. The formation of this isomer is confirmed by the presence of 1,2-di/2-pyridyl/-ethene, which will be discussed later. It can thus be concluded that the very strong peak 1 in the gas chromatogram (Figure 1) is due to a mixture of 1,2-di/2-pyridyl/-ethane **1** with at least one of the isomers **2**. The fragmentation pathways of this isomer is shown in Figure 2.

Peak 3 of the chromatogram is due to a compound with MW of 182.0838, molecular formula $C_{12}H_{10}N_2$. The mass spectrum of this compound and the suggested fragmentation pathways are shown in Figure 3. The molcular formula fits to the composition of 1,2-di/2-pyridyl/-ethene **3** which arises by dehydrogenation of compound **1**. Its structure is confirmed by the mass spectrum. The base peak is that at m/z 181 (M-1), as the fragmentation affords a stable cation (2-pyridyl)—$\overset{+}{C}$=CH—(2-pyridyl). A fragment ion at m/z 104 (M-78) is less intense. The remaining ions appearing in the spectrum are formed by ejection of HCN.

Molecular weight of the products due to peaks 4 and 5 of the gas chromatogram is 216. In the spectrum of the separated mixture, only one such ion with accurate mass of 216.0752, $C_{12}H_{12}N_2S$, was observed. This leads to conclusion

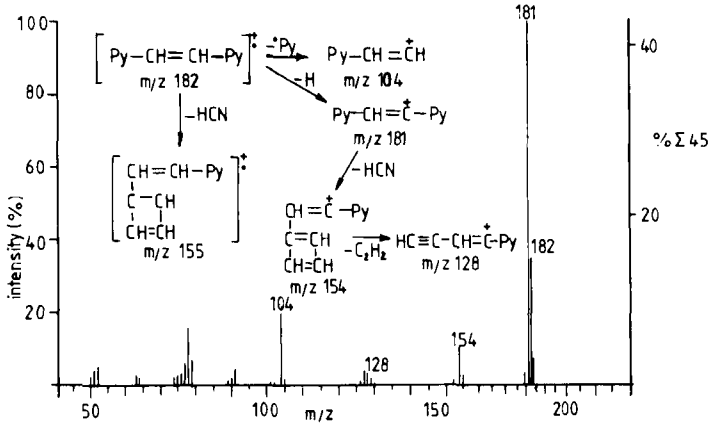


FIGURE 3 Mass spectrum and fragmentation pathways of compound **3**.

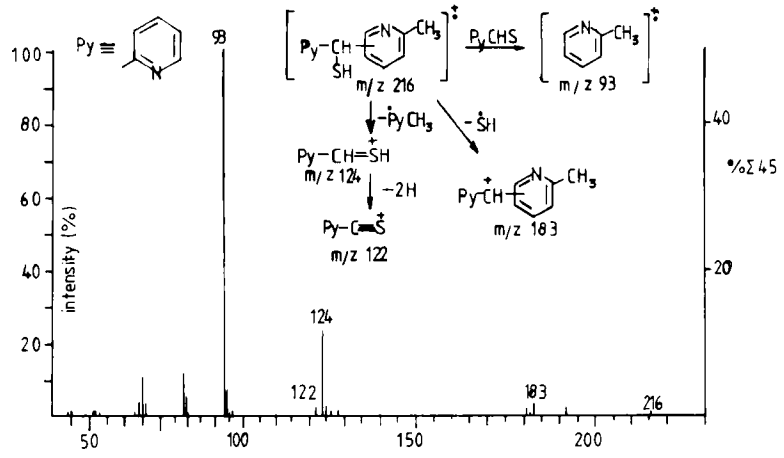


FIGURE 4 Mass spectrum and fragmentation pathways of compound **4**.

that both peaks can be assigned to isomers of identical mass spectral patterns (Figure 4). The peaks at m/z 124 and 122 ascribed to (2-pyridyl)—$\overset{+}{C}H=\overset{+}{S}H$ and (2-pyridyl)—$C\overset{+}{S}$, respectively, revealed the presence of sulfur in the molecule. Examination of the structure of these compounds offers five possibilities as shown in Figure 5. In the mass spectrum (Figure 4) a peak at m/z 183 (M-SH) is observed, whereas that at m/z 138, which should have been formed during fragmentation of RCH_2SR' into $CH_2=\overset{+}{S}R'$ is missing. Consequently, compounds resulting from this reaction are thiols, and sulfide structures D and E (Figure 5) can be ruled out. In the mass spectra of both peaks, an ion with m/z 47 ($CH_2=\overset{+}{S}H$) which should have been formed in the spectrum of the C type isomers,[9] is missing. Hence, it can be concluded that peaks 4 and 5 of the gas chromatogram correspond to compounds A and B. A study on separation of products of the reaction of toluene with sulfur[10] has shown that under similar separation conditions the retention time of the linear isomer (B) is shorter than that of ring-substituted compounds. Bearing this in mind, one may speculate that peak 4 corresponds to compound **5** whereas peak 5 to isomer or mixture of isomers **4**.

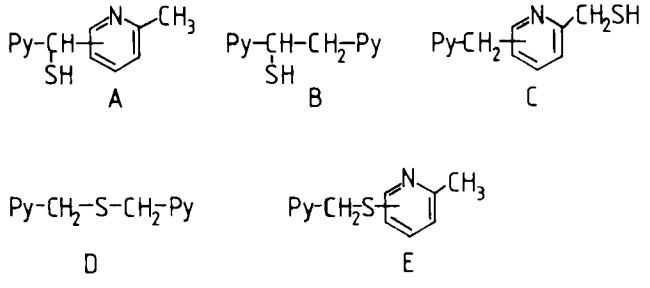


FIGURE 5 The possible structures of compounds of molecular formula $C_{12}H_{12}N_2S$ (MW 216).

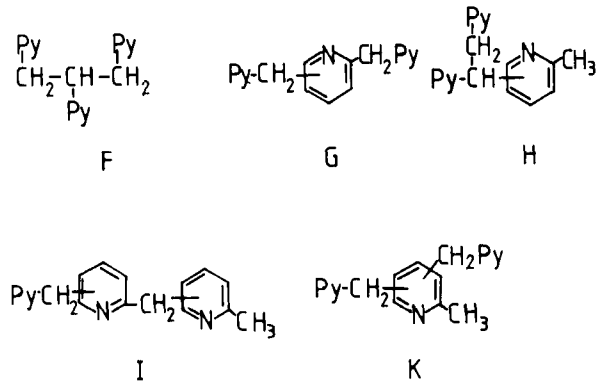


FIGURE 6 The possible structures of compounds of molecular formula $C_{18}H_{17}N_3$ (MW 275).

Peaks 6 and 7 in the chromatogram (Figure 1) correspond to two isomers of molecular weight 275. A mass spectrum of the mixture of products revealed one ion at m/z 275 with accurate mass 275.1395 ($C_{18}H_{17}N_3$) to which a number of structures can be assigned (see Figure 6). Product F arises from the reaction of 2-picoline with dipyridylethane **1**, whilst products G and H might have been formed both in the reaction with **1** and with its nonlinear isomers **2** which are the only starting reagents in the synthesis of compounds I and K. The mass spectra of both peaks are much alike. Minor differences can only be noted in the intensity of some fragment ions. In the spectrum of peak 7 (Figure 7) appears an ion at m/z 260 (intensity 1.4%) which is missing in the spectrum of peak 6. This is the only feature differentiating the two spectra. The fragment ion at m/z 93 arises from elimination of 1,2-dipyridylethene concerted with hydrogen transfer. Bearing this in mind, the products cannot have structures G, I and K. The missing peak of the

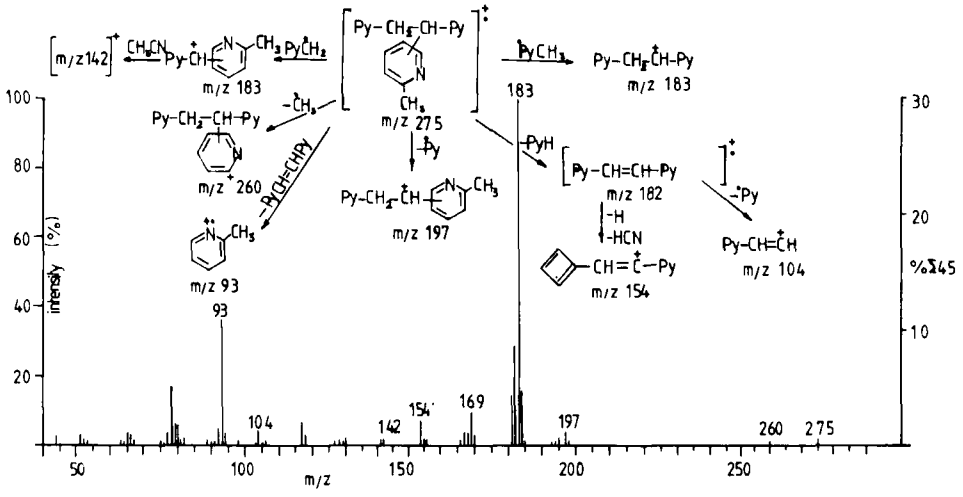


FIGURE 7 Mass spectrum and fragmentation pathways of compound **7**.

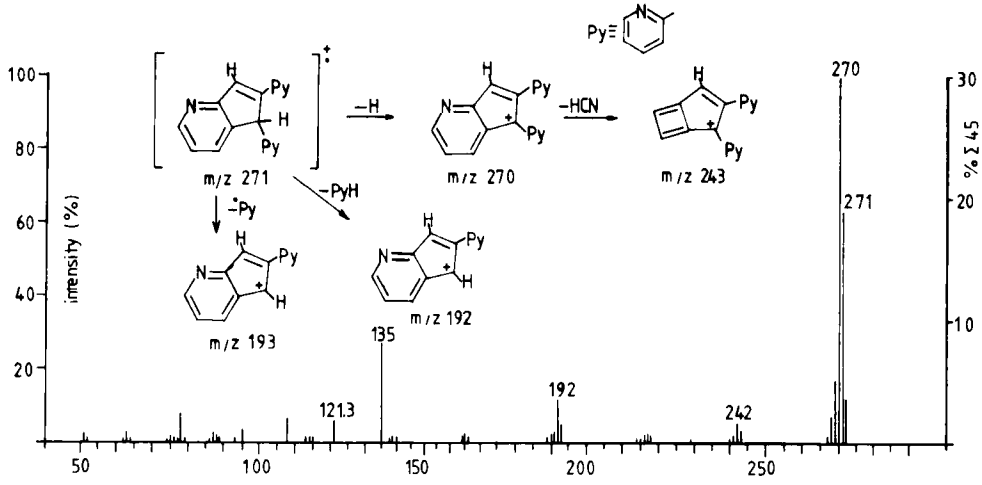
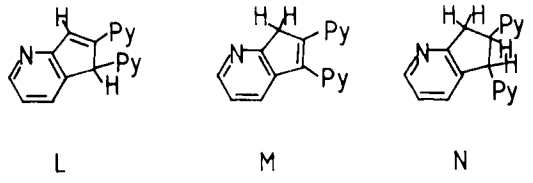


FIGURE 8 Mass spectrum and fragmentation pathways of compound **8**.

ion at m/z 106 in the spectrum, appearing in the spectrum of compound **2** resulting from β-decay of ring-substituted picolines,[8,11] affords another argument in favor of the absence of compound I. Consequently, chromatographic peaks 6 and 7 (Figure 1) correspond to isomers of structure of F and H respectively. In the mass spectrum of peak 7, an ion at m/z 260 (M-15) appears which allows to assign structure H (**7**) to the product, whereas compound producing peak 6, whose spectrum is devoid of the fragment ion M-15, is tri(2-pyridyl)-propane **6**.

Products giving peaks 8 and 9 in the chromatogram could not be separated for taking their mass spectra. The spectra of the mixtures were only recorded, each containing an excess of another product. Both spectra are identical. As in the spectra the base peak appears at m/z 270 and the highest mass occurs at m/z 271 it is concluded that peaks 8 and 9 are due to isomers of molecular weight 271. Both the mass spectrum and the fragmentation pathways of one of the isomers are shown in Figure 8. The molecular peak at m/z 271 (accurate mass 271.1074) can be assigned molecular formula $C_{18}H_{13}N_3$ and structure L or M (Figure 9). The two compounds may be products of dehydrogenation of compound N formed by intramolecular cyclization of **6**. It must be emphasized that a compound with MW 273 was not detected in the reaction mixture. Hence, it seems to be very prone to dehydrogenation. Isomers **8** and **9** differ in the position of the double bond. Their mass spectrum is rather poor. The major fragment ions are those at



L M N

FIGURE 9 Product of compound **6** cyclization (N) and its dehydrogenation products (L and M).

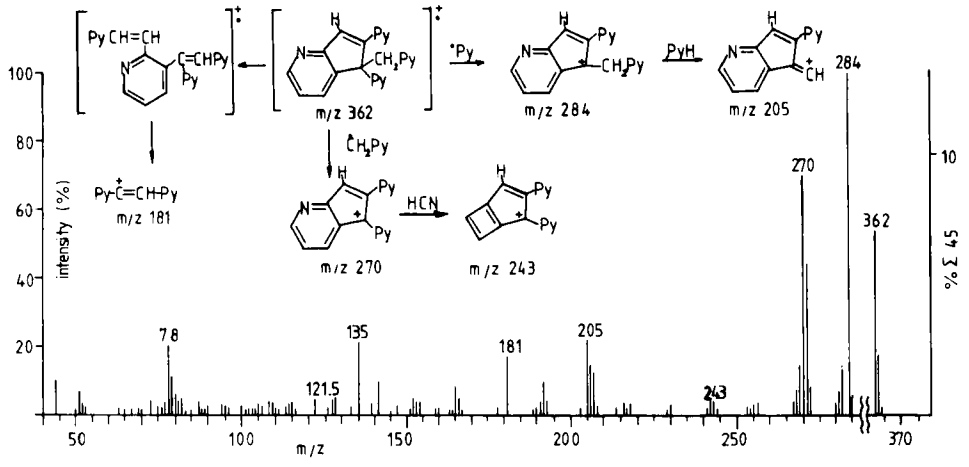


FIGURE 10 Mass spectrum and fragmentation pathways of compound **10**.

m/z 270 (M-1), 193 (M-78) and 192 (M-79). Relatively intense ions at m/z 135 and 121.5 are double charged ions of MW 270 and 243 respectively.

The suggested structure of isomers **8** and **9** (L and M) is at the same time part of the structure of two further products (chromatographic peaks 10 and 11). Their spectra and fragmentation pathways are shown in Figures 10 and 11.

In both cases the molecular ion occurs at m/z 362. The accurate mass (362.1498) fits to molecular formula $C_{24}H_{18}N_4$ for which four structures can be suggested (Figure 12).

In the spectra of both isomers the fragment ion at m/z 270 (M-92) arises by abstraction of the $Py\dot{C}H_2$ radical. This allows to eliminate structure S i.e. the linear, dehydrogenated product of condensation of four picoline molecules. Compounds O and P might have arisen from isomer **8** and product R from isomer **9**.

In the mass spectrum of peak 10, the ion at m/z 284 (M-78) has intensity of

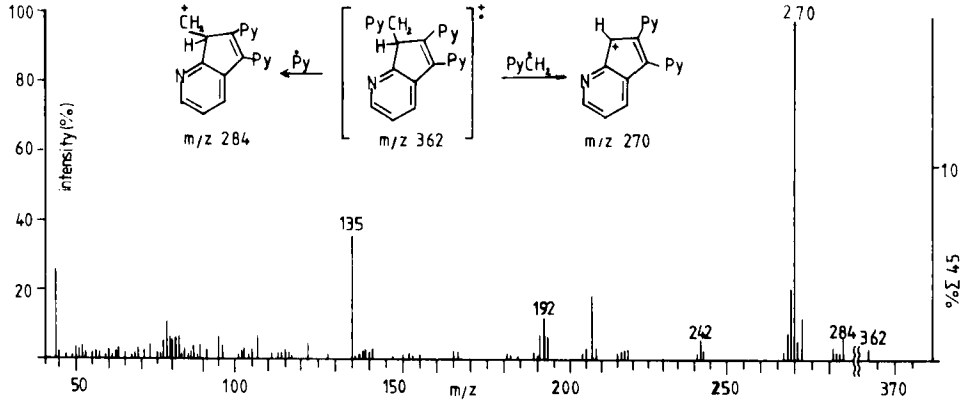


FIGURE 11 Mass spectrum and fragmentation pathways of compound **11**.

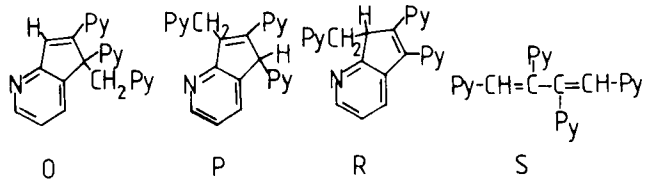


FIGURE 12 The possible structures of compounds of molecular formula $C_{24}H_{18}N_4$ (MW 362).

100%. Also the ion at m/z 270 has a high intensity (70%). In the spectrum of peak 11, the ion at m/z 270 has a 100% intensity, whereas that at m/z 284 only 7%. Structural examination of molecules O, P and R (Figure 12) from the standpoint of the stability of the cations produced during fragmentation (M-78 and M-92) shows that product **10** is likely to have structure O, whereas product **11** structure R. These are thus products of hydrogen substitution at the saturated carbon atom in isomers **8** and **9**.

Emmert and Grolle[7] isolated a base of the formula $C_{36}H_{24}N_6S_2$ from the reaction mixture. It was only slightly volatile and attempts to characterize it by GC-MS failed. In this study, however, it occurred at higher concentration in the hexane extract and could be isolated by column chromatography. Its mass spectrum is shown in Figure 13.

The molecular weight (604) was determined by the FD technique. In the spectrum taken by the EI technique, the molecular peak at m/z 604 was missing, this making the determination of the accurate molecular weight and molecular formula impossible. However, the results of elemental analysis confirmed the formula suggested by Emmert and Groll.[7] In the EI mass spectrum there was one peak at m/z 302 (accurate mass 302.0735) indicating a symmetric structure of the

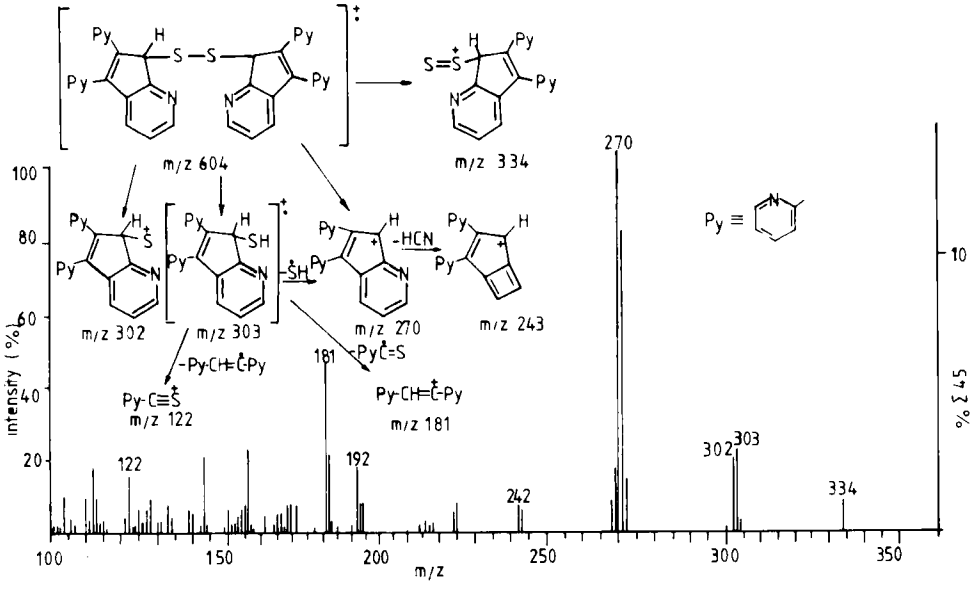
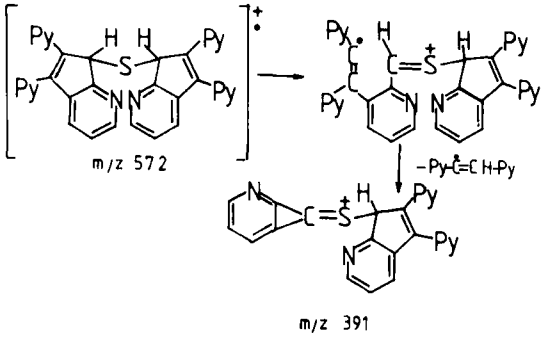


FIGURE 13 Mass spectrum and fragmentation pathways of compound **12**.

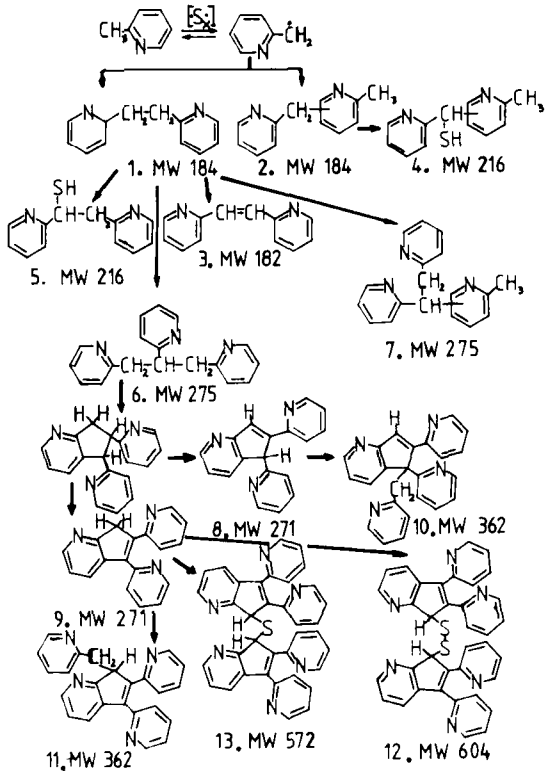
molecule. The symmetry is displayed by disulfides, whose fragmentation often results in fission of the S—S bond.[8] A fragment ion at m/z 334 (M-270) in the spectrum suggests that the compound of MW 604 a structure of R—S—S—R can be described, where R has a mass of 270. Among the products so far considered there are only two substrates for the formation of the discussed compound. These are isomers **8** and **9** (MW 271). Their spectrum (Figure 8) exhibits peaks at m/z 270, 243 and 192 occurring likewise in the spectrum of the product under consideration. In view of the facts that hydrogen attached to aliphatic carbon undergoes radical substitution and that steric factors facilitate the reaction of sulfur with isomer **9** rather than **8**, the compound was assigned structure **12**.

As in the case of compound with MW 604, the intensity of the molecular peak of product **13** at m/z 572 was too weak to ensure accurate determination of its molecular (2.1%). A column chromatographic separation gave one fraction in which it occurred as a component of the highest molecular weight. The FD mass spectrum showed that the fraction contained also compounds of molecular weights 184, 271 and 362. In the EI mass spectrum the base ion was at m/z 391 resulting from elimination of the Py—Ċ = CH—Py radical. A scheme of this process is outlined in Scheme 1. The possibility of elimination of this fragment confirms the suggested sulfide structure of this product, similar to the disulfide structure **12**. It should be noted that the fragment ion at m/z 303 (Figure 13) also decays with the loss of the Py—CH = Ċ—Py radical.

To sum up, it can be said that the reaction of elemental sulfur with 2-picoline, similar to that of 4-picoline,[1] is a radical consecutive-parallel process outlined in Scheme 2. Its major product is the disulfide **12**, whereas in the reaction of 4-picoline tetrapyridylthiophene was the main product, which could not be found now. This fundamental difference shows that the methyl group at position 2 has an enhanced influence, as compared to the substituent at position 4, on substitution of hydrogen in the ring. Accordingly, intramolecular alkylation of product **6** gave two isomers **8** and **9**. As tri(4-pyridyl)-propane does not undergo this reaction,[1] this synthetic pathway is ruled out. Again, the presence of thiols **4** and **5** among the reaction products of 2-picoline, is indicative of their enhanced stability. Unlike the derivatives of 4-picoline, they do not react with di(2-pyridyl)-thene, which would have afforded substituted thiopenes.



Scheme 1 Fragmentation pathway of compound **13**.



Scheme 2 Reaction of 2-picoline with elemental sulfur.

EXPERIMENTAL

The reaction of sulfur with 2-picoline. To 16 g of elemental sulfur 100 ccm of 2-picoline was added and the mixture was refluxed under argon for 48 hours. Then it was cooled, the excess of sulfur filtered off and the unreacted 2-picoline was removed in vacuo at room temperature to leave a dense, dark brown oil which still contained sulfur. Other components of the mixture were separated by leaching with an ethanol–benzene (5:1) solution. The total quantity of recovered sulfur was 3.1 g (ca 20%).

The ethanol–benzene solution was evaporated to dryness in vacuo at room temperature and the residue was repeatedly extracted with hexane. Both the hexane extracts and the insoluble residue were further examined.

Mass spectrometry. The mass spectra were taken on the mass spectrometer Varian MAT 711 furnished with the combined source EI, FI and FD. Low-resolution spectra for R = 1000 and high-resolution spectra for 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 mass spectra by GC-MS were recorded on the LKB 2090 spectrometer equipped with a two-stage Ryhage separator. The columns were connected in the make-up system. The resolution was R = 600 and the ionisation energy 70 eV.

Gas chromatography. Separations were carried out with the Varian Aerograph model 1400 gas chromatograph adapted for work with capillary columns. The columns were coated with OV-1 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 to 2×10^{-12} AmV^{-1}.

Thin Layer Chromatography (TLC). The course of the reaction and the composition of the eluate obtained from liquid chromatography was searched by TLC method (DC-Plastikfolien, Kieselgel 60, Merck). The plates were developed by using chloroform-methanol (10:1) or benzene-methanol (10:1) mixtures. Substances were detected on the chromatogram visually in UV light or by using an iodine atmosphere as a detection reagent.

Liquid chromatography. The products were chromatographed on the MN-Kieselgel finer than 200 mesh on a column 75 × 2 cm with the system chloroform-methanol (30:1). Before the separation, the column was conditioned with the same system. The products of the liquid chromatography were investigated by means of TLC, GC and MS methods.

REFERENCES

1. E. Gleich, Z. Warnke, J. Szafranek and E. Maliński, *Phosphorus and Sulfur*, **28,** 315 (1986).
2. A. S. Sadikov, O. S. Otroshchenko and T. K. Yunusov, *Polish Journal of Chemistry*, **53,** 367 (1979).
3. D. J. Casagrande, N. Ng, *Nature*, **282,** 598 (1979).
4. D. J. Casagrande, G. Idowu, A. Friedman, P. Rickert, K. Siefert and D. Schlenz, *Nature*, **282,** 599 (1979).
5. Y. Mehmet, The occurrence and origins of sulfur compounds in crude oils—a review, *Alta. Sulfur Res. Ltd., Q. Bull.*, **8(1),** 1 (1971).
6. H. I. Thayer, USA-Pat. 2496319 (7.02.1950), *C.*, **1950** II, 1511.
7. B. Emmert and M. Groll, *Chem. Ber.*, **86,** 205 (1953).
8. S. R. Heller, G. W. A. Milne, *EPA/NIH Mass Spectral Data Base*, vol. 1–4, U.S. Department of Commerce, National Bureau of Standards, December 1978.
9. H. Kienitz, *Massenspektrometrie*, p. 501, Verlag Chemie GmbH, Weinheim/Bergstrasse 1968.
10. K. Przewocki, E. Maliński and J. Szafranek, *Chemical Geology*, **47,** 347 (1984).
11. H. Budzikiewicz, C. Djerassi, D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds*, p. 255, Holden-Day, Inc. San Francisco 1965.