# SULPHUR COMPOUNDS IN THE KEROSINE BOILING RANGE OF MIDDLE EAST DISTILLATES

# OCCURRENCE OF A BICYCLIC THIOPHENE AND A THIENYL SULPHIDE

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Abstract—A bicyclic thiophene, 1,4,4-trimethyl-4,5,6,7-tetrahydroisothianaphthene, and a thienyl sulphide, methyl 3, 4, 5-trimethyl-2-thienyl sulphide, have been isolated from a concentrate of sulphur compounds obtained in the refining of a Middle East kerosine. The structures of these compounds have been established.

In recent years numerous investigations have been carried out into the nature of sulphur compounds in petroleum, particularly in distillates. The major components present in the gasoline range are thiols, alkane sulphides and cyclic sulphides<sup>1-4</sup> whilst in the kerosine boiling range we have shown<sup>5,6</sup> the additional presence of polycyclic sulphides and alkylthiophenes. Confirmation of the presence of alkylthiophenes in the lower boiling distillates has been afforded by the work of the American Petroleum Institute Research Project 487 which has conclusively identified thiophene and its 2-methylderivative. Considerably less is known of the sulphur compounds in the higher boiling distillates, e.g. gas oil and lubricating oil, and attention is now being directed toward materials in this boiling range. Unpublished work in these laboratories indicates that these sulphur compounds are predominantly thiophenic in character and this observation is substantiated by the work of Lumpkin and Johnson<sup>8</sup> who conclude from mass spectrometric data that the predominant type of sulphur compound is based on the thianaphthene ring, as well as by the data reported by Drushell and Miller.<sup>9</sup> In addition it should be pointed out that Cook et al.<sup>10</sup> have isolated three sulphur compounds, possessing a thiophene ring from a Kuwait gas oil.

Examination of the fractions obtained by us from the kerosine extract tar oil previously described<sup>5,6</sup> has therefore been concentrated upon the higher boiling materials with particular reference to the thiophenic compounds and other nonaliphatic sulphur compounds in the hope that identification of individual compounds

<sup>&</sup>lt;sup>1</sup> R. Emmott, J. Inst. Petroleum 39, 695 (1953).

<sup>&</sup>lt;sup>2</sup> F. Challenger, Manuf. Chem. 25, 151 (1954).

<sup>&</sup>lt;sup>3</sup> C. J. Thompson, H. J. Coleman, H. T. Rall and H. M. Smith, Analyt. Chem. 27, 175 (1955).

<sup>&</sup>lt;sup>4</sup> H. J. Coleman, N. G. Adams, B. H. Eccleston, R. L. Hopkins, L. Mikkelsen, H. T. Rall, D. Richardson, C. J. Thompson and H. M. Smith, *Analyt. Chem.* 28, 1380 (1956).

<sup>&</sup>lt;sup>6</sup> S. F. Birch, T. V. Cullum, R. A. Dean and R. L. Denyer, *Industr. Engng. Chem.* 47, 240 (1955).
<sup>6</sup> S. F. Birch, T. V. Cullum and R. A. Dean, *Chemical and Engineering Data Series* 3, 359 (1958).
<sup>7</sup> C. J. Thompson, H. J. Coleman, L. Mikkelsen, D. Yee, C. C. Ward and H. T. Rall, *Analyt. Chem.* 28, 1384 (1956).

<sup>&</sup>lt;sup>8</sup> H. E. Lumpkin and B. H. Johnson, Analyt. Chem. 26, 1719 (1954).

 <sup>&</sup>lt;sup>9</sup> H. V. Drushell and J. F. Miller, Analyt. Chem. 30, 1271 (1958).
 <sup>10</sup> J. W. Cook, W. Carruthers and D. L. Woodhouse, Brit. Med. Bull. 14, 132 (1958).

may be of assistance in the examination of those present in the higher boiling ranges. As a result we have identified in the fractions boiling around 250° two sulphur compounds possessing structures of a type not previously identified in naturally occurring materials viz. 1,4,4-trimethyl-4,5,6,7-tetrahydroisothianaphthene (1) and methyl 3,4,5-trimethyl-2-thienyl sulphide (II). It must be appreciated that these compounds



have been isolated by a combination of physical and chemical methods from a spent refining agent but we believe<sup>5</sup> that they have survived unchanged from the original petroleum distillate.

The identification of the thienyl sulphide is, as far as we know, the first occasion on which it has been demonstrated that petroleum contains sulphur compounds possessing more than one sulphur atom per molecule, apart from vicinal disulphides, which appear to arise very largely if not completely from the oxidation of mercaptans during processing of the crude. The immediate implications of this discovery are quite apparent when it is realized that the tentative attempts to analyse higher boiling fractions have always been based on the assumption that only one sulphur atom is present per molecule. Further consequences, e.g. the effect on the stability of petroleum products and on desulphurization processes, must await an evaluation of the percentage contribution of this type of sulphur compound and further study of its chemistry. By analogy with the sulphides the discovery of the bicyclic thiophene is not surprising since there appears to be a tendency in the sulphur compounds for an increase in the number of rings per molecule to take place with increase in boiling point, rather than for the length of chains to increase. One interesting point in the structure of I is its striking analogy with the pyridine (III) and acid (IV) which have been isolated from Californian distillates<sup>11,12</sup> and its slight similarity to Vitamin A. These analogies may



be compared with those already pointed out for hydrocarbons and sulphur compounds<sup>6</sup> and may possibly be of some assistance in considerations of the origin of petroleum.

## Isolation and structure determination

The preparation of the fraction (XXVII b.p. 245-249°) has been previously described,<sup>5,6</sup> as has the extraction of this fraction with aqueous mercuric acetate solution to yield a sulphide fraction, which has been shown to consist of mono- and poly-cyclic sulphides, a solid acetoxymercurithiophene and an unextracted portion.

B. Shive, S. M. Roberts, R. I. Mahan and J. R. Bailey, J. Amer. Chem. Soc. 64, 909 (1942).
 W. O. Ney, W. W. Crouch, C. E. Rannefeld and H. L. Lochte, J. Amer. Chem. Soc. 65, 770 (1943).

The latter was assumed to consist of tetra-alkylthiophenes together with small amounts of aromatic hydrocarbons and oxygenated materials.<sup>5</sup> The acetoxymercurithiophene after crystallization to constant melting point analysed as the monoacetoxy mercuriderivative of a trialkylthiophene. However, analysis of the thiophene itself gave the formula  $C_{11}H_{16}S$  and this together with its high refractive index,  $n_{10}^{20}$  1.5393, suggested the presence, in the molecule, of a naphthene ring. Desulphurization of the thiophene was carried out by the normal technique<sup>6</sup> and the product and the original thiophene were examined by mass, infra-red, ultra-violet and proton magnetic resonance spectrometry. It was known, from a bromine number determination, that the desulphurization product contained an appreciable amount of olefinic material and gas-liquid chromatography indicated that this was 50 per cent of the mixture. Infra-red and proton magnetic resonance spectra demonstrated that the olefin had no hydrogen atoms attached to the doubly bonded carbon atoms and the mass spectrum confirmed that the olefin content was of the order of 50 per cent (assuming equal sensitivities for the olefin and the naphthene). Further information obtained was the presence of an  $\alpha$ -methyl group on the thiophene (m/e peak at 59), one hydrogen atom attached to the thiophene ring (proton magnetic resonance) and an indication of the presence of a gem-dimethyl group (infra-red doublet at 7.22  $\mu$ and 7.32  $\mu$ ) in the thiophene. The presence of this gem-dimethyl group in the desulphurization product was confirmed by the existence of a main band at 7.26  $\mu$  with shoulders at 7.22  $\mu$  and 7.32  $\mu$  in the infra-red spectrum of the naphthene, which was separated from the olefin by the Fluorescent Indicator Adsorption technique.<sup>13</sup>

From all these data it appeared probable that the thiophene possessed a methyl group and a hydrogen atom in the  $\alpha$ -positions and that a naphthene ring with a gem-dimethyl group was fused in the  $\beta$ -positions, but it was not possible to say whether this was a five-membered ring with three methyl substituents or a six-membered with two. This problem was resolved by comparison of the dehydrogenation of the naphthene with that of model compounds, when it was shown to behave as a six-membered ring with a gem-dimethyl group and to yield methane and ethyl-2,3-dimethylbenzene. Final proof of the structure (I), which was now clearly indicated was obtained by the synthesis of ethyl-2,3,3-trimethylcyclohexane (IX) and its identification with the naphthene formed on desulphurization of I. The synthesis of IX was carried out by normal procedures from 3,3-dimethyl-2,carbethoxycyclohexanone (V),<sup>14</sup> via 2,3,3-trimethylcyclohexanone (VI), ethyl-2,3,3-trimethylcyclohexanol (VIII) and ethyl-2,3,3-trimethylcyclohexenes (mixed olefins) (VIII).

The occurrence of the bicyclic thiophene suggested that a tetrasubstituted analogue might be present in the portion not extracted by mercuric acetate solution and this was accordingly investigated. Fractionation, by gradient elution chromatography on silica gel, gave appreciable separation and a pronounced refractive index peak  $(n_D^{20} \ 1.5600)$  occurred in the material eluted by a cyclohexane/benzene mixture. The sulphur content (32 per cent) of the fraction of this refractive index and the m/e ratio (172) of a large peak in the mass spectrum suggested the presence of a thienyl sulphide. Gas-liquid chromatographic and infra-red spectroscopic data were obtained, the former suggested that one component accounted for 70-80 per cent of the fraction

<sup>&</sup>lt;sup>18</sup> ASTM Standards on Petroleum Products and Lubricants (with Related Information), D. 1319-56T. American Society for Testing Materials, Philadelphia 3, Pa. (1956).

<sup>&</sup>lt;sup>14</sup> U. Steiner and B. Willhalm, *Helv. Chim. Acta* 35, 1752 (1952). 10A-(4 pp.)

but no conclusion could be drawn from the latter. Examination of the desulphurization product by gas-liquid chromatography and mass spectrometry demonstrated that it was a mixture of a C<sub>7</sub> paraffin and olefin possibly 2,3-dimethylpentane or 3-methylhexane and 2,3-dimethylpentene-1. Since the thienyl sulphide was probably tetra-substituted (unreactive toward mercuric acetate solution) the only two feasible compounds that could satisfy these requirements appeared to be methyl 3,4,5-trimethyl-2-thienyl sulphide (II) and methyl 2,4,5-trimethyl-3-thienyl sulphide and these were accordingly synthesized. Comparison of the infra-red spectra of these compounds with that of the fraction  $n_D^{20}$  1.5600 showed that the compound present was II, the only significant adsorption present in the spectrum not accounted for by this compound (13.55  $\mu$  and 14.31  $\mu$ ) being attributable to aromatic hydrocarbons.

The syntheses of the two thienyl sulphides also followed normal procedures, from 2,3,4-trimethylthiophene and 2,3,5-trimethylthiophene.

#### **EXPERIMENTAL\***

Spectra. The infra-red<sup>†</sup> spectra were determined on a Grubb Parsons Double Beam Recording Infra-red Spectrometer; the ultra-violet spectra<sup>†</sup> on a Carey Recording Spectrophotometer Model 11, the mass spectra on a Metropolitan Vickers M.S.2. Mass Spectrometer and the nuclear magnetic resonance spectra on a Varian Nuclear Magnetic Resonance Spectrometer.

#### Isolation and characterization of the bicyclic thiophene (I)

The crude acetoxymercurithiophene isolated from fraction XXVII of the tar oil, b.p. 245-249<sup>-6.6</sup> was crystallized from acetone and methanol, m.p. 163-165°. A total of 38.5 g of pure derivative was obtained (Found: C, 35.8; H, 4.2; S, 7.7. C<sub>1s</sub>H<sub>18</sub>O<sub>1</sub>SHg requires: C, 35.6; H, 4.1; S, 7.3%). A suspension of this derivative in 5 N hydrochloric acid was refluxed and the thiophene (12 g) which was separated from the distillate using an oil/water separator, had the following physical properties b.p. 66-70°/0·3 mm, m.p. 21-22°, n<sup>20</sup> 1.5393 (supercooled liquid) (Found: C, 72.9; H, 8.8; S, 17.8. C<sub>1</sub>,H<sub>14</sub>S requires: C, 73.3; H, 9.0; S, 17.8%). By reaction of the acetoxymercuriderivative with sodium chloride, a chloromercuri-derivative was formed, m.p. 197-199° from benzene/ethanol (Found: C, 31.9; H, 3.7; S, 7.8; Cl, 8.4. C<sub>11</sub>H<sub>13</sub>SClHg requires: C, 31.8; H, 3.6; S, 7.7; Cl, 8.5%). A mercury dithienyl, m.p. 179-180° from benzene/ethanol, was obtained by reaction of the acetoxymercuri-derivative with sodium iodide (Found: C, 47.0; H, 5.4; S, 11.4. C22H30S2Hg requires: C, 47.3; H, 5.4; S, 11.5%). Gas-liquid chromatography of the thiophene showed one peak only of retention volume 41.8 relative to n-octane with a silicone oil as stationary phase at 134°, and of 0.68 relative to n-hexadecane with Apiezon grease L as stationary phase at 245°. The infra-red spectrum showed absorption at 7.22  $\mu$  and 7.32  $\mu$  attributed to a gem-dimethyl group, the mass spectrum a significant peak at m/e 59 indicative of an  $\alpha$ -methyl group on the thiophene ring and a parent peak at m/e 180, and the nuclear magnetic resonance spectrum a peak attributable to a proton on the thiophene ring having an area approximately 1/16 of the total proton peaks.

#### Desulphurization of the bicyclic thiophene (I)

Treatment of the thiophene with Raney nickel in Carbitol (the monoethyl ether of diethyleneglycol) by the usual technique<sup>8</sup> gave a 75 per cent yield of product,  $n_D^{10}$  1.4586. Gas-liquid chromatography showed the presence of two equal peaks of retention volumes 5.80 and 5.95 relative to n-octane with a silicone oil stationary phase at 130°. The latter was shown to be the naphthene and the former the cyclic olefin by comparison with the relative retention volumes of the separated hydrocarbons (*vide infra*). The olefin and naphthene had retention volumes of 5.6 and 6.6 respectively relative to n-octane with n-tetratriacontane as stationary phase at 145°. Although the bromine number of an olefin C<sub>11</sub>H<sub>20</sub> would be expected to be 105, that of the desulphurization product was 115. The components

\* All melting points are corrected. Some of the analyses were performed by Dr. Ing. A. Schoeller of Kronach/Oberfranken, Bambergerstrasse 20, Germany.

<sup>†</sup> These spectra are being submitted for inclusion in the American Petroleum Institute's Catalogue of Spectral Data.

of the desulphurization product  $(1\cdot10 \text{ g})$  were separated by the Fluorescent Indicator Adsorption technique<sup>13</sup> modified by continuing the isopropanol elution to displace the bands from the column. Four fractions were collected,  $(1) 0\cdot50$  g, colourless material,  $(2) 0\cdot10$  g, an intermediate fraction at the junction of the colourless and yellow bands of material,  $(3) 0\cdot42$  g, yellow coloured material,  $(4) 0\cdot13$  g, an intermediate fraction between (3) and the isopropanol. Fraction (1) was shown by mass spectrometry to be the naphthene (m/e 154 : m/e 152 : 580 : 1) and fraction (3) to be the olefin with a small amount of naphthene still present (m/e 152 : m/e 154 : 36 : 1). The results indicate that the desulphurization product was a 1 : 1 mixture of naphthene and olefin—which must have an anomalous bromine number. The infra-red spectrum of the naphthene showed large absorption at 7.26  $\mu$  with shoulders at 7.22  $\mu$  and 7.32  $\mu$  suggesting the presence of a gem-dimethyl group. The fact that no absorption was observed at 3.29  $\mu$  in the infra-red spectrum of the olefin demonstrated the absence

of hydrogen atoms attached to the doubly bonded carbon atoms and this was confirmed by the ultraviolet iodine absorption complex method.<sup>15</sup> The nuclear magnetic resonance spectrum of the desulphurization product had no peak corresponding to a proton on the doubly bonded carbon atoms.

#### Dehydrogenation of the naphthene (IX)

A commercial platinum on alumina catalyst (200 g) was dried at 425° for 30 min and then stirred with a solution of sodium acetate trihydrate (32 g in 300 ml water). After decanting off the excess aqueous phase, the catalyst was heated in an oven at  $150-170^{\circ}$  (7 hr) and finally in a current of hydrogen at 500°. This catalyst was used to study the dehydrogenation of various model compounds in an atmosphere of hydrogen at 350° and a space velocity of 0.5 v/v per hr. Analyses of the products were carried out by a combination of gas-liquid chromatography and mass spectrometry and the results together with those from the naphthene are given below.

Compound	Conversion to aromatic (mol %)	
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1,1,3-Trimethylcyclopentane	3 to 4	
n-Propylcyclopentane	>5	
1,1-Dimethylcyclohexane	30	
Naphthene (IX)	33	
cis-Ethyl-2-methylcyclohexane	85	

The evolution of methane during the dehydrogenation of the naphthene was demonstrated by taking a sample of the effluent gases; the methane content of the effluent gases was 12.6 per cent w/w compared with 0.2 per cent w/w in an experiment with benzene. One of the peaks in the gas-liquid chromatogram of the product from the dehydrogenation of the naphthene had the same retention volume as that of ethyl-2,3-dimethylbenzene (8.9 relative to n-octane with a silicone oil stationary phase at 130°). The material having this retention volume was collected and its ultra-violet spectrum obtained; ethyl-2,3-dimethylbenzene was the only  $C_{10}$  aromatic with this spectrum.

#### Synthesis of ethyl-2,3,3-trimethylcyclohexane (IX)

3,3-Dimethyl-2-carbethoxycyclohexanone (V), was prepared in 23 per cent yield from mesityl oxide as previously described,<sup>14</sup> b.p. 69-73°/0·3 mm,  $n_D^{10}$  1·4638, 2,4-dinitrophenylhydrazone m.p. 117° (Steiner and Willhalm<sup>14</sup> quote m.p. 116-116·5°). The sodium salt of V was reacted with methyl iodide by a modification<sup>16</sup> of the method of Linstead and Meade to give a 75 per cent yield of 2,3,3-*trimethyl-2-carbethoxycyclohexanone*, b.p. 105-114°/0·3 mm,  $n_D^{10}$  1·4657, retention volume 1·57 relative to naphthalene with Apiezon grease N as stationary phase at 197°. The 2,4-*dinitrophenyl-hydrazone* had m.p. 119·5-120° (from ethanol) (Found: C, 55·2; H, 6·4; N, 14·1. C<sub>18</sub>H<sub>46</sub>O<sub>6</sub>N<sub>4</sub> requires: C, 55·1; H, 6·2; N, 14·3%). The semicarbazone had m.p. 185·5-186·5° (from ethanol)

<sup>&</sup>lt;sup>18</sup> D. R. Long and R. W. Neuzil, Analyt. Chem. 27, 1110 (1955).

<sup>&</sup>lt;sup>16</sup> S. F. Birch, R. A. Dean and E. V. Whitehead, J. Org. Chem. 23, 783 (1958).

(Found: C, 58-1; H, 8-8; N, 15-8. C<sub>18</sub>H<sub>23</sub>O<sub>3</sub>N<sub>3</sub> requires: C, 58-0; H, 8-6; N, 15-6%). Decarboxylation and hydrolysis of the keto-ester (8.8 g) was carried out by refluxing it with a mixture of glacial acetic acid (60 ml) and conc. hydrochloric acid (40 ml).<sup>12</sup> The course of decarboxylation was followed by gas-liquid chromatography, and was only 80 per cent complete after 200 hr and still not complete after 344 hr when the reaction was stopped. The crude product was found to be a mixture of 2,3,3trimethyl-2-carbethoxycyclohexanone, 2,3,3-trimethylcyclohexanone (VI) and 3,3-dimethylcyclohexanone. Pure VI was isolated by gas-liquid chromatography using a commercial alkylarylsulphonate detergent as stationary phase<sup>18</sup> at 138° (the charge was ca. 1.5 g per run using a column 15 m long and 2.2 cm dia.). Yield 60 per cent, b.p.  $63^{3}/8$  mm,  $n_{20}^{20}$  1.4557, retention volume 5.22 relative to n-octane with n-tetratriacontane as stationary phase at 145°, oxime m.p. 92-93° (from aqueous ethanol) (Crossley and Renouf<sup>19</sup> quote m.p. 95°). The ketone (VI, 1.85 g) in ether (10 ml) was reacted in the usual way with excess ethylmagnesium bromide (from magnesium 1/3 g). The alcohol (VII), retention volume 14.2 relative to n-octane with n-tetratriacontane as stationary phase at 145°, was used without further purification for the next step in the synthesis. (Gas-liquid chromatography indicated the presence of a small amount of ether and a small amount of VI (not more than 2 per cent of the product). Dehydration was carried out by heating the alcohol with naphthalene-2-sulphonic acid<sup>20</sup> at 150°. The mixture of olefins (VIII) was extracted with ether, dried with potassium carbonate and finally redistilled. Yield 60 per cent, b.p.  $85^{\circ}/18$  mm,  $n_{20}^{20}$  1.4642. Examination of the product by gas-liquid chromatography showed two incompletely separated peaks of retention volumes 5.6 and 6.1 respectively relative to n-octane with n-tetratriacontane as stationary phase at 145. The infra-red spectrum demonstrated the presence of olefins with protons on the carbon atoms attached by the double bonds and this was confirmed by the ultra-violet iodine complex method<sup>16</sup> (the peak with retention volume 6.1 is presumably due to this type of olefin). VIII (0.55 g) was heated in Carbitol with Raney nickel at 100° for 90 min, (this method of hydrogenation was chosen to increase the probability of the naphthene having the same stereochemical configuration (which is unknown) as that produced by the desulphurization process from the thiophene), and the product (0.16 g),  $n_{\rm D}^{\rm so}$ 1.4562, worked up in the usual way. Gas-liquid chromatography showed the presence of two peaks of retention volumes 5.6 and 6.6 respectively relative to n-octane with n-tetratriacontane as stationary phase at 145. No peak of retention volume 6.1 could be seen (limit of detection 5 per cent of the sample). The product was separated by the Fluorescent Indicator Adsorption technique into naphthenic (0.03 g) and olefinic (0.05 g) fractions. The infra-red spectrum of the former was identical with that of the naphthene isolated from the desulphurization product of the thiophene. The latter was shown by spectroscopic methods to be fully alkylated and must therefore be ethyl-2,3,3-trimethylcyclohexene-1.

#### Isolation and desulphurization of the thienyl sulphide (II)

The unextracted portion from fraction XXVII of the tar oil after treatment with aqueous mercuric acetate solution was exhaustively extracted with further aqueous mercuric acetate until only traces of sulphides were extracted, it was then distilled under reduced pressure, wt. 39 g,  $n_{10}^{20}$  1.5211, thiophene content 70-80 per cent (ultra-violet spectroscopy). Part of this material (11 g) was given a preliminary chromatographic separation using silica gel (213 g, 28-200 mesh) with pentane/benzene/ ethanol as successive eluants. A portion (59 g,  $n_0^{20}$  1 5328) of the benzene-eluted material was chromatographed over silica gel (186 g), pre-wetted with cyclohexane, using the technique of gradient elution with a stirred mixing chamber,<sup>11</sup> cyclohexane (100 ml), benzene (150 ml) and ethanol (45 ml) being used as eluants. Solvents were removed by distillation and the residues combined, as indicated by refractive index, to give the fractions listed in the table on p. 317.

An infra-red spectrum on the fraction  $n_D^{20}$  1.5359 indicated a very complex mixture but showed absorption at 13.55  $\mu$  and 14.31  $\mu$  attributable to aromatic hydrocarbons. This absorption was absent in a sample that had been washed with conc. sulphuric acid, confirming this assignment. An infra-red spectrum of the fraction  $n_D^{30}$  1 5600, sulphur content 32.0 per cent w/w, was recorded, as

- <sup>18</sup> D. H. Desty and C. L. A. Harbourn, Divisions of Petroleum and Analytical Chemistry, Symposium on Advances in Gas Chromatography p. D-157. 132nd Meeting, ACS, New York, Sept. (1957).
- <sup>20</sup> A. W. Crossley and N. Renouf, J. Chem. Soc. **99**, 1101 (1911).
   <sup>20</sup> E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, J. Amer. Chem. Soc. **61**, 1057 (1939).
   <sup>21</sup> D. W. Bannister, C. S. G. Phillips and R. J. P. Williams, Analyt. Chem. **26**, 1451 (1954).

<sup>&</sup>lt;sup>17</sup> R. H. Martin and Sir R. Robinson, J. Chem. Soc. 491 (1943).

Solvents in eluant	Total volume – of eluant (ml)	Residue	
		Wt. (g)	n <sup>\$0</sup>
Cvclohexane	47	1.25	1.5200
Cyclohexane/benzene	68	2.60	1-5359
Cyclohexane/benzenc	88	0.75	1.5600
Cyclohexane/benzene	173	0.20	1.5445-1.4969
Cyclohexane/benzene/ethanol	178	0.15	1.5100
Cyclohexane/benzene/ethanol	350	0.10	

was also its mass spectrum which showed a large peak at m/e 172 (11 has a molecular weight of 172). The gas-liquid chromatogram had a peak (accounting for approximately 70 per cent of the sample) with a retention volume of 3.85 relative to n-dodecane with a solid synthetic detergent as stationary phase<sup>18</sup> at 245<sup>-</sup>. Desulphurization of the fraction was carried out by the normal method<sup>6</sup> and the gas-liquid chromatogram obtained. Peaks were present corresponding in retention volume to heptanes but no definite assignment could be made and no quantitative estimate was possible. Other minor peaks were present in the region of hydrocarbons formed from sulphur compounds possessing one sulphur atom per molecule and some peaks were present of retention volume comparable with the original sulphur compound fraction suggesting the presence of non-sulphur compound impurities. The cracking pattern of the desulphurization product indicated that a heptene, possibly, 2,3-dimethylpentene-1 was present as well as heptanes.

#### Synthesis of methyl 3,4,5-trimethyl-2-thienyl sulphide (II)

2,3,4-Trimethylthiophene (5.6 g, 0.044 mole) was dissolved in benzene (40 ml) and mercuric oxide (7.9 g, 0.037 molc) and iodine (11.6 g, 0.091 g atom) were added alternately in small portions with vigorous stirring.<sup>22</sup> Mercuric iodide was filtered off and from the filtrate there was obtained, by distillation, 2-iodo-3, 4, 5-trimethylthiophene (9 g) in 79 per cent yield, b.p. 134°/20 mm. The thienyl-magnesium iodide was prepared<sup>23</sup> by the reaction of the iodo-compound (9 g, 0.036 mole) with magnesium (1 g, 0.041 g atom) in ether under a nitrogen atmosphere, sulphur (1.2 g, 0.038 g atom) was added, with stirring, the reaction mixture refluxed for 2 hr and decomposed with dil. HCl. The trimethylthiophenethiol was extracted from the ether with 4 N caustic soda solution (20 ml), ethanol (25 ml) and methyl iodide (5.1 g, 0.036 mole) were added to the alkaline layer and the solution was refluxed for 2 hr. Dilution of the reaction mixture with water, extraction with pentane and distillation of the extract gave 11 in 17 per cent overall yield, b.p. 124–126°/18 mm,  $n_{20}^{20}$  1.5688 (Found: C, 55.6; H, 7.1; S, 37.5.  $C_8H_{12}S_2$  requires: C, 55.8; H, 7.0; S, 37.2%). The ethanol solution from the Grignard reaction, after extraction with alkali, was evaporated to dryness and the residue on crystalization from cyclohexane gave the *di*-(3,4,5-*trimethyl*-2-*thienyl*) *disulphide* (0. 8g) as yellow crystals m.p.  $89.5^{-}-90.5^{-2}$  (Found: C, 53.6; H, 6.2; S, 40.5.  $C_{14}H_{1x}S_4$  requires: C, 53.5; H, 5.8; S, 40.8%).

#### Synthesis of methyl 2,4,5-trimethyl-3-thienyl sulphide

2,3,5-Trimethylthiophene (1.05 g, 0.0084 mole) was heated at 40° with sulphuric acid (4.05 g, 0.042 mole) for 1 hr, the cooled reaction mixture was poured into water and the aqueous solution was neutralized with sodium hydroxide and evaporated to dryness under reduced pressure. The sodium thiophenesulphonate (0.95 g), 50 per cent yield, was isolated by extraction of the dry solid with ethanol: a total of 3 g was prepared by this method. Conversion to the sulphonyl chloride was effected by heating the sodium salt with phosphorus oxychloride at 130–150° for 2.5 hr and the sulphonyl chloride was isolated by addition of the reaction mixture to water, followed by extraction with ether, (1.2 g), 40 per cent yield, b.p.  $154^{\circ}/15$  mm. This sulphonyl chloride (1.2 g, 0.0053 mole) was reduced in the usual manner<sup>34</sup> with lithium aluminium hydride (1.2 g, 0.03 mole), the product

22 W. Minnis, Organic Syntheses Coll. Vol. II, p. 357. John Wiley, New York (1943).

<sup>&</sup>lt;sup>25</sup> P. D. Caesar and P. D. Branton, Industr. Engng. Chem. 44, 122 (1952).

<sup>&</sup>lt;sup>24</sup> C. S. Marvel and P. D. Caesar, J. Amer. Chem. Soc. 72, 1033 (1950).

was extracted into an aqueous solution of sodium hydroxide and reacted with methyl iodide (vide supra) to give the required sulphide (0.45 g), 53 per cent yield, b.p.  $120^{\circ}/18$  mm,  $n_D^{20}$  1.5640.

The infra-red spectrum of this sulphide was obtained and none of it could be detected in the thienyl sulphide fraction of the tar oil (limit of detection ca. 3 per cent).

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