

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

ELEMENTAL SULFUR REACTIONS WITH 4-PICOLINE

E. Gleich^a; Z. Warnke^a; J. Szafranek^a; E. Malinski^a

^a Institute of Chemistry, University of Gdańsk, Gdańsk, Poland

To cite this Article Gleich, E. , Warnke, Z. , Szafranek, J. and Malinski, E.(1986) 'ELEMENTAL SULFUR REACTIONS WITH 4-PICOLINE', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 28: 3, 315 — 325

To link to this Article: DOI: 10.1080/03086648608072823

URL: <http://dx.doi.org/10.1080/03086648608072823>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ELEMENTAL SULFUR REACTIONS WITH 4-PICOLINE

E. GLEICH, Z. WARNKE,* J. SZAFRANEK and E. MALINSKI

*Institute of Chemistry, University of Gdańsk, ul. Sobieskiego 18,
80-952 Gdańsk, Poland*

(Received October 28, 1985; in final form December 9, 1985)

A study of the reaction of the elemental sulfur 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 reaction products were identified by means of LC, GC, and GC-MS. The following products have been identified: 1,2-di[4-pyridyl]-ethane, 1,2-di[4-pyridyl]-ethene, 1,2,3-tri[4-pyridyl]-propane, tetra[4-pyridyl]-thiophene, E and Z isomers of 1,2,3-tri[4-pyridyl]-propene, 6-[4-pyridyl]-thieno[3,2-c]pyridine and 10-[4-pyridyl]-pyrido[3''4'':5',4']cyclopenta[2',3':4,5]thieno[2,3-c]pyridine.

Radical mechanisms for the reactions have been proposed. The catalytic effect of sodium hydroxide on this reaction has also been confirmed as well as the mechanism of the catalysis has been suggested. This study corroborates suggestions concerning the mechanisms of formation of the heterocyclic nitrogen- and sulfur-containing compounds from an organic matter under geological conditions.

INTRODUCTION

The reactivity of elemental sulfur has attracted the interest of many scientists representing various disciplines,^{1,2} including geochemistry.^{3,4} Sulfur and its compounds occur in various deposits of organic origin, including coal and oil.^{5,6,7} A model chemical reaction of simple organic compounds with sulfur may enhance our insight into biogeochemical processes leading to conversion of an organic material to relevant deposits. It has been known that the concentration of sulfur in an organic material both of plant and animal origin seems to be too small for producing as large amount of organic sulfur compounds as is actually observed in some solid and liquid fuels.⁸ Therefore, it is believed that many of these compounds originate from thermal reactions between an organic material and elemental sulfur.⁹

Apart from substances containing sulfur, solid and liquid fuels contain also the following nitrogen organic compounds: pyridine benzologs, diaza compounds, amides and carbazoles.¹⁰ Derivatives containing sulfur and nitrogen in the same molecule have also been isolated.^{11,12} It is believed that the latter resulted from direct reactions between sulfur and organic compounds containing nitrogen.⁴

A considerable amount of work has been devoted to studies of the reactivity of sulfur with hydrocarbons.² Much less attention has been paid to a study how sulfur interacts with heterocycles containing nitrogen. The purpose of this work has been an investigation of the reaction of sulfur with 4-picoline. This reaction has been little studied. Thayer and Corson¹³ have only identified a part of the products on the

*Author to whom all correspondence should be sent.

preparative way. In this work, by means of GC-MS technique, we have confirmed their results as well as discovered and identified a few more products.

RESULTS

We began the study of the reaction of sulfur with 4-picoline from the identification of the chemical structure of products obtained during the 48 hour-long heating of the substrates. Mass spectrometry was employed for the determination of the molecular weights and formulas. The results obtained by means of the EI technique [at 15 eV] as well those obtained by means of high-resolution MS are summarized in Table I.

TABLE I

Low- and high-resolution mass spectra of products of the reaction of sulfur with 4-picoline [48 hours, reflux at the boiling point]

| Relative intensity [%] | Precise mass [measured] | Elemental composition | Compound* |
|------------------------|-------------------------|-----------------------|---|
| 7.6 | 212.0405 | $C_{12}H_8N_2S$ | 6-[4-pyridyl]thieno-[3,2-c]pyridine [7] |
| 11.2 | 182.0874 | $C_{12}H_{10}N_2$ | 1,2-di[4-pyridyl]-ethene [2] |
| 100.0 | 184.1009 | $C_{12}H_{12}N_2$ | 1,2-di[4-pyridyl]-ethane [1] |
| 18.4 | 275.1438 | $C_{18}H_{17}N_3$ | 1,2,3-tri[4-pyridyl]-propane [3] |
| 10.0 | 392.1120 | $C_{24}H_{16}N_4S$ | tetra[4-pyridyl]thiophene [8] |

*The numbering of the compounds in tables and in figures is consistent with the numbering defined in the reaction scheme, Scheme 1.

TABLE II

Results of the separation of the products of the reaction of 4-picoline with sulfur by means of the liquid chromatography

| Fraction | Volume [cm ³] | Molecular weight | Formula | Compound |
|----------|---------------------------|------------------|--------------------|---|
| 1 | 100 | 301 | $C_{18}H_{11}N_3S$ | 10-[4-pyridyl]-pyrido-[3'',4'':5',4']cyclopenta-[2',3':4,5]thieno[2,3-c]-pyridine [6] |
| 2 | 30 | 182 | $C_{12}H_{10}N_2$ | 1,2-di[4-pyridyl]-ethene [2] |
| | | 184 | $C_{12}H_{12}N_2$ | 1,2-di[4-pyridyl]-ethane [1] |
| 3 | 45 | 182 | $C_{12}H_{10}N_2$ | [2] |
| | | 184 | $C_{12}H_{12}N_2$ | [1] |
| 4 | 130 | 273 | $C_{18}H_{15}N_3$ | 1,2,3-tri[4-pyridyl]-propene [4] |
| | | 273 | $C_{18}H_{15}N_3$ | [5] |
| | | 392 | $C_{24}H_{16}N_4S$ | tetra-[4-pyridyl]thiophene [8] |
| 5 | 200 | 392 | $C_{24}H_{16}N_4S$ | [8] |
| 6 | 250 | 275 | $C_{18}H_{17}N_3$ | 1,2,3-tri[4-pyridyl]-propane [3] |

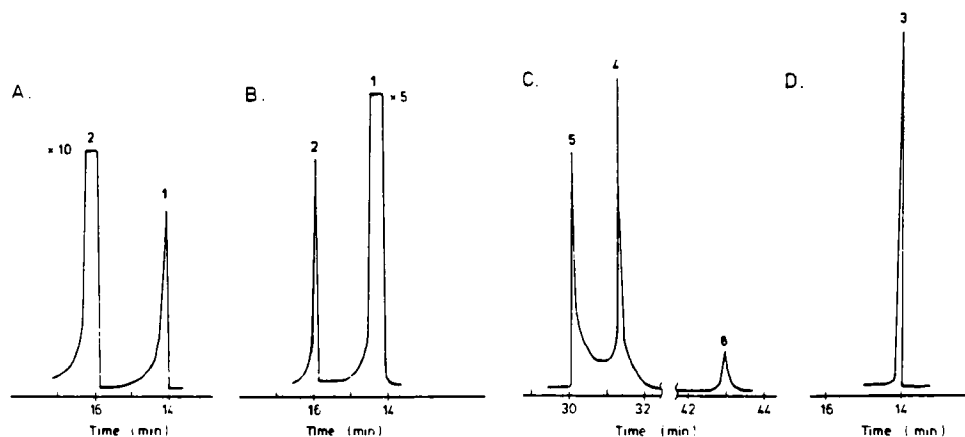


FIGURE 1 GC analysis of the fraction obtained by means of the liquid chromatography. A. Fraction 2. Capillary column Dexsil 300. Initial temp. 90°C, 4°/min. B. Fraction 3. Capillary column Dexsil 300. Initial temp. 90°C, 4°/min. C. Fraction 4. Capillary column OV-1. Initial temp. 50°C, 3°/min. D. Fraction 6. Capillary column SE-30. Initial temp. 130°C, 4°/min.

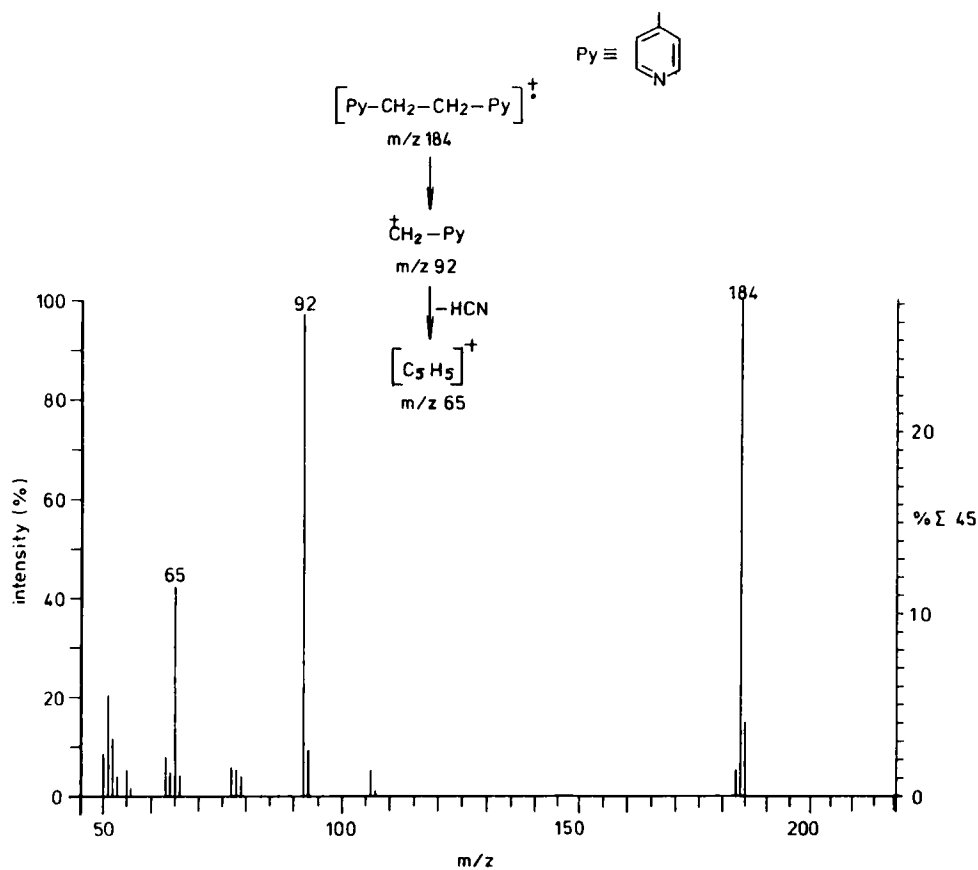


FIGURE 2 Mass spectrum and fragmentation pathways of compound 1.

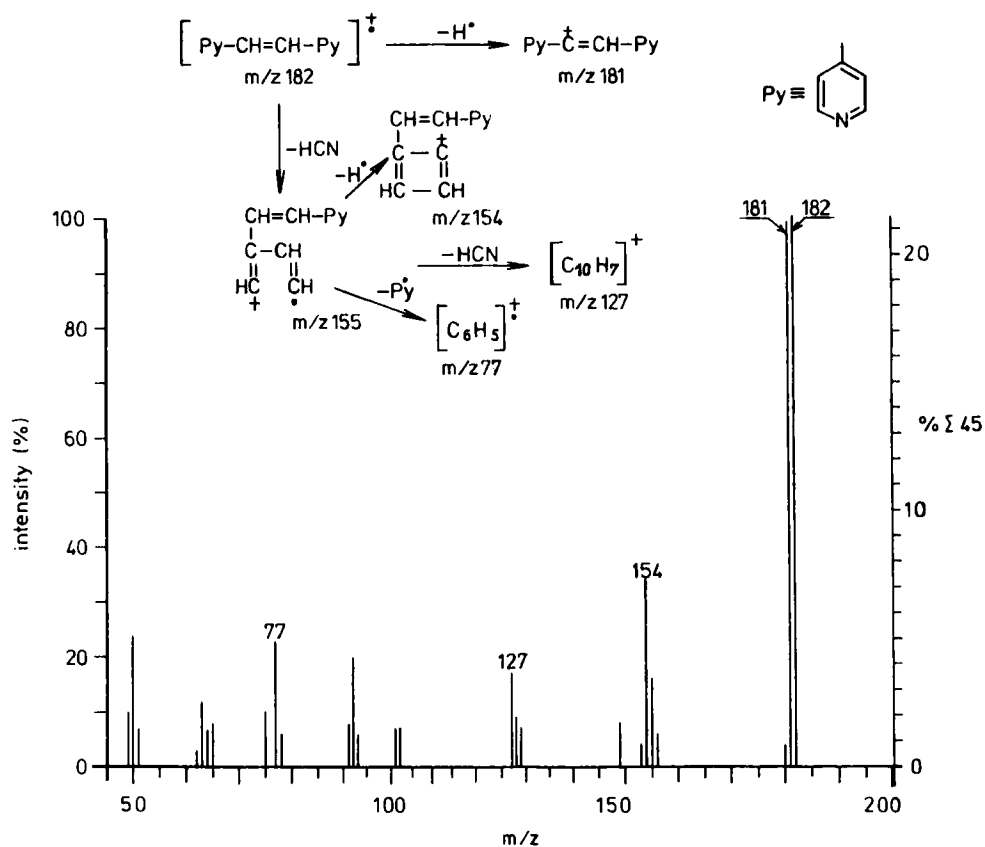


FIGURE 3 Mass spectrum and fragmentation pathways of compound 2.

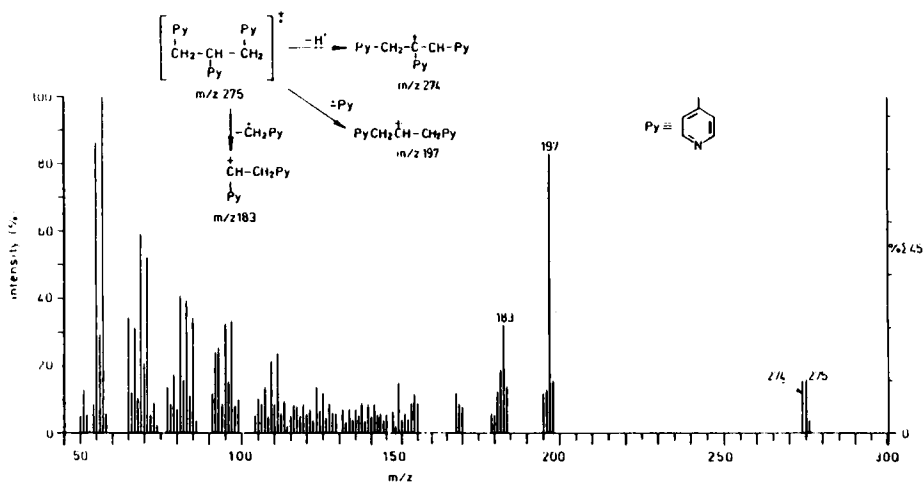


FIGURE 4 Mass spectrum and fragmentation pathways of compound 3.

After the separation of the reaction products by liquid chromatography six fractions were obtained whose constitution was then investigated by means of MS and GC-MS. The results are presented in Table II and in Figures 1A through 1D. The mass spectra and the proposed fragmentation patterns are shown in Figures 2 through 7. The proposed structures are based on these patterns.

Once the reaction products had been established, it was possible to investigate the reaction mechanism. To this aim time-variations in the concentrations of products were analysed. In Figure 8 the chromatograms of the mixtures of products obtained from the reaction carried out over 9, 22, and 34 hours are presented while in Figure

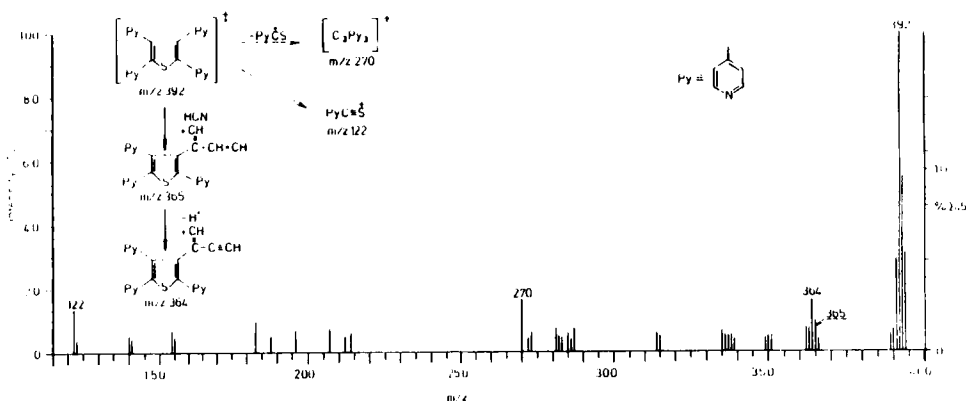


FIGURE 5 Mass spectrum and fragmentation pathways of compound 8.

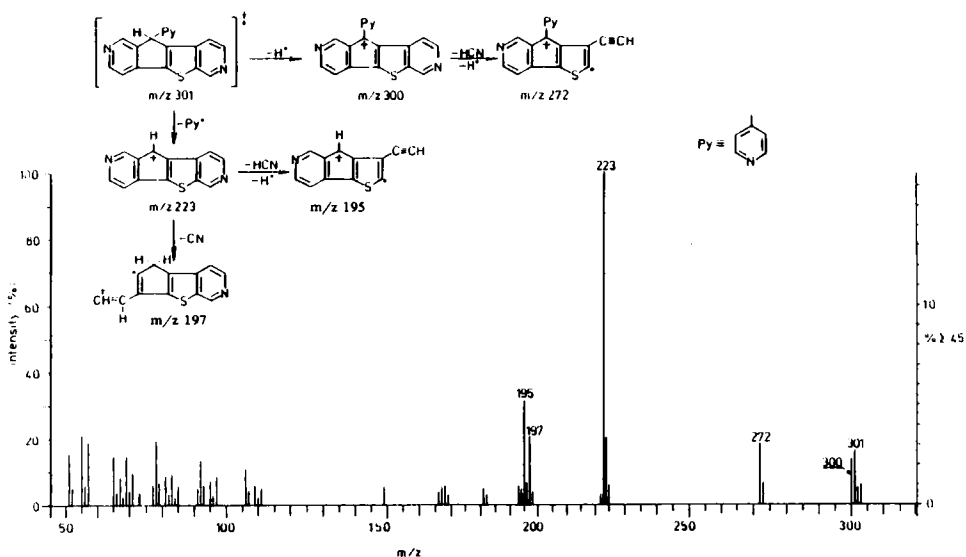


FIGURE 6 Mass spectrum and fragmentation pathways of compound 6.

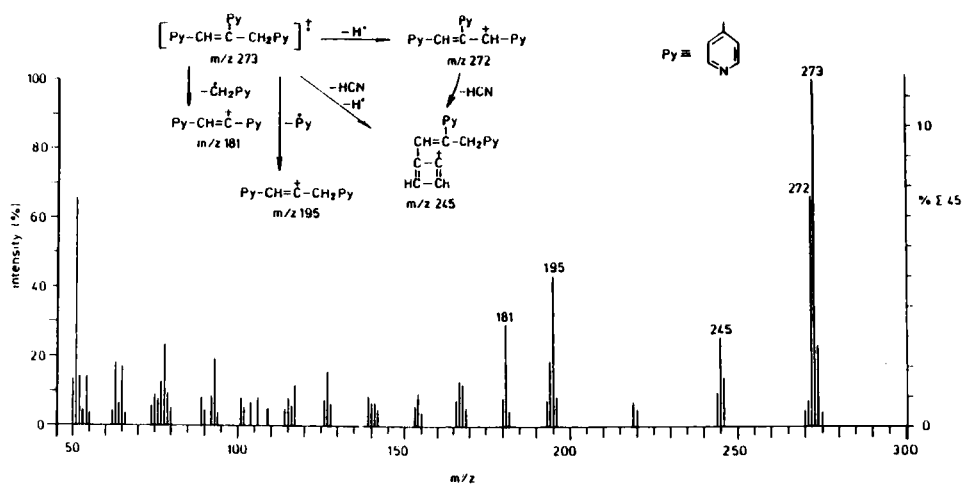


FIGURE 7 Mass spectrum and fragmentation pathways of compound 4 or 5.

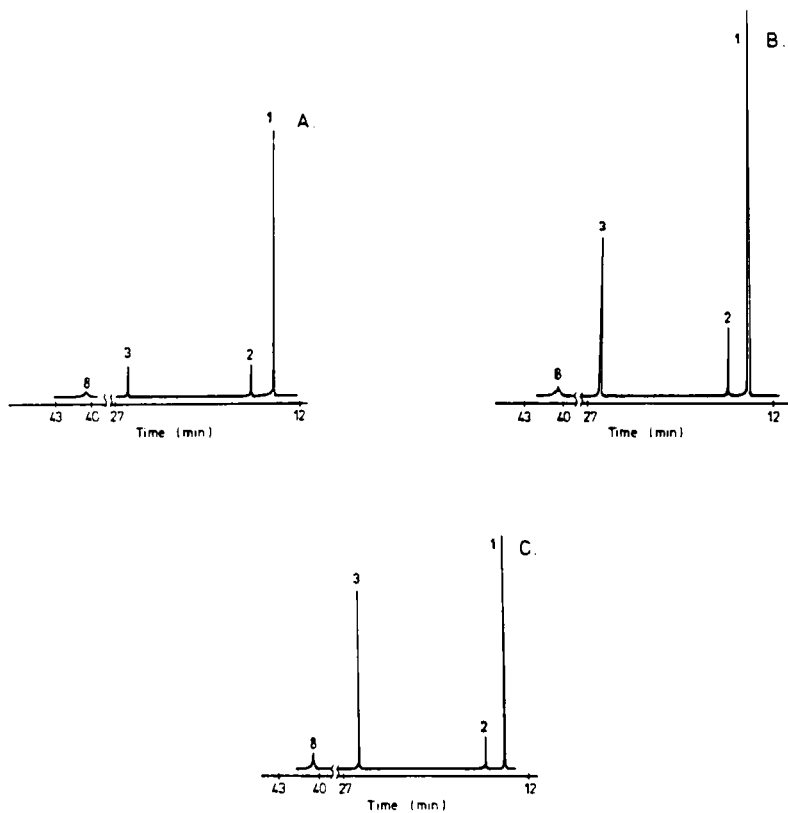


FIGURE 8 GC analysis of products of the reaction of 4-picoline with sulfur. A. after 9 hours, B. after 22 hours, C. after 34 hours. Capillary column Dexsil 300, initial temp. 90°C, 4°/min.

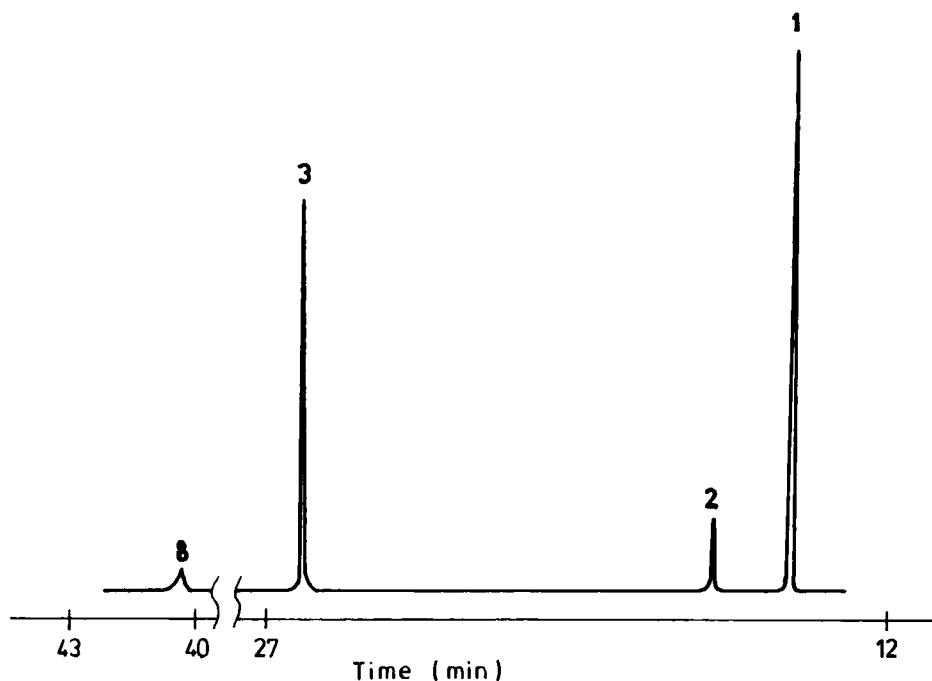


FIGURE 9 GC analysis of products of the reaction of 4-picoline with sulfur in the presence of sodium hydroxide. Reaction time 9 hours. Capillary column Dexsil 300, initial temp. 85°C, 4°/min.

9 the chromatogram of the mixture of products obtained after the reaction carried out over 9 hours, with the admixture of sodium hydroxide.

The intensity of each peak was integrated thus enabling determination of the relative amounts of products. The concentration of 1,2-di[4-pyridyl]-ethane was arbitrarily assumed to be 100%. The variation of all concentrations with time was also determined. The results are presented in Table III.

TABLE III

Time-variation of the concentration of products of the reaction of sulfur with 4-picoline. Concentration of di-[4-pyridyl]ethane equals to 100%

| Time [hr.] | Compound | | |
|---------------|----------|------|-----|
| | 2 | 3 | 8 |
| 9 | 12.0 | 11.0 | 1.7 |
| 22 | 17.5 | 40.0 | 5.0 |
| 34 | 16.0 | 83.0 | 8.0 |
| 9* | 12.0 | 72.0 | 6.0 |

*Reaction with a catalytic amount of sodium hydroxide.

DISCUSSION

Our initial analysis provided the identification of five compounds, Table I. The chemical constitution of four of them has been established by means of the GC-MS method, Fig. 2–5. They are 1,2-di[4-pyridyl]-ethane [1], 1,2-di[4-pyridyl]-ethene [2], 1,2,3-tri[4-pyridyl]-propane [3], tetra[4-pyridyl]-thiophene [8]. The formation of these compounds was proposed by H. I. Thayer and B. B. Corson¹³ who determined their chemical structure by chemical methods and elemental analysis.

Liquid chromatography, applied by us for the initial separation of the products, enabled us to remove tars and to determine the presence of three additional compounds. Their concentration was low, therefore they were not seen in the mass spectrum of the mixture. The results of the separation are presented in Table II and in Figure 1.

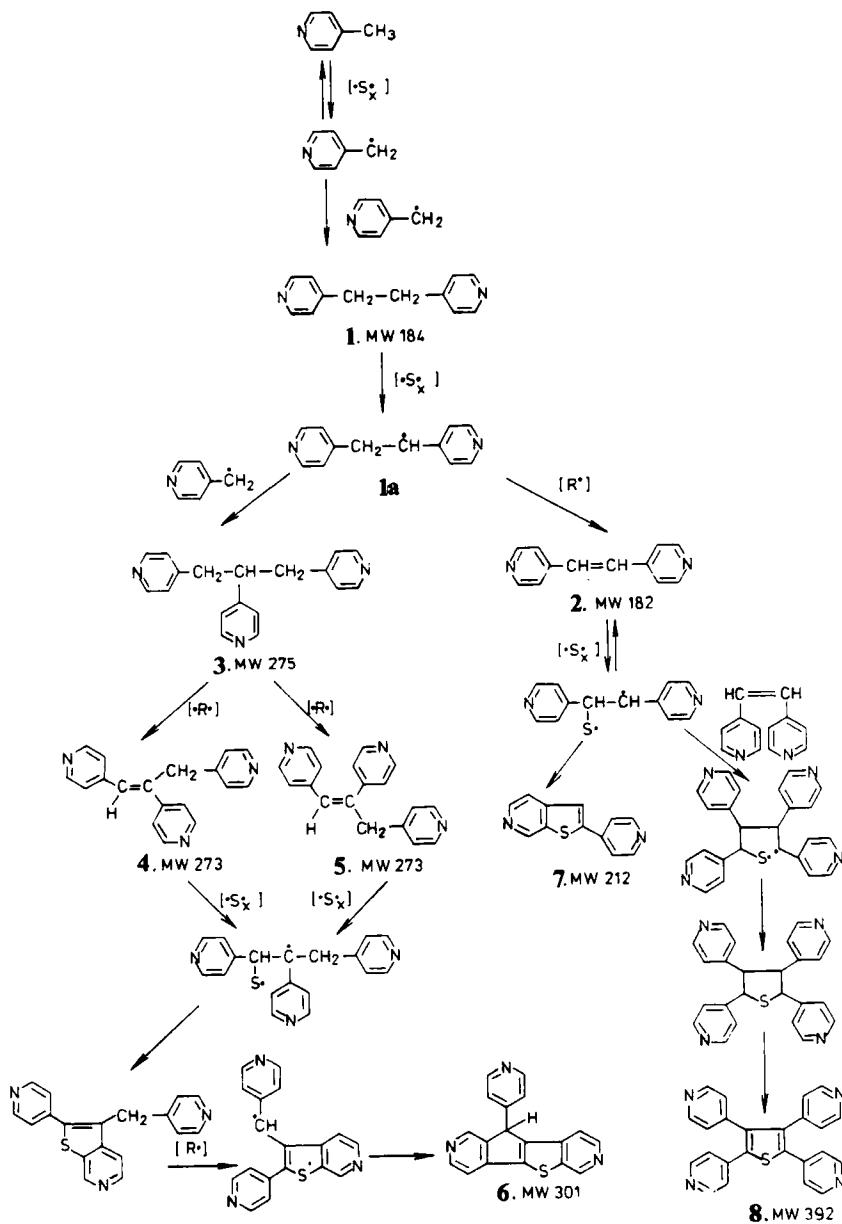
Fraction 1 contains a small amount of a compound of molecular weight equal to 301. The mass spectrum, Figure 6, is characterised by the intensive ion of m/z 223 and moderately intensive ions m/z 300, 272, 197 and 195. Two fragmentation paths, namely the M-1 and M-78 ones are competitive and should take place on the same atom since their secondary fragmentations correspond only to eliminations typical of a pyridine system. Having accounted for the chemical precursors and the mass spectrum, we propose the structure which is 10-[4-pyridyl]-pyrido-[3'4'':5',4']cyclopenta[2',3':4,5]thieno[2,3-c]pyridine.

Fraction 4 [Figure 1C], apart from a small amount of 8, contains two so far unknown compounds. They are characterized by the same molecular weight 273 and identical mass spectra [Figure 7] so that they should be isomers. The presence of two isomers with their masses differing by two mass units from a compound whose structure determination suggested tri[4-pyridyl]-propane, as well as the fragmentation indicating the presence of the pyridine rings suggests that the unknown compounds may be attributed the formulas of the E- and Z-isomers of 1,2,3-tri[4-pyridyl]-propene [4 and 5]. It is likely that the less abundant compound characterized by the shorter retention time [Figure 1C] might be the sterically less stable isomer Z [5].

Unfortunately, we did not succeed in isolating and taking mass spectra of compound 7 [Table I]. Its suggested constitution [6-[4-pyridyl]-thieno[3,2-c]pyridine] was based on the composition, which was determined by means of the high resolution MS [found 212.0405 amu, calculated 212.0407 amu]. This assumption may be supported by the fact that the reaction of sulfur with toluene results in the analogous 2-phenyl-benzo[b]thiophene.¹⁴

The studies of the time-dependence of the concentration of the main products [Figure 8] have revealed that the concentration of the products 1 and 2 initially increases and then decreases. The concentration of the products 3 and 8 increases continually. Their contribution relatively to 1 increases while the relative contribution of 2 practically remains unchanged [Table III]. Both facts and also the type of the products permits us to conclude that the reaction of 4-picoline with sulfur, with no oxygen present is a consecutive-parallel process, most likely of radical character, in accordance with Scheme 1.

The radicals $C_5H_4NCH_2^{\cdot}$ resulting from the action of sulfur on picoline, recombine to give di[4-pyridyl]-ethane [1], which in turn in the reaction with the radical



SCHEME 1 Reaction of 4-picoline with elemental sulfur.

$·S_x$ gives the radical **1a**. The latter recombines with $C_5H_4NCH_2·$ to give **3**. The radical **1a** in the presence of sulfur or other radicals may also undergo dehydration giving olefine **2**. The above mechanism can serve as a pattern for another one, explaining in a similar way the formation of the isomers **4** and **5** from compound **3**. The unsaturated products **2**, **4** and **5** undergo the reaction with sulfur to give dehydrogenated and sulfur-containing cyclic products **6**, **7** and **8**.

Thus, we have found that the course of the reaction of sulfur with picoline is similar to that of the reaction of sulfur with toluene.¹⁴ The fact that the former one takes place at slightly milder conditions [b.p. of 4-picoline is 145°C while the temperature of the reaction with toluene is 200°C] may be explained if the role of a tertiary amine in the activation of sulfur is accounted for. The tertiary amine mediates in the formation of a donor-acceptor complex which is more active than cyclo-S₈.¹⁵ On the other hand, such amine may bind evolving hydrogen sulfide forming the thiophilic HS⁻ which facilitates opening of the S₈ ring.¹⁶ The role of sodium hydroxide also is rationalized in the activation of sulfur due forming sodium sulfide with the evolving hydrogen sulfide, which is low soluble under the reaction conditions. Sodium sulfide is a very thiophilic agent¹⁵ and therefore disrupts the sulfuric ring easily. The resulting polysulfide undergoes thermolysis much faster than cyclo-S₈. Presumably sodium hydroxide has no directional property favouring any particular reaction course in contrast to the opinion of Thayer and Corson.¹³ Rather, it increases the reaction speed resulting in faster consumption of intermediate products in a chain of consecutive reactions illustrated in Scheme 1. Reactions leading to the formation of the thiophene ring are irreversible, hence tetra[4-pyridyl]-thiophene is cumulated. This conclusion is confirmed by the composition of the reaction products after 9 hours [Figure 9], which is similar to that obtained after 34 hours with no NaOH [Figure 8].

By reaction of 4-picoline with elemental sulfur two groups of products are formed: heterocycles containing nitrogen and heterocycles containing both nitrogen and sulfur. The formation of products **6**, **7** and **8** conforms to the suggestion that naturally occurring products containing nitrogen and sulfur could be formed by interactions of elemental sulfur with nitrogen-organic compounds.⁴ Under anaerobic and reductive conditions which preclude catagenesis, nitrogen-organic components of precursors of oil are stable, yet submitted to sulfurization which should lead to the formation of oils with a large amount of asphalts and tars.

EXPERIMENTAL

The reaction of sulfur with 4-picoline. To 3.2 g [0.1 mole] of elemental sulfur 20 ccm [0.2 mole] of 4-picoline were added and the mixture was refluxed under argon atmosphere for 48 hours. In order to investigate an effect of bases on the course of the reaction, a separate run was carried out, in which 120 mg [3×10^{-3} mole] of sodium hydroxide were added to the reaction mixture. In both cases samples were taken after 9, 22 and 34 hours. After cooling, the excess of the liquid material was evaporated under vacuum or in a nitrogen stream at room temperature and all reaction products were separated from an excess of sulfur by the extraction of the remaining solid with anhydrous ethanol-benzene [5 : 1]. 0.74 g [25%] of sulfur were recovered in the noncatalysed reaction.

In order to study an effect of time on the progress of the reaction, 0.25 ccm aliquots of the solution were taken in the course of the reaction and an excess of the substrates was removed. The mixture of products was dissolved in 5 ccm of anhydrous ethanol-benzene [5 : 1]. The injected sample volumes [GC] were identical after 9, 22 and 34 hours and amounted to 0.8 μ l.

Liquid chromatography. The products were chromatographed on the MN-Kieselgel'finer than 200 mesh on a column 73 \times 2 cm with the system benzene-methanol [10 : 1]. Before the separation, the column was conditioned with the same system. The products of the liquid chromatography were investigated by means of GC, MS and GC-MS methods.

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 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 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 [GC]. Separations were carried out with the Varian Aerograph model 1400 gas chromatograph adapted for work with capillary columns. The columns were coated with Dexsil 300, SE 30 or 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 $25 \text{ cm}^3 \text{ min}^{-1}$. The sensitivity employed equalled to $2 \times 10^{-12} \text{ AmV}^{-1}$.

REFERENCES

1. H. Schumann, Reactions of elemental sulfur with inorganic, organic and metal-organic compounds, in *Sulfur in Organic and Inorganic Chemistry*, vol. 3, pp. 1–18, A. Senning, Ed., Marcel Dekker Inc., New York, 1972.
2. M. G. Voronkov, *Reaktsii Sery s Organicheskimi Soedinenami*, Izd. Nauka, Sibirskoe Otdelene, Novosibirsk, USSR, 1979.
3. J. de Roo, G. W. Hodgson, *Chem. Geol.*, **22**, 71 (1978).
4. I. V. Gontcharov and L. N. Lebedeva, *Geokhimiya*, **12**, 1873 (1984).
5. D. J. Casagrande and N. Ng, *Nature*, **282**, 598 (1979).
6. D. J. Casagrande, G. Idowu, A. Friedman, P. Rickert, K. Siefert and D. Schlenz, *Nature*, **282**, 599 (1979).
7. Y. Mehmet, "The occurrence and origins of sulfur compounds in crude oils—a review", *Alta. Sulfur Res. Ltd., Q. Bull.*, **8**[1], 1 (1971).
8. A. G. Douglas and B. J. Mair, *Science*, **147**, 499 (1965).
9. W. E. Hanson, Origin of petroleum, in *Chemical Technology of Petroleum*, W. A. Gruse and D. R. Stevens, Eds., McGraw-Hill, New York, Chapter 5 (1971).
10. J. F. McKay, J. H. Weber and D. R. Lathan, *Anal. Chem.*, **48**, 891 (1976).
11. L. R. Snyder, *Anal. Chem.*, **41**, 1084 (1969).
12. P. Burchill, A. A. Herod and E. Pritchard, *Fuel*, **62**, 20 (1983).
13. H. I. Thayer and B. B. Corson, *J. Am. Chem. Soc.*, **70**, 2330 (1948).
14. K. Przewocki, E. Malinski and J. Szafranek, *Chemical Geology*, **47**, 347 (1984).
15. R. Mayer, *Zeitschrift für Chemie*, **13**[9], 321 (1973).
16. P. D. Bartlett, E. F. Cox and R. E. Davis, *J. Am. Chem. Soc.*, **83**, 103 (1961).