

Maria Curie-Skłodowska University

WAWRZYNIEC PODKOŚCIELNY\*. WANDA KOWALEWSKA\*

*The synthesis, structure and properties  
of 2,3,5,6-tetramethyl-benzene-1,4-dithiol  
and some of its derivatives*

---

Synteza, struktura i właściwości 2,3,5,6-tetrametylobenzeno-1,4-ditiolu  
oraz jego niektórych pochodnych

A systematic study related to the synthesis, properties and application of the sulfur containing organic compounds has been carried out in our laboratory for over 15 years. The objects of our special interest were the dithiol derivatives of the aromatic hydrocarbons, used as monomers to the synthesis of macromolecular compounds and, to a less degree, as the output products to the synthesis of the compounds characteristic due to their biological activity. Two kinds of dithiols were used to the synthesis of polymers.

The first kind of monomers (of a strong acidic character) were the dithiol derivatives of biphenyl, diphenylmethane, diphenylsulfide, diphenylsulfone and 2,3,5,6-tetramethylbenzene. Another kind of dithiols (of a smaller acidity but close to that of the phenols) were bis-(mercaptomethyl) – derivatives of benzene, toluene, xylenes, trimethylbenzenes, tetramethylbenzene, biphenyl, naphthalene, diphenylsulfide, diphenylsulfone, diphenylmethane as well as benzophenone. The above mentioned dithiols were used to the synthesis, of polymers containing a sulfur atom in the main chain, such as polythioesters, polysulfides and thioetheroglycidyl resins. The polythioesters, received in the result of poly-

---

\* Department of Organic Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Plac M. Curie-Skłodowskiej 3, Poland.

condensation in a low or high boiling solvent and, especially, by the interfacial polycondensation.

An example of a polythioester, received according to the above mentioned methods of polycondensation, can be the products of reaction between 2,5-bis-mercaptomethyl-1,4-dimethylbenzene and some aliphatic and isomeric phthaloyl dichlorides [1].

The polysulfides were received from 4,4'-bis(mercaptomethyl)-biphenyl and dibromoalkanes, or bis(chloromethyl)aryls. The reaction had been carried out in the presence of KOH in a polar solvent of a high boiling temperature, best of all in dimethyl acetamide (DMAC) [2].

An example of thioetherglycidyl resins can be the products of the reaction between bis (4-mercaptomethylphenyl) ether and bis (4-mercaptomethylphenyl) methane and epichlorohydrine which takes place during the process of a hetero-phase condensation in the alkaline solution (NaOH) in water or isopropanol [3].

The aromatic dithiols with the SH groups directly connected to the aromatic ring or via the groups of  $-\text{CH}_2-$  have been used to the synthesis of certain compounds of a potential biological activity. In the condensation reaction of the natrium salts of various dithiols in the water/acetone medium with 2-chloro-4,6-dimethoxy- or 2-chloro-4,6-diphenoxy-S-triazine we received more than a dozen of new compounds; among those newly received compounds the 4,6-methoxy-derivatives of s-triazine with bis(4-mercaptophenyl) sulfides and 1,4-bis-(mercaptomethyl) tetramethylbenzene show some fungicidal properties [4].

The main purpose of the present article is to present an investigation related to the synthesis and the structure determination as well as properties of 2,3,5,6-tetramethylbenzene-1,4-dithiol and its application to the synthesis of the corresponding dithioacids and dithioethanol, and in the future, to the synthesis of polyesters and polyurethanes. It should be stressed in this place that the dithiol had already been previously the object of our interest. The condition of their synthesis had been elaborated, its fundamental physicochemical properties had been determined and it was successfully used to the synthesis of polythioesters by the polycondensation with the aromatic and aliphatic acid chlorides [5].

Presently due to the fact of application of 2,3,5,6-tetramethyl-benzene-1,4-dithiol to the synthesis of the monomers of the kind of dithioacids and dithioalcohols, it seems indispensable to describe the unpublished procedure of its synthesis, a clear determination of its structure and properties and the publication of the related bibliographic information.

2,3,5,6-Tetramethylbenzene-1,4-dithiol was received in 1979 by R a s c h [6] with the help of an indirect method by using tetramethylquinone as the out-

put substance which with the dimethylthiocarbamyl chloride ( $\text{Me}_2\text{NCSCl}$ ) in the temperature of  $200^\circ\text{C}$  in the quinoline solution reacted to give the tetramethyl-p-phenylene-0,0'-bis(dimethylthio)-carbamate.

The 0,0'-diester in the nitrogen atmosphere at about  $280^\circ\text{C}$  changes into the tetramethyl-p-phenylene-S,S'-bis(dimethylthiocarbamate). The hydrolysis of the above S,S'-diester (KOH in the water/pyridine/ /methanol solution) in the nitrogen atmosphere resulted in receiving the tetramethylbenzene-1,4-dithiol of the melting temperature about  $195\text{--}198.5^\circ\text{C}$ . The structure of this compound has been confirmed with the help of the elementary analysis as well as by the spectral method ( $^1\text{H-NMR}$  in relation to TMS in  $\text{CDCl}_3$ ). The single signals at 2.37ppm were attributed to the hydrogen atoms in four  $\text{CH}_3$  groups, and at 3.12 to the protons of the two SH groups. It witnesses in favour of a symmetrical composition of the compound and the situation of the two SH groups in position 1,4.

Because of the toilsome and time consuming method of synthesis of the above mentioned compound, and due to a difficulty to get the output tetramethylquinone we tried to find an indirect method in order to receive the tetramethylbenzene-1,4-dithiol. In order to do so the tetramethylbenzene was sulphonated with the help of 25% oleum. This way the corresponding disulphonic acid was received and, then, separated in the form of its disodium salt. In the reaction with  $\text{PCl}_5$  the disodium disulphonate produced the disulphochloride. This product in reaction with  $\text{SnCl}_2$  in acetic acid saturated with dry HCl produced the desired tetramethylbenzene-1,4-dithiol of a melting point of  $201^\circ\text{C}$  ( $195\text{--}198^\circ\text{C}$  according to the literature [5]).

It should be stressed that already in 1886 J a c o b s o n [7] obtained the tetramethyldisulphonic acid in the reaction of the Nordhausen sulphuric acid with 2,3,5,6-tetramethylbenzene; he characterized the received product by its diamide of a melting point  $310^\circ\text{C}$  (583K). The diamide and also (independently) the disulphonic acid while heated in the temperature  $170^\circ\text{C}$  disintegrated, producing in the first mentioned case the 2,3,5,6-tetramethylbenzene, ammonia gas and sulphuric acid, and in the second case the hydrocarbon and sulphuric acid. The result of the above experiments made it possible to formulate a conclusion: the substitution of the sulphonic groups in 2,3,5,6,-tetramethylbenzene (in reaction with oleum) takes place in position 1,4.

Our IR investigation of the structure, and especially the  $^1\text{H-NMR}$  data for the product, received in the reaction of the corresponding disulphochloride and diamide, confirmed Jacobsen's suggestion. The results of  $^1\text{H-NMR}$  analysis — one signal at 2.73 ppm for the protons of the 4  $\text{CH}_3$  groups of the disulphochlo-

ride, and for the amide, two singlets at 2.50 ppm for the protons of the 4 methyl groups, and at 7.50 ppm for the protons of  $\text{NH}_2$  groups, confirm the symmetrical structure of the system and the substitution in position 1,4.

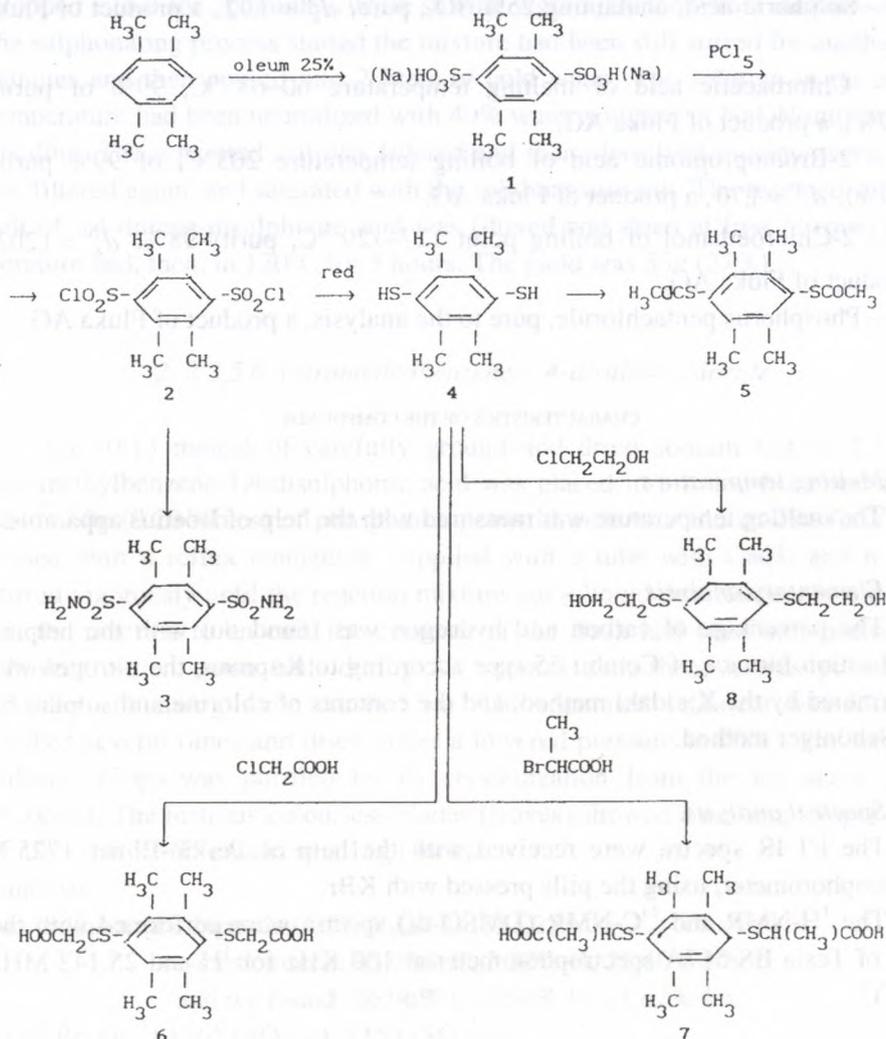
Attention should be paid to the work by A. K o e b e r g - T e l d e r and H. C e r f o n t a i n (1982) [8] where the authors presented a method of receiving the 2,3,5,6-tetramethyl-1,4-disulphonic acid. The structure of the acid (in the form of its dipotassium salt) was confirmed without any doubts by the  $^1\text{H-NMR}$  analysis (one signal at 3.17 ppm for four  $\text{CH}_3$  groups).

The dipotassium salt was received in a two-stage synthesis. 2,3,5,6-Tetramethylbenzene (20g) was treated at first with 98.4% sulphuric acid for 3hrs. The separated free 1-sulphonic acid (6g) reacted in the second stage with 107%  $\text{H}_2\text{SO}_4$  for 20 hrs. The disulphonic acid was finally separated as its dipotassium salt (2.9g, about 5.3% of the theoretical yield) by the reacting of the free acid with 10% ethanolic solution of KOH. Such a two-stage method lasting many hours and not assuring any good yield was not a satisfactory one in our opinion.

While carrying out the sulphonating reaction of 2,3,5,6-tetramethylbenzene we took into consideration the fact of J a c o b s e n ' s reaction [7] connected with a migration of the alkyl group in the tetramethyl-1-sulphonic acid which was formed in the first stage of the synthesis, and being in contact with the sulphuric acid in the reaction mixture. The migrations of the methyl groups in Jacobsen's reaction can be classified into two main kinds: an intermolecular, taking place within one and the same molecule, and an intermolecular one, occurring between two different molecules; both of them are connected with the isomerization and disproportionation of products. In consequence we paid special attention to the interpretation of the results of the spectral analysis which arise no doubts. The disulphonic acid (1) was characterized by its transformation into the disulphochloride (2) and diamide (3). The disulphochloride was reduced with  $\text{SnCl}_2$  in acetic acid saturated with dry gas HCl and the dithiol (4) was received. The dithiol was transformed into the dithioacyl compound (5) and the investigation of its structure was also carried out. In order to receive the monomers, the 2,3,5,6-tetra-methylbenzene-1,4-dithiol in the water solution of 20% NaOH was condensed with chloroacetic and  $\alpha$ -bromopropionic acid, and, the corresponding acids were received, i.e. 2,3,5,6-tetramethylbenzene-1,4-dithioacetic acid (6) and -benzene-1,4-di- $\alpha$ -thiopropionic one (7). As a result of the reaction of chloroethanol in the solution of 20% NaOH with dithiol we also received 2,3,5,6-tetramethylbenzene-1,4-dithioethanol (8). The experiments we carried out are represented on the scheme.

The basic physicochemical properties of the newly received compounds have been determined. Their structure was confirmed by the results of the elementary analysis and by the spectral analysis in the infrared area and  $^1\text{H-NMR}$  as well as  $^{13}\text{C-NMR}$  analysis for the dithiol.

## Scheme



## EXPERIMENTAL

## MATERIALS

- 1,2,4,5-Tetramethylbenzene of melting point 78–80 °C and 99% of purity (=99%), a product of Fluka AG.
- Sulphuric acid, containing 25% SO<sub>3</sub>, pure,  $d_4^{20} = 1.92$ , a product of Fluka AG.
- Chloroacetic acid of melting temperature 60–63 °C, 99% of purity (=99%), a product of Fluka AG.
- 2-Bromopropionic acid of boiling temperature 203°C, of 99% purity (=99%),  $d_4^{20} = 1.70$ , a product of Fluka AG.
- 2-Chloroethanol of boiling point 127–129 °C, purity-98%,  $d_4^{20} = 1.202$ , a product of Fluka AG.
- Phosphorus pentachloride, pure to the analysis, a product of Fluka AG.

## CHARACTERISTICS OF THE COMPOUNDS

*Melting temperature*

The melting temperature was measured with the help of Böetius apparatus.

*Elementary analysis*

The percentage of carbon and hydrogen was found out with the help of combustion furnace of Combii 55 type according to Kupman; the nitrogen was determined by the Kjeldahl method, and the contents of chlorine and sulphur by the Schöniger method.

*Spectral analysis*

The FT-IR spectra were received with the help of Perkin-Elmer 1725 X spectrophotometer, using the pills pressed with KBr.

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) spectra were performed with the help of Tesla BS-567A spectrophotometer at 100 KHz for <sup>1</sup>H and 25.142 MHz for <sup>13</sup>C.

### 1. *Sodium salt of 2,3,5,6-tetramethylbenzene-1,4-disulphonic acid*

In a round-bottomed three-necked flask, supplied with a mechanical stirrer, a dropper and a reflux condenser, 53g (0.4 moles) of carefully powdered 2,3,5,6-tetramethylbenzene was placed and 300cm<sup>3</sup> of 25% oleum had been dropped into it for 20 minutes while stirring vigorously the whole mixture. After the sulphonating process started the mixture had been still stirred for another 20 minutes and then poured into 2 liters of cold water. The solution in the room temperature had been neutralized with 40% water solution of NaOH until it was alkaline. The separated salt was filtered and then, dissolved in some warm water, filtered again, and saturated with the solid sodium salt. The received sodium salt of 1,4-durene-disulphonic acid was filtered and dried at first in room temperature and, then, in 120°C for 5 hours. The yield was 35g (27%).

### 2. *2,3,5,6-Tetramethylbenzene-1,4-disulphochloride*

35g (0.13 moles) of carefully ground and dried sodium salt of 2,3,5,6-tetramethylbenzene-1,4-disulphonic acid was placed in a round-bottomed flask where 60g (0.29 moles) of phosphorus pentachloride was added. The flask was closed with a reflux condenser, supplied with a tube with CaCl<sub>2</sub> and it was stirred vigorously until the reaction mixture got a liquid consistence. In order to put the reaction to an end, the contents of the flask had been still heated on a boiling water steam bath during 30 minutes and, then, it was poured to a beaker containing some crushed ice. The separated sediment was filtered, washed several times and dried under a lowered pressure in 60°C. The sulphochloride (20g) was purified by its crystallization from the icy acetic acid (120cm<sup>3</sup>). The lustrous colourless blades (leaves) showed a melting temperature of 167–168 °C. The yield was 15g (44%).

Analysis:

According to the formula C<sub>10</sub>H<sub>12</sub>S<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub> (331.25)

we calculated: 36.06% C, 3.32% H, 21.40% Cl;

and we found: 36.06% C, 3.54% H, 21.62% Cl.

IR (KBr, cm<sup>-1</sup>) 1361 (SO<sub>2</sub>, v); 1153 (SO<sub>2</sub>, v).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm) 2.73 (s-12H; 4xCH<sub>3</sub>).

### 3. 2,3,5,6-Tetramethylbenzene-1,4-disulphonylamide

1 g (0.003 mole) of 2,3,5,6-tetramethylbenzene-1,4-disulphochloride was placed in a 100cm<sup>3</sup> beaker and treated with 40cm<sup>3</sup> of 25% water solution of ammonia and, then, evaporated on the steam bath to receive a dry residue. The received disulphonylamide (0.8g) was purified by crystallization from 45cm<sup>3</sup> of 40% ethanol, yielding 0.5g (57%) of colourless, lustrous blades (leaves) of a melting point 310°C.

Analysis:

For the formula C<sub>10</sub>H<sub>16</sub>S<sub>2</sub>O<sub>4</sub>N<sub>2</sub> (292.39)

we calculated: 9.5% N;

and we found: 9.5% N.

IR (KBr, cm<sup>-1</sup>) 3364 and 3273 (SO<sub>2</sub>NH<sub>2</sub>, v<sub>s</sub>); 1354 (SO<sub>2</sub>, v<sub>as</sub>); 1137 (SO, v<sub>s</sub>).

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm) 2.50 (s-12H; 4xCH<sub>3</sub>); 7.50 (s-4H; 2xNH<sub>2</sub>).

### 4. 2,3,5,6-Tetramethylbenzene-1,4-dithiol

In a round-bottomed three-necked flask supplied with a mechanical stirrer, a reflux condenser and a tube to introduce the HCl gas, 180g of SnCl<sub>2</sub>·2H<sub>2</sub>O and 640cm<sup>3</sup> of icy acetic acid was placed. The dry gas of HCl had been passing through the mixture until the stannic chloride (II) dissolved completely and, then, the whole mixture was cooled down to 0°C and, while stirring it, 17g (0.05 mole) of 2,3,5,6-tetramethylbenzene-1,4-disulphochloride was added. The cooling mixture was put aside and the stirring continued for 5 hours in room temperature. Then, the whole mixture had been warmed up to about 40–50 °C and the contents of the flask was poured to 64cm<sup>3</sup> of the concentrated hydrochloric acid. The separated dithiol was filtered off and washed with water and, then, dissolved in 500cm<sup>3</sup> of hot 20% water solution of NaOH. The solution was filtered again and acidified with a diluted (1:1) water solution of HCl. The separated sediment was filtered, dried in the air and purified by crystallization (10g) from cyclohexane (120cm<sup>3</sup>). Pale yellow well-shaped needles were received, they had a melting point of 201°C. The yield was 6g (60%).

Analysis:

For the formula C<sub>10</sub>H<sub>14</sub>S<sub>2</sub> (398.35)

we calculated: 60.55% C, 7.11% H, 32.40% S;

and we found: 60.33% C, 7.21% H, 32.48% S.

IR (KBr,  $\text{cm}^{-1}$ ) 2551 (S–H,  $\nu_s$ ); 715 (C–S,  $\nu_s$ ).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm) 2.35 (s-12H; 4x $\text{CH}_3$ ); 2.14 (s-2H; 2xSH).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , ppm) 19.41 (4x $\text{CH}_3$ ); 12.85 (4xC– $\text{CH}_3$ ); 132.8 (2xC–SH).

#### 5. 1,4-Diacetyl-thio-2,3,5,6-tetramethylbenzene

In around bottomed flask supplied with a reflux condenser 4g (0.02 mole) of 1,4-dimercapto-2,3,5,6-tetramethylbenzene, 40 $\text{cm}^3$  of acetic acid anhydride and two drops of concentrated sulphuric acid was placed. The whole mixture was heated on the boiling water bath during 30 minutes. After it was cooled, the separated sediment was filtered, washed with a small amount of water and dried out. 4g of 1,4-diacetyl-mercapto-2,3,5,6-tetramethylbenzene (4g) was crystallized from 50 $\text{cm}^3$  of ethanol. 3.4g (60%) of colourless, lustrous blades (leaves) was received; they melted in 167°C.

Analysis:

For the formula  $\text{C}_{14}\text{H}_{18}\text{S}_2\text{O}_2$

we calculated: 59.53% C, 6.42% H;

and we found: 59.71% C, 6.12% H.

IR (KBr,  $\text{cm}^{-1}$ ) 1354 ( $\text{COCH}_3$ ,  $\delta$ ); 1699 (C=O,  $\nu_s$ ); 626 (CS,  $\nu_s$ ).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm) 2.37 (s-12H; 4x $\text{CH}_3$ ); 2.39 (s-6H; 2x $\text{COCH}_3$ ).

#### 6. 2,3,5,6-Tetramethylbenzene-1,4-dithioacetic acid

4g (0.02 mole) of 2,3,5,6-tetramethylbenzene-1,4-dithiol was dissolved in 100 $\text{cm}^3$  of 20% water solution of NaOH. Then, while it had been vigorously stirred, a water solution of natrium chloroacetate was added to the mixture (the solution was prepared by neutralization of 5g (0.05 mole) of chloroacetic acid in 20 $\text{cm}^3$  of water). The reaction mixture was heated on a boiling water bath during 30 minutes and, then, it was allowed to stay in room temperature during 12 hours. The natrium salt of the dithioacetic acid was filtered off and dissolved in 100 $\text{cm}^3$  of hot water. While adding some diluted solution (1:1) of hydrochloric acid a sediment of the free acid separated; it was filtered, washed twice with water (2 x 30 $\text{cm}^3$ ) and dried. The raw product (6g) was purified by crystallization from 75% ethanol (40 $\text{cm}^3$ ). Colourless needles were received, they melted at 227°C. The yield was 4.5g (71%).

Analysis:

For the formula  $C_{14}H_{18}S_2O_4$

we calculated: 53.48% C, 5.77% H;

and we found: 53.50% C, 5.62% H.

IR (KBr,  $cm^{-1}$ ) 2995–2687 (OH,  $\nu_s$ ); 1698 (C=O).

$^1H$ -NMR (DMSO- $d_6$ , ppm) 2.56 (s-12H; 4xCH<sub>3</sub>); 3.32 (s-4H; 2xCH<sub>2</sub>COOH), 12.56 (s-2H; 2xCOOH).

### 7. 2,3,5,6-Tetramethylbenzene-1,4-dithio- $\alpha$ -methylpropionic acid

4g (0.02 mole) of 2,3,5,6-tetramethylbenzene-1,4-dithiol was dissolved in 50cm<sup>3</sup> of 20% water solution of NaOH and, while stirring it vigorously, a neutralized (with the solid NaHCO<sub>3</sub>) solution of 4.5g (0.054 moles) of  $\alpha$ -bromopropionic acid in 20cm<sup>3</sup> of water was added. The whole mixture was heated up in the boiling water bath during 20 minutes and, then, allowed to stay in room temperature during 12 hours. The separated sodium salt was filtered and, then, dissolved in 100cm<sup>3</sup> of water and acidified with some diluted (1:1) hydrochloric acid. The separated tiny crystalline sediment was filtered and dried. The received 2,3,5,6-tetramethylbenzene-1,4-bis(thio- $\alpha$ -propionic) acid was purified by crystallization from ethanol. It resulted in the form of colourless needles of melting point 168°C. The yield was 4.3g (63%).

Analysis:

For the formula  $C_{16}H_{22}S_2O_4$  (342.49)

we calculated: 56.11% C, 6.47% H;

and we found: 55.84% C, 6.20% H.

IR (KBr,  $cm^{-1}$ ) 2995–2550 (OH,  $\nu_s$ ); 1703 (C=O,  $\nu_s$ ).

$^1H$ -NMR (DMSO- $d_6$ , ppm) 2.52 (s-12H; 4xCH<sub>3</sub>); 1.25–1.32 (d-6H; 2xCH<sub>3</sub>), 3.30–3.45 (q-2H; 2xCH); 12.54 (s-2H; 2xCOOH).

### 8. 2,3,5,6-Tetramethylbenzene-1,4-bis(thioethanol)

In a three-necked round bottomed flask supplied with a mechanical stirrer, a reflux condenser and a dropper. 4g (0.02 moles) of 2,3,5,6-tetramethylbenzene-1,4-dithiol and 50cm<sup>3</sup> of 20% water solution of NaOH was placed. Then, while stirring vigorously the mixture, 5g (0.04 mole) of chloroethanol dissolved in 10cm<sup>3</sup> of ethanol had been dropped into it. The reaction mixture had been heated

on the boiling water bath during 30 minutes and, then, cooled down. The separated bis(thioethanol) (5g) was purified by crystallization from 48% ethanol (70cm<sup>3</sup>). The received product had a melting point of 156°C. The yield was 4g (70%).

Analysis:

For the formula C<sub>14</sub>H<sub>22</sub>S<sub>2</sub>O<sub>6</sub> (286.46)

we calculated: 58.70% C, 7.74% H;

and we found: 58.43% C, 7.35% H.

IR (KBr, cm<sup>-1</sup>) 3273 (OH, ν<sub>s</sub>); 1698 (C=O); 669 (C-S, ν<sub>s</sub>).

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm) 2.50 (s-12H; 4xCH<sub>3</sub>); 2.61–2.75 (t-4H; 2-CH<sub>2</sub>CH<sub>2</sub>-), 3.28–3.48 (q-4H; 2xCH<sub>2</sub>CH<sub>2</sub>OH); 3.79 (s-2H; 2xOH).

## REFERENCES

- [1] Podkościelny W., Szubińska S., *J. Appl. Polym. Sci.*, 32, 3277 (1996).
- [2] Podkościelny W., Tarasiuk B., *Angew. Makromol. Chem.*, 234, 145 (1996).
- [3] Charmas W., Podkościelny W., *J. Appl. Polym. Sci.*, 27, 1455, (1982).
- [4] Podkościelny W., Kowalewska W., Tarasiuk B., Rudź W., Maziarczyk H., Morytz B., Zimińska Z., *Przemysł Chemiczny*, 70/3, 113, (1991).
- [5] Podkościelny W., Kowalewska W., *J. Appl. Polym. Sci.*, 39, 1649, (1990).
- [6] Raasch M.S., *J. Org. Chem.*, 44, No 15, 2629 (1979).
- [7] Jacobsen O., *Ber. Deut. Chem. Ges.*, 19, 1209 (1886).
- [8] Koeberg-Telder A., Cerfontain H., *Reci. Trav. Chim., Pays-Bas*, 101, 41 (1982).

## STRESZCZENIE

Poprzez bezpośrednie sulfonowanie 2,3,5,6-tetrametylobenzenu za pomocą 25% oleum otrzymano kwas 2,3,5,6-tetrametylobenzeno-1,4-disulfonowy, który wyodrębniono w postaci soli disodowej. Sól disodową przez działanie PCl<sub>5</sub> przeprowadzono w nieopisany dotychczas 2,3,5,6-tetrametylobenzeno-1,4-disulfochlordek, który wykorzystano do syntezy odpowiedniego diamidu przez działanie stężonym roztworem amoniaku, a przez redukcję SnCl<sub>2</sub> do syntezy interesującego nas tetrametylobenzo-1,4-ditiolu.

Ditiol w reakcji z solami sodowymi kwasów chlorooctowego i alfa-bromopropionowego oraz z bezwodnikiem kwasu octowego i chloroetanolem przeprowadzono w kilka nowych związków.

Dla ditiolu i pozostałych związków dokonano jednoznacznego określenia struktury przy użyciu analiz elementarnej, spektralnej w podczerwieni i <sup>1</sup>H-NMR oraz dla ditiolu dodatkowo <sup>13</sup>C-NMR.

