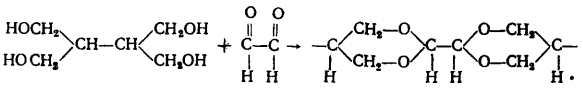
Recently[47] a new class of linear polycycloacetals was reported. The reaction of dialdehydes with tetrahydric alcohols, which contain two 1,2- or 1,3-diol groupings, easily produces linear polycycloacetals, in which each unit contains a ring:



In this reaction the dialdehydes and tetrols can be considered as bifunctional compounds. The reaction of more stable acetals of aliphatic aldehydes of the general formula $(C_2H_5O)_2CH(CH_2)_nCH(OC_2H_5)_2$ with various tetrols, such as pentaerythritol or $(HOCH_2)_2CH(CH_2)_mCH(CH_2OH)_2$, where $m = n = 6-10$, gives yellow or white solid polymers, m.p. 146°–205°, which are soluble in chlorinated hydrocarbons and have film- or fibre-forming properties. The dielectric constant of these polymers is 2.1–2.4, the dielectric loss 0.03, and the resistivity $10^{16}-10^{17}$ ohm cm.

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THE SATURATED CYCLIC SULPHIDES OF PETROLEUM AND THEIR SYNTHESIS

Yu. K. Yur'ev and E. G. Rozantsev

CONTENTS

Introduction 88

I. Synthesis of saturated cyclic sulphides 88

1. Action of Alkali Metal Sulphides on δ- and ε-Dihalides 88

2. Catalytic Conversion of γ- and δ-oxides into Saturated Cyclic Sulphides 90
3. Reduction and Catalytic Hydrogenation of Thiophens 92
4. Reduction of Sulphones 92
5. Intramolecular Cyclisation 92
6. Reduction of Carbonyl Derivatives of Cyclic Sulphides 93
7. Other Methods 94

II. Spectra of Sulphides of the Thiophan and Thiacyclohexane series 96
1. Ultra-Violet Spectra 96
2. Raman Spectra 96
3. Infra-Red Spectra 97

INTRODUCTION

A high sulphur content is typical of many petroleum deposits. Thus Californian petroleum (Santa Maria Valley deposit) contains 4.5% total sulphur, Venezuelan (Boscan) 4.8%,[1] and Iraq up to 7.8%.[2] In Russian petroleums, a high sulphur content is found in the deposits of the Bashkir and Tartar Autonomous Soviet Socialist Republics, the Kuibyshev region, and particularly South Uzbekistan, where, for example, Uch-Kizyl petroleum contains 6.3% total sulphur[3]. This sulphur occurs mainly as organosulphur compounds, particularly cyclic and aliphatic sulphides.

Since Mabery first separated saturated cyclic sulphides of the general formula $C_nH_{2n}S$ from North American petroleum[4,5], these sulphides have been detected in all sulphur-containing petroleums: for instance, thiophan has been found in petroleums from Iran[6,7], Turkey[8], USA[9], Mexico[10-13], and USSR[3,14,15]. Many homologues of thiophan and tetrahydrothiopyran can now be separated from petroleum and identified, by using mercury salts[16,17,18], sulphur dioxide, alumina[19], silica gel[20-22], or hydrofluoric acid[23], together with spectrometry, thermal diffusion, and accurate rectification methods.

Hartough[24] has given the physical properties of all cyclic organosulphur compounds detected in petroleum up to 1951. It was remarked that it was very difficult to establish the structure of the saturated cyclic sulphides, because of the absence of synthetic model compounds[25].

Thiophan, 2- and 3-methylthiophan, 2-ethylthiophan, 2,3- and 2,4-dimethylthiophan, 2,3,4- and 2,3,5-trimethylthiophan, tetrahydrothiopyran, 2-, 3-, and 4-methyltetrahydrothiopyran[7,26], and thiaadamantane[27] have been separated from Iranian petroleum and identified, and tetrahydrothiopyran and 3-butyltetrahydrothiopyran[28] from Kuwait petroleum. The structures of the following nine saturated cyclic sulphides from American petroleum (Wasson deposit) have been accurately established: thiophan, 2- and 3-methylthiophan, tetrahydrothiopyran, *cis*- and *trans*-2,5-dimethylthiophan, and 2-, 3-, and 4-methyltetrahydrothiopyran[9]. In the USSR, 2-methylthiophan has been isolated from South Uzbekistan petroleum[3], 2,5-dimethylthiophan from the Ishimbaev deposit[29], and 3-butylthiophan from the Tuimazinsk deposit[30].

Saturated cyclic sulphides are thus components of all sulphur-containing petroleums. Since by 1955 more than half of the petroleum worked in the USSR was of the sulphur-containing type from the Urals–Volga oil-bearing region[31], organosulphur compounds of this type merit as deep a study as the hydrocarbons themselves. Studies in this field would form the basis of a more rational and efficient utilisation of the ready-made organosulphur compounds presented to us by nature, in the national economy and industry[32-37].

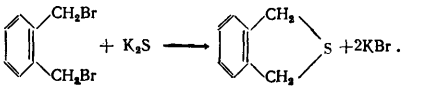
I. SYNTHESIS OF SATURATED CYCLIC SULPHIDES

The term "thiophan" has been most widely used to designate tetrahydrothiophen in Soviet and foreign literature, and we shall use it here.

The following are the most general of the existing methods for the synthesis of saturated cyclic sulphides.

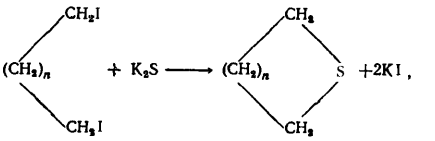
1. Action of Alkali Metal Sulphides on δ- and ε-Dihalides

In 1884 Leser[38] and somewhat later Hjelt[39] obtained 3,4-benzothiophan by the action of potassium sulphide on *o*-xylylene dibromide:



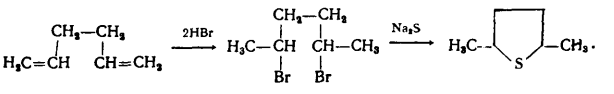
The same compound was prepared by von Braun, Bayer, and Kaiser[40] using sodium sulphide.

Thiophan itself and tetrahydrothiopyran were first prepared in 1910 by von Braun and Trümpler[41] by the action of potassium sulphide on alcoholic solutions of 1,4-diiodobutane and 1,5-diiodopentane respectively; high yields were obtained:



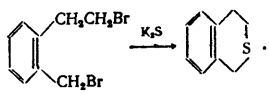
where n = 2 or 3. 2-Methylthiophan was prepared analogously[42].

In 1916 Grishkevich-Trokhimovskii made a detailed study of the reaction of α,ω-dihalides with sodium sulphide in aqueous-alcoholic solution, and used this method to prepare a large number of saturated cyclic sulphides, including several homologues of thiophan and tetrahydrothiopyran[43]. 2,5-Dimethylthiophan was prepared from *meso*-2,5-dibromohexane, itself obtained by addition of hydrogen bromide to diallyl[44]:

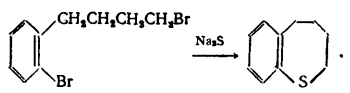


In this preparation of 2,5-dibromohexane, in addition to the crystalline dibromide a liquid isomer was obtained; in 1901 Wislicenus showed that the solid dibromide is the *meso*-form, and the liquid the racemic form[45].

von Braun and Zobel prepared 3,4-benzotetrahydrothiopyran by the action of potassium sulphide on the corresponding dibromide[46]:



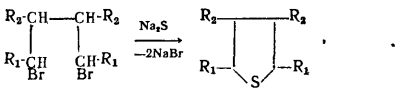
von Braun, Bayer, and Kaiser[40] obtained 2,3-benzohexamethylene sulphide (homothiochroman) in 40% yield by an analogous method from 2-(4-bromobutyl)bromobenzene:



1930 saw the start of an intensive investigation of possibilities for purifying petroleum fractions from sulphides, thiophans, and tetrahydrothiopyran[20]. To this period belong the studies of Bost and Conn on the properties of organic sulphides, including thiophan and tetrahydrothiopyran, and these compounds were used in developing methods for the preparation of sulphones, double compounds with mercuric chloride and iodide, and methyltetra- and methylpenta--methylenesulphonium halides; the synthesis of the cyclic sulphides themselves was considerably improved[47-49].

In 1938 Müller and his coworkers used the reaction of α,ω-dihalides with sodium sulphide to prepare a series of macrocyclic sulphides of the general formula $C_nH_{2n}S$ (n = = 12–14)[50,51], and later, hexa-, octa-, and nona-methylenesulphides[51].

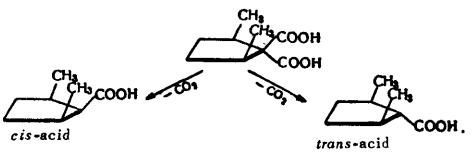
In preparing new cyclic sulphones, Marvel and Williams synthesised 3,4- and 2,5-dipropylthiophan by a complex route in yields of 77.5 and 77% respectively[52]:



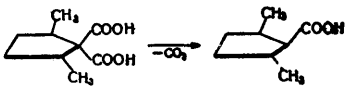
where R_1 = H, R_2 = C_3H_7; R_1 = C_3H_7, R_2 = H.

In 1951 Whitehead, Dean, and Fidler published an interesting study on the synthesis of homologues of thiophan and tetrahydrothiopyran by the action of sodium sulphide on 1,4- and 1,5-dibromides. In addition to the known thiophan, 2- and 3-methylthiophan, tetrahydrothiopyran and 2-methyltetrahydrothiopyran, the compounds 3- and 4-methyltetrahydrothiopyran, and *cis*- and *trans*-2,5--dimethylthiophan were obtained for the first time[53].

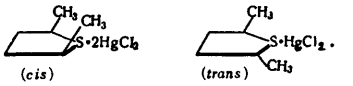
It was mentioned above that the solid 2,5-dibromohexane is the *meso*-form, and the liquid is the racemic form[45]. Condensation of *meso*-2,5-dibromohexane with disodio--malonic ester and saponification of the reaction product produces *cis*-2,5-dimethylcyclopentane-1,1-dicarboxylic acid; on decarboxylation this acid gives two acids of different melting point, thus proving the *cis*-configuration of the starting acid:



Condensation of racemic 2,5-dibromohexane with disodio-malonic ester gives *trans*-2,5-dimethylcyclopentane-1,1-dicarboxylic acid, from which only one acid, *trans*-2,5-dimethylcyclopentane carboxylic acid, is obtained by decarboxylation:

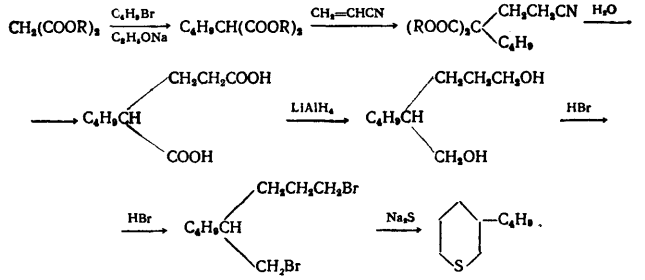


We may conclude from these data that the 2,5-dimethylthiophan obtained by the action of sodium sulphide on *meso*-2,5-dibromohexane is the *cis*-form, while the isomer obtained from racemic 2,5-dibromohexane has the *trans*-configuration. The former gives a complex with two molecules of mercuric chloride (m.p. 180°), and the latter a complex with one molecule of mercuric chloride (m.p. 110°–111°):

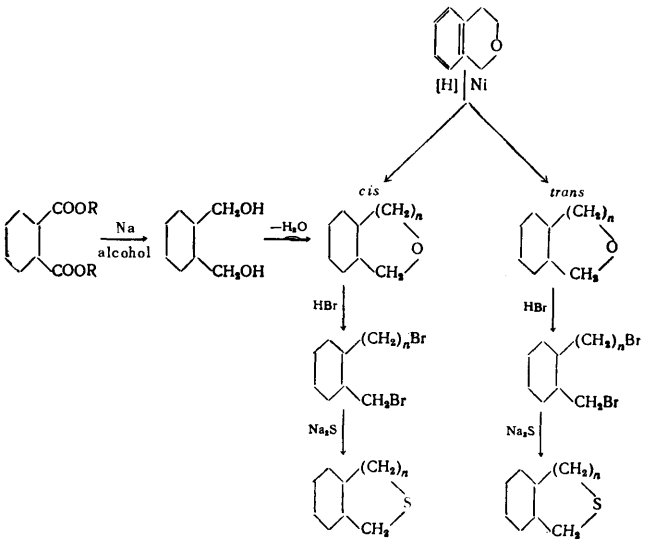


In this connection, the mercuric chloride complex of 2,5-dimethylthiophan (m.p. 109°–110°) prepared by Grishkevich-Trokhimovskii from *meso*-2,5-dibromohexane[43] corresponds, from the melting point, not to *cis*-2,5--dimethylthiophan, but to the *trans*-form. Apparently the composition and so the melting point of the mercuric chloride complexes depends on their method of preparation. Obolentsev and Dronov[54] obtained *cis*- and *trans*--2,5-dipropylthiophan[52] analogously from 4,7-dibromodecane and sodium sulphide.

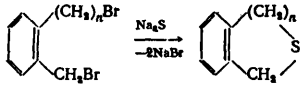
Emmott[28] prepared 3-butyltetrahydrothiopyran in 22% yield by the following series of reactions:



In 1954 several papers appeared on the synthesis of various bicyclic sulphides similar in type to those found in petroleum. Thus Birch, Dean, and Whitehead[55] prepared *cis*- and *trans*-2-thiahydrindanes and *cis*- and *trans*-2-thiadecalins as follows:



The stereoisomeric cyclic oxides were separated by rectification. The configuration of the resulting dibromides was established by Wislicenus's method[45]. High yields of the bicyclic sulphides were obtained: *cis*- and *trans*-2--thiahydrindane 75% and 91% respectively, and *cis*- and *trans*-thiadecalin 83.5% and 86.5% respectively. These workers also prepared 2-thiaindane and 2-thiatetralin in yields of 67% and 59% respectively[56]:



where n = 1 or 2.

In 1955 the American Petroleum Institute, the United States National Bureau of Stan ards and the United States Bureau of Mines prepared, in accordance with plan 48A†, 25 sulphur compounds in a high state of purity, including thietan, thiophan, and tetrahydrothiopyran. In the same year, in accordance with a decision of the Seventh Italian National Chemical Congress, work was begun on the synthesis of various cyclic sulphides so that they could be thoroughly investigated; Onesta and Ferretti[57] prepared a series of 2-alkylthiophans by the action of sodium sulphide on the corresponding dibromides (alkyl = C_3H_7, C_4H_9, iso-C_4H_9, iso-C_5H_{11}).

It is interesting that the melting points of the mercuric chloride complexes given by the Italian workers differ from those given by Yur'ev and Gragerov[58] (Table 1).

The unsatisfactory nature of the explanations for the different melting points of the mercuric chloride complexes[59] led to the appearance of a special study, which showed that the composition of the monoalkylthiophan–mercuric chloride double compounds, and therefore their melting points, depends on the method of their preparation[60]. We have already referred to a similar discrepancy in the melting points of mercuric chloride complexes, in discussing the work of Whitehead and coworkers[53].

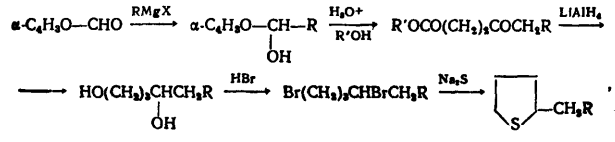
TABLE 1.

Mercuric chloride complex of	M.p., °C	References
2-Propylthiophan	132—133	57
2-Propylthiophan	51—52	58
2-Butylthiophan	111—113	57
2-Butylthiophan	39.5—41	58

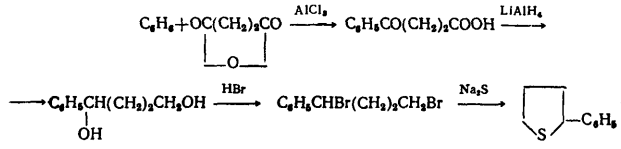
† In 1948 the American Petroleum Institute put forward two projects of study, named 48A and 48B, connected with the presence in petroleum of various organosulphur compounds and the great increase in the working of high-sulphur petroleum. Work on project 48A (the synthesis, purification and properties of the sulphur compounds in petroleum) was carried out at two Bureau of Mines stations – the Petroleum and Shale Experimental Station at Laramie (Wyoming) [Laramie Petroleum Research Center (Ed. of Translation)], and the Petroleum Experiment Station at Bartlesville (Oklahoma). The group at Laramie is concerned with the preparation, purification and study of the properties of such compounds, including the preparation of 1.5 litres of highly pure (99.9 mole %) compound in each case, and the determination of their physical and thermodynamic properties and their spectroscopic characteristics.

In 1958 Obolentsev and his coworkers[61] prepared a number of sulphides, including the saturated cyclic sulphides 2-pentylthiophan, tetrahydrothiopyran, and thiacycloheptane, by the action of sodium sulphide on the corresponding dihalides.

Later, Obolentsev and Bukharov[62] reported the synthesis of ten 2-alkyl- and 2-aralkyl-thiophans starting from furfural:



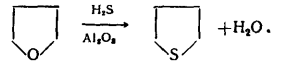
where R = CH_3, C_2H_5, C_3H_7, iso-C_3H_7, iso-C_4H_9, t-C_4H_9, iso-C_5H_{11}, iso-C_8H_{17}, $C_6H_5CH_2$, or $C_6H_5CH_2CH_2$. These workers also prepared 2-phenylthiophan by a slightly different route:



Onesta and Ferretti's data on the boiling point of 2-butylthiophan[57,63] have not been confirmed; the boiling point given by Obolentsev and Bukharov coincides with that given earlier by Yur'ev and Gragerov[58] and is the true figure.

2. Catalytic Conversion of γ- and δ-Oxides into Saturated Cyclic Sulphides

In 1937 Yur'ev and Prokina[64] obtained thiophan in a high yield by passing tetrahydrofuran in a current of hydrogen sulphide through a tube containing alumina and heated to 400°:



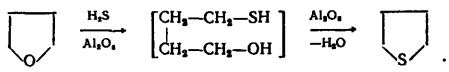
Yur'ev and Tronova passed tetrahydrofuran over pyrites (FeS_2) and the easily hydrolysed aluminium sulphide, but no sulphur-containing heterocyclic compounds were formed in the temperature range 350°–600°; when, however, a mixture of tetrahydrofuran and water was passed over aluminium sulphide at 300° or 350°, thiophan was obtained in yields of 32.5% and 30.5% respectively[65].

This new reaction provided the possibility of systematic synthesis and detailed study of this important group of saturated cyclic sulphides. The reaction linked the saturated oxygen-containing heterocyclic compounds with the corresponding sulphur compounds, showed their genetic relationship, and provided an approach towards the elucidation of the complex natural processes producing the sulphur-containing heterocyclic compounds in petroleum‡.

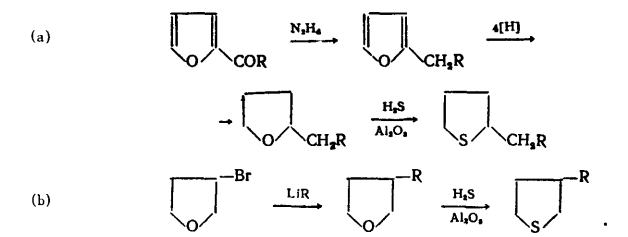
‡ Postovskii, Bednyagina, and Mikhailova[66] and Birch[7] consider that under conditions pertaining in nature, oxygen- and nitrogen-containing heterocyclic compounds can be converted into cyclic sulphides by the Yur'ev reaction.

By this method Yur'ev prepared 2-methylthiophan from 2-methyltetrahydrofuran in 69% yield[67].

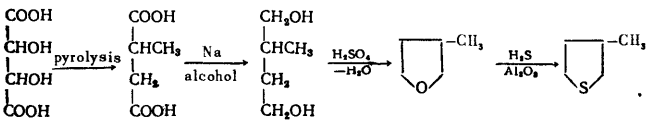
Yur'ev, Minachev, and Samurskaya have shown[68] that, at elevated temperature in the presence of alumina, 4-mercaptobutanol produces thiophan almost quantitatively§. This reaction confirmed the mechanism put forward by Yur'ev for the catalytic conversion of tetrahydrofuran into thiophan in the presence of hydrogen sulphide[64,68,70], which includes the intermediate formation of a 1-mercapto-4--hydroxy compound (4-mercaptobutanol) by ring-opening of the tetrahydrofuran at a carbon–oxygen bond and addition of the elements of hydrogen sulphide:



This reaction was later applied to other tetrahydrofuran homologues[58,71-73]; thus in 1949 Yur'ev and Gragerov prepared a number of 2- and 3-alkylthiophans as follows[58,73]:

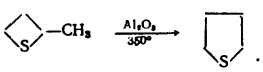


2-Ethyl-, 2-propyl-, 2-butyl-, 3-methyl-, 3-propyl-, and 3-butyl-thiophan were obtained in this way. 3-Methylthiophan was prepared by the following series of reactions:



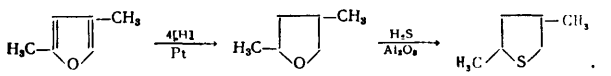
In the study of the catalytic interconversions of tetrahydrofuran, thiophan, and pyrrolidine, Yur'ev and Bugorkova obtained thiophan in 33.5% yield by the action of hydrogen sulphide on pyrrolidine[74].

Yur'ev, Dyatlovitskaya, and Levi[75] achieved an interesting synthesis of thiophan by the contact isomerisation of 2-methylthietan at 350° in the presence of alumina:



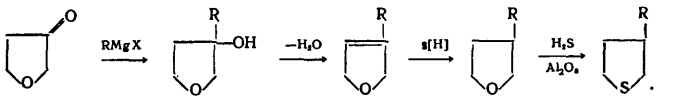
When 3-oxotetrahydrofuran was passed over alumina at 350° in a current of hydrogen sulphide, thiophan was obtained, in place of the expected 3-oxothiophan[76].

Yur'ev, Kondrat'eva and Kartashevskii have described the catalytic conversion of 2,4-dimethyltetrahydrofuran into 2,4-dimethylthiophan in 58% yield[77]:



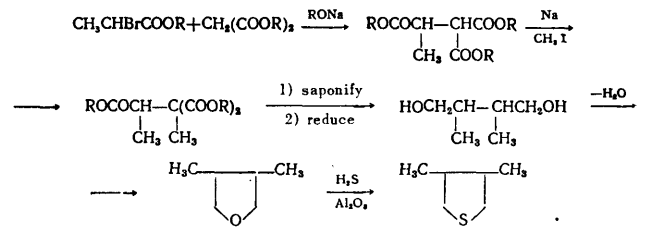
Although 3,3-dimethylthiophan was obtained in 73% yield by Yur'ev, Kondrat'eva, and Sadovaya[78], 2,2-dimethylthiophan was obtained in only 27% yield by Yur'ev, Kondrat'eva, and Akishin[79]; Yur'ev and his coworkers also obtained 2,5-diethylthiophan in a yield of only 12%.[80] These effects are due to an increased steric effect around the hetero--atom because of the introduction of the alkyl groups into the tetrahydrofuran ring (see Figure).

In 1954 Yur'ev, Lukina, and their coworkers developed a general method for the preparation of 3-alkyl- and 3-aryl-thiophans from 3-oxotetrahydrofuran by the following series of reactions:

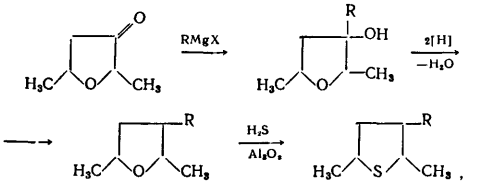


This method was used to prepare 3-pentyl- and 3-phenyl--thiophan in 64% and 58% yields respectively[81], and, later, 3-isopentyl-, 3-hexyl-, and 3-*p*-tolyl-thiophan in yields of 60%, 57%, and 51%.[82]

Yur'ev and Kondrat'eva prepared 3,4-dimethylthiophan as follows, with a 71% yield on the last step[83]:



Later Yur'ev, Rozantsev, and Godovikova put forward a new general method for the preparation of the difficultly attainable 2,3,5-substituted thiophans[84], by the action of hydrogen sulphide on the 2,3,5-substituted tetrahydrofurans[85]:



where R = CH_3, C_2H_5, or C_3H_7. Yur'ev, Rozantsev, and Gribov have also described the preparation of 3-butyl-, 3-isobutyl-, 3-pentyl-, and 3-isopentyl-2,5-dimethylthiophans by the same method[86].

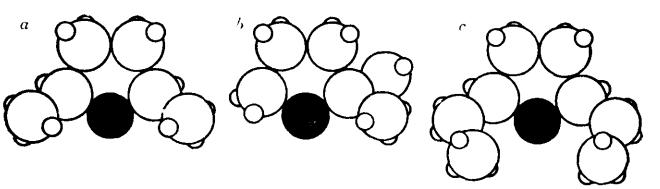
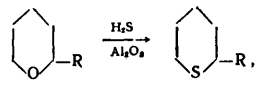


Figure. *a*) 2,5-dimethylthiophan (68% yield); *b*) 2,2-dimethylthiophan (27% yield); *c*) diethylthiophan (12% yield).

§ Under these conditions thiophans are also formed from 1,4-diols[69] and 4-chlorobutanol in the presence of hydrogen sulphide.

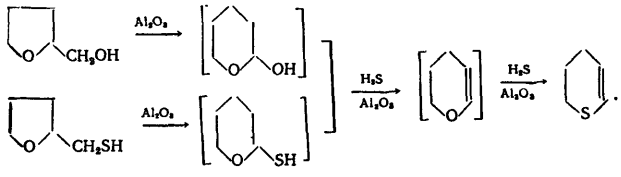
The six-membered tetrahydrothiopyran and its homologues were prepared by this method in 1939 by Yur'ev, Pervova, and Sazonova [87] and later by Yur'ev and Revenko [88]:



where R = H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, or iso-C_4H_9.

The preparation of unsaturated cyclic sulphides with the double bond in a definite position presented great difficulties. Δ^2-Dihydrothiopyran was first obtained by Yur'ev, Dubrovina, and Tregubov [89] by the action of hydrogen sulphide on Δ^2-dihydropyran at 300° in the presence of alumina.

Yur'ev and Vendel'shtein prepared Δ^2-dihydrothiopyran by the catalytic conversion of tetrahydrofurfuryl alcohol with hydrogen sulphide at 300 (yield 27%) and by passing 2-(tetrahydrofuryl)methanethiol over alumina at 300° (yield 22%) [90]:



When tetrahydrofurfuryl alcohol is reacted as above at 450°, in addition to Δ^2-dihydrothiopyran a mixture of thiopyran and tetrahydrothiopyran is obtained [91].

3. Reduction and Catalytic Hydrogenation of Thiophens

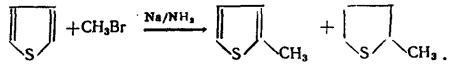
Attempts have been made to hydrogenate the comparatively easily available thiophen homologues into the corresponding thiophans, but the early experiments had little success [92-95].

In 1925 Fricke and Spilker showed [96,97] that benzothiophen is reduced by sodium in boiling alcohol to give 2,3-benzothiophan in 17% yield. Mozingo and his coworkers were able to hydrogenate thiophen and some of its derivatives under moderate hydrogen pressure in the presence of palladium catalysts; the yields reached 71%. [98,99]

Later Wender, Levine, and Orchin [100,101] hydrogenated some thiophen homologues at 185° at elevated hydrogen pressure in the presence of cobalt carbonyl, and obtained thiophan, 2-methylthiophan, 2-ethylthiophan, and 2,5-dimethylthiophan, in yields of 66, 77, 82, and 22% respectively.

Birch and McAllan [102] attempted the reduction of 3-methyl- and 2,5-dimethyl-thiophen with nascent hydrogen (sodium in liquid ammonia), and obtained mixtures of the dihydro- and tetrahydro-thiophen homologues.

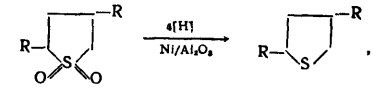
Zimmerschied and Arnold [103] reported the reduction of the thiophen ring as a side reaction in the alkylation of thiophen in liquid ammonia: on reacting the metallised thiophen with methyl bromide in liquid ammonia, 2-methylthiophan was obtained in 29% yield, in addition to the 2-methylthiophen:



Hydrogenation of thiophen, 2-isobutylthiophen, and 2-isooctylthiophen with sulphide catalysts — nickel, molybdenum, and tungsten sulphides — produced thiophan, 2-isobutylthiophan, and 2-isooctylthiophan in yields of 59, 22.2, and 35% respectively [104]. Bateman and Shipley [105] have successfully hydrogenated homologues of dihydrothiophen and dihydrothiopyran with palladium on carbon and palladium on barium sulphate catalysts.

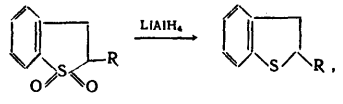
4. Reduction of Sulphones

In 1949 Moore and Trimble [106] catalytically reduced thiophan and 2,4-dimethylthiophan *S*-dioxides in the presence of nickel on alumina to thiophan and 2,4-dimethylthiophan respectively:



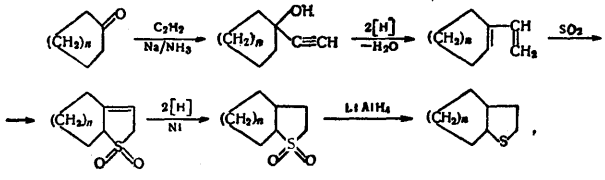
where R = H or CH_3.

Bordwell and McKellin [107] obtained benzothiophan and 2-methylbenzothiophan by reducing the corresponding *S*-dioxides [108] with lithium aluminium hydride:



where R = H or CH_3.

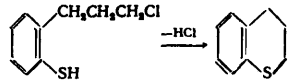
Later Birch *et al.* [109] described the preparation of *cis*-2-thiabicyclo[3,3,0]octane and *cis*- and *trans*-7-thiabicyclo[4,3,0]nonane by the following method:



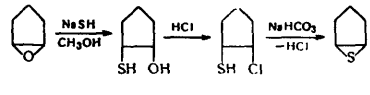
where *n* = 1 or 2, and they also prepared *cis*- and *trans*-3-thiabicyclo[3,3,0]octane. An attempt to prepare *trans*-2-thiabicyclo[3,3,0]octane [110] *via* isomerising the *cis*-sulphone intermediate [111] was unsuccessful, although this method has been successfully used for obtaining *trans*-7-thiabicyclo[4,3,0]nonane.

5. Intramolecular Cyclisation

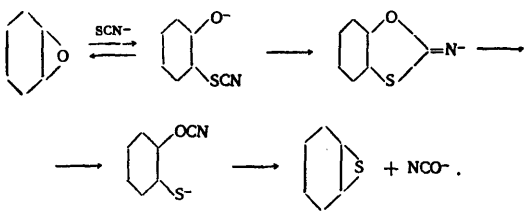
In 1910 von Braun obtained 2,3-benzotetrahydrothiopyran by the intramolecular condensation of 2-(3-chloropropyl)thiophenol [42]:



and by an analogous method van Tamelen [112] prepared cyclohexene sulphide and cyclopentene sulphide in yields of 73 and 75% respectively, starting from the corresponding oxides:

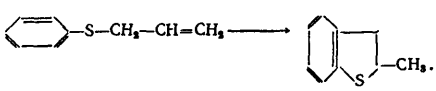


Culvenor, Davies, and Pausacker[113] obtained cyclohexene sulphide in 60% yield by the action of potassium or ammonium thiocyanate on cyclohexene oxide in an alkaline medium; Snyder, Stewart, and Ziegler[114] used this method for the preparation of several ethylene sulphide homologues, including cyclohexene sulphide, and suggested the following mechanism for this reaction:

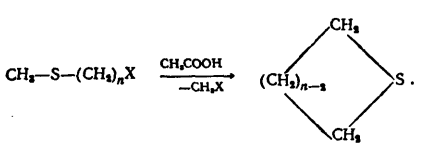


Many ethylene sulphide homologues are known[115-120], but up to the present have not been found in petroleum. However, they may be of interest in the study of, for instance, the spectrographic features of cyclic sulphides, or in the calculation of various physicochemical and thermodynamic values, and this is also true of trimethylene sulphide and its homologues[121,122].

Hurd and Greengard[123] have reported the isolation of 2-methylbenzothiophan from the pyrolysis products of phenyl allyl sulphide:

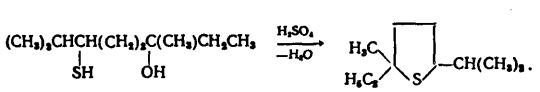


Bennett and Gudgeon suggested that macrocyclic sulphides could be obtained by eliminating methyl halide from ω-halogenoalkyl methyl sulphides, *e.g.* by heating with acetic acid or sodium iodide, and used this method to prepare cyclic sulphides with 14, 16, and 18 methylene groups[124]:

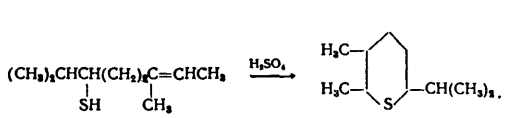


In 1951 a group of American workers reported the formation of sulphides by adding hydrogen sulphide to olefines in the presence of aluminium bromide or sulphuric acid, with subsequent addition of the resulting thiol to a second olefine molecule[59].

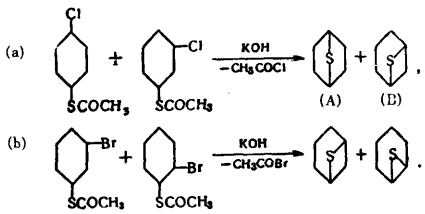
Bateman and Glazebrook used this reaction for the preparation of many thiacycloalkenes, using the corresponding mercaptoketones as starting compounds[125,126]. Glazebrook and Saville[127] then applied the method to 4-mercaptoalcohols, and so obtained 2-methyl-2-ethyl-5-isopropylthiophan:



Bateman, Glazebrook, and Moore showed that the intramolecular addition of a thiol group to a double bond also produces saturated cyclic sulphides, and obtained 2,3-dimethyl-6-isopropyltetrahydrothiopyran by this method[128]:

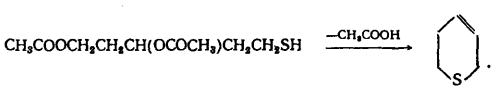


Intramolecular condensation was used in 1958 by Birch, Dean, and Hunter for the preparation of 7-thiabicyclo-[2,2,1]heptane (A) and 6-thiabicyclo[3,1,1]heptane (B):



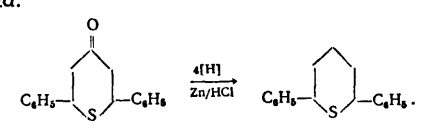
The resulting mixtures of bicyclic sulphides were separated by azeotropic distillation and chromatography; the by-product of cyclohexene sulphide — reaction (b) — was identified spectroscopically[129].

Olsen and Rutland suggested a method for the preparation of Δ^3-dihydrothiopyrans by the intramolecular condensation of 3,5-diacetoxypentan-1-thiol, with the elimination of acetic acid: Δ^3-dihydrothiopyran was obtained in 37% yield[130]:

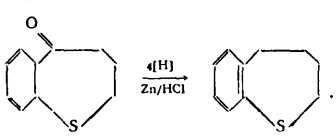


6. Reduction of Carbonyl Derivatives of Cyclic Sulphides

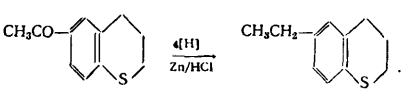
The possibility of obtaining cyclic sulphides from thiabenz-4-one and tetrahydrothiabenz-4-one has long attracted the attention of chemists[131-136]. Arndt and Schauder[135] obtained 2,6-diphenyltetrahydrothiabenz-4-one in 40% yield by reducing 2,6-diphenyltetrahydrothiabenz-4-one in hydrochloric acid:



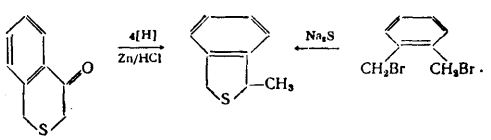
Cagniant and Deluzarche[137] and then Truce and Milionis[108] prepared 2,3-benzothiacycloheptane (homothiochroman) by the reduction of 2,3-benzo-4-thiacycloheptanone:



Krollpfeiffer *et al.* prepared 1-thiatetralin (thiochroman) and then 6-methyl- and 6,8-dimethyl-1-thiatetralin[138,139]. Cagniant and Deluzarche obtained 6-ethyl-1-thiatetralin by Clemmensen reduction of 6-acetyl-1-thiatetralin[140]:

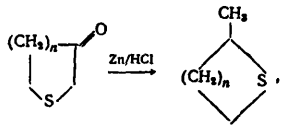


In an attempt to reduce 1,2,3,4-tetrahydro-2-thianaphthalen-4-one by the Clemmensen method, von Braun and Weissbach[141] obtained 2-methyl-3,4-benzothiophan, the structure of which was established by synthesis:



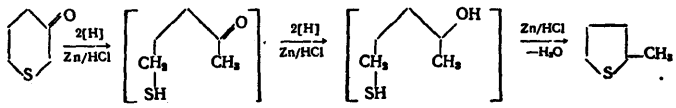
The reduction of 1,2-dihydro-2-thianaphthalen-5-ol under the same conditions produced 1,2-dihydro-2-thianaphthalene, described earlier by von Braun and Zobel[46].

The same anomalous reaction was observed later by Leonard and Figueras[142] in the reduction of 1-thiacyclohexan-3-one and 1-thiacycloheptan-3-one to 2-methylthiophan and 2-methylthiacyclohexane respectively:

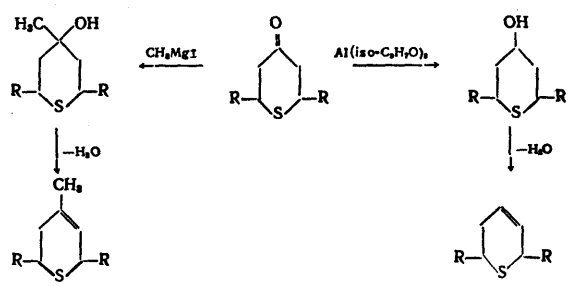


where n = 2 or 3.

This reaction apparently passes through the intermediate formation of the methyl ω-mercaptoalkyl ketone, which is then reduced to the corresponding mercapto-alcohol, which by the elimination of water gives the cyclic sulphide with one methylene group less in the ring[143,144]:



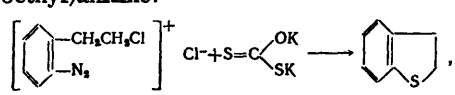
Naylor[91] prepared Δ^3-dihydrothiapyran and its homologues from tetrahydrothiabenz-4-one and its homologues:



where R = H or CH_3. 2,2,6,6-Tetramethyl- and 2,2,4,6,6-pentamethyl-Δ^3-dihydrothiapyrans were prepared similarly.

7. Other Methods

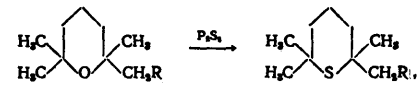
von Braun, Bayer, and Kaiser[40] and Challenger and Clapham[145] have described the preparation of 2,3-benzothiophan by the action of potassium xanthate on diazotised 2-(2-chloroethyl)aniline:



and Bennett and Hafez[146] described its analogous preparation from diazotised 2-(2-hydroxyethyl)aniline.

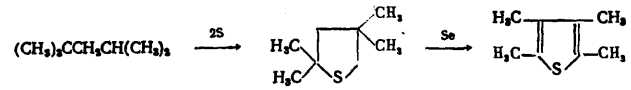
In 1947 Farmer and Shipley observed the formation of 2,2-dimethyl-5-isobutylthiophan, 2,3-dimethyl-5-isobutylthiophan, 2,2,6,6-tetramethylthiacyclohexane, 2,2,6-trimethyl-6-ethylthiacyclohexane, and 2,3-dimethyl-6-isopropylthiacyclohexane when dienoid hydrocarbons were heated at 140° with elementary sulphur; unsaturated cyclic sulphides were also formed. The cyclic sulphides were said to be formed by the addition of hydrogen sulphide across the double bonds of the dienes[147]. The structures of the compounds were established by comparing their infra-red absorption spectra with those of synthetic models[148]. The difficulties of identification were made worse because some of the products contained a tertiary carbon atom attached to sulphur, so that the solid mercuric chloride derivatives could not be obtained[149].

In the same year Naylor added hydrogen sulphide to geraniolene, dihydromyrcene, and 2,6-dimethylocta-2,6-diene[150] to obtain 2,2,6,6-tetramethyl-, 2,2,6-trimethyl-6-ethyl-, and 2,3-dimethyl-6-isopropyl-thiacyclohexane. He also prepared the two former compounds by the action of phosphorus pentasulphide on the corresponding tetrahydropyran derivative[151]:

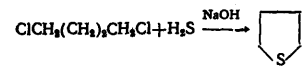


where R = H or CH_3.

Friedmann[152] reported an interesting synthesis of 2,2,4,4-tetramethylthiophane by boiling 2,2,4-trimethylpentane with sulphur; when the reaction product was dehydrogenated with selenium, isomerisation occurred to form 2,3,4,5-tetramethylthiophen:



A convenient method from the preparative point of view is the preparation of thiophan from 1,4-dichlorobutane and hydrogen sulphide in alcoholic alkali (yield 70%)[153]:



Birch and Dean obtained *cis*-3-thiabicyclo[3,2,1]octane in 77% yield from sodium sulphide and, instead of the α,ω-dihalide, cyclopentane-1,3-dimethoxy di-*p*-toluenesulphonate[154]:

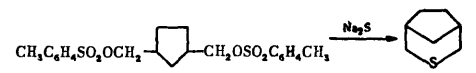


TABLE 2. Physical properties and yields of saturated cyclic sulphides of the thiophan and tetrahydrothiopyran series*.

No.	Compound	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	Yield, %	Reference
1.	Thiophan	121.1 (760)	1.5047	0.9998	91	18, 21, 41—43, 47, 48, 53, 64, 65, 68, 69, 74—76, 92—95, 98—101, 104, 106, 153, 202, 208, 209, 210—217
		120—120.5 (767)	1.5054	0.9961	90.5	
2.	2-Methylthiophan	132.4 (760)	1.4909	0.9552	90	42, 43, 53, 67, 77, 95, 101, 103, 142, 151, 189, 200, 218,
		131.2—131.9 (747)	1.4927	0.9553	69	
3.	3-Methylthiophan	138.2 (760)	1.4924	0.9634	82	43, 53, 58, 73, 200
		136.9—137.3 (747)	1.4932	0.9630	81	
4.	2,2-Dimethylthiophan	138—138.8 (750)	1.4807	0.9220	27	79
5.	2,4-Dimethylthiophan	147—148 (742)	1.4818	0.9265	58	77, 106
6.	2,5-Dimethylthiophan	140.2—140.8 (758)	1.4822	0.9220	68	71, 199, 204
7.	*cis*-2,5-Dimethylthiophan	60 (45)	1.4799	0.9222	73	43, 53
8.	*trans*-2,5-Dimethylthiophan	58 (44)	1.4776	0.9188	—	53
9.	3,3-Dimethylthiophan	144—145 (755)	1.4861	0.9374	73	78
10.	2-Ethylthiophan	156.8—156.4 (745)	1.4900	0.9433	71	58, 72, 73, 101, 205
11.	3-Ethylthiophan	164.5—165.4 (750)	1.4911	0.9497	80	58, 73, 205

* Literature references printed in heavy type are those containing constants and yields of the cyclic sulphides.

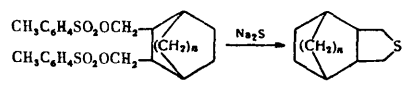
TABLE 2 (contd.)

No.	Compound	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	Yield, %	Reference
12.	2-Propylthiophan	180.4 (766)	1.4859	0.9259	62	57, 58, 63, 73
		179.3—179.8 (743)	1.4862	0.9308	63	
13.	3-Propylthiophan	187.1—187.6 (733)	1.4886	0.9375	72	58, 73
14.	2,3,5-Trimethylthiophan	162—163 (751)	1.4786	0.9104	56	84
15.	2-Butylthiophan	201.5—202 (753)	1.4862	0.9221	60	57, 58, 63, 73
16.	2-Isobutylthiophan	192.5 (766)	1.4800	0.9114	58	57, 63
17.	2-t-Butylthiophan	186—187 (760)	1.4850	—	60	104
18.	2,5-Diethylthiophan	183.5—184.5 (760)	1.4825	0.9104	12	80
19.	2,2,4,4-Tetramethylthiophan	m.p. 158—161°	—	—	—	152
20.	2,5-Dimethyl-3-ethylthiophan	172—173 (744)	1.4782	0.9094	56.5	84
21.	3-Butylthiophan	209.5—209.9 (733)	1.4868	0.9271	79	58, 73
22.	2-Isopentylthiophan	218.4 (764)	1.4821	0.9193	56	57, 63
23.	2,5-Dimethyl-3-propylthiophan	197—198 (747)	1.4770	0.8989	52	84
24.	3-Pentylthiophan	92—93 (10)	1.4870	0.9151	64	81
25.	3-Isopentylthiophan	87—88 (10)	1.4868	0.9196	60	82
26.	3-Phenylthiophan	112—113 (5)	1.6000	1.1009	58	81
27.	2,5-Dipropylthiophan	74—75 (1)	1.4795	0.8955	77	52
28.	*cis*-2,5-Dipropylthiophan	78.5—79.5 (4)	1.4786	0.8979	—	54
29.	*trans*-2,5-Dipropylthiophan	78.5—79.5 (4)	1.4770	0.8944	—	54
30.	2-Methyl-2-ethyl-5-isopropylthiophan	87 (10)	1.4765	—	77	127
31.	2,5-Dimethyl-3-butylthiophan	210—211 (748)	1.4557	0.8930	26	86
32.	2,5-Dimethyl-3-isobutylthiophan	208—209 (752)	1.4740	0.8922	36	86
33.	3-Hexylthiophan	121—122 (16)	1.4870	0.9170	57	82
34.	3,4-Dipropylthiophan	65—66 (1)	1.4830	0.9129	77.5	52
35.	3-*p*-Tolylthiophan	127,5—128 (4)	1.5847	1.0645	51	82
36.	2,5-Dimethyl-3-pentylthiophan	237—238 (765)	1.4734	0.8868	22	86
37.	2,5-Dimethyl-3-isopentylthiophan	233—234 (752)	1.4736	0.8862	19	86
38.	2-Isooctylthiophan	252—253 (760)	1.4801	—	—	104
39.	7-Thiabicyclo[2,2,1]heptane	164 (765)	1.517 (in dibutyl sulphide)	—	low	129
40.	*cis*-2-Thiabicyclo[3,3,0]octane	87.7—88 (25)	1.52424	1.0419	63	109
41.	*cis*-3-Thiabicyclo[3,3,0]octane	88.3—88.5 (25)	1.52328	1.0427	79	109, 160
42.	*trans*-3-Thiabicyclo[3,3,0]-octane	95.5—96 (28)	1.52099	1.0294 (30°)	76	109, 160
43.	2,3-Benzothiophan	235.68 (760)	—	1.1398	26	40, 58, 107 145, 146
44.	3,4-Benzothiophan	241.5 (760)	—	1.1446 (25°)	67	38—40, 56
45.	*cis*-7-Thiabicyclo[4,3,0]nonane	102—102.5 (20)	1.52716	1.0383	54	109
46.	*trans*-7-Thiabicyclo[4,3,0]-nonane	102.7—103.7 (21)	1.52115	1.0209	55	109
47.	*cis*-8-Thiabicyclo[4,3,0]nonane	108.5 (21)	1.53215	1.0430	75	55
48.	*trans*-8-Thiabicyclo[4,3,0]-nonane	104.6—105.6 (20)	1.52481	1.0203	91	55
49.	5-Methyl-2,3-benzothiophan	m.p. 114—115°	—	—	49	206
50.	4-Methyl-2,3-benzothiophan	96.5—97 (6)	1.5969	1.0980	67	206, 207
51.	2-Methyl-3,4-benzothiophan	m.p. 115—116°	—	—	70	141
52.	*cis*-4-Thiatricyclo[5,2,1,$0^{2,6}$]-decane	m.p. 123.5—125°	—	—	18	155
53.	*cis*-4-Thiatricyclo[5,2,2,$0^{2,6}$]-undecane	m.p. 56—58°	—	—	47	155
54.	Tetrahydrothiapyran	141.6 (760)	1.5067	0.9855	80	21, 28, 41—43, 47, 48, 51, 53, 61, 87, 142, 151 167, 202, 203
55.	2-Methyl-tetrahydrothiopyran	151—151.5 (750)	1.4906	0.9427	55.5	13, 48, 53, 88, 142
56.	3-Methyl-tetrahydrothiopyran	157.9 (760)	1.4922	0.9473	82	53
57.	4-Methyl-tetrahydrothiopyran	54 (22)	1.4923	0.9471	80	53
58.	2-Ethyl-tetrahydrothiopyran	107.5—108.5 (45)	1.4874	0.9427	50	88
59.	2-Propyl-tetrahydrothiopyran	89—89.5	1.4860	0.9164	48	88
60.	2-Isopropyl-tetrahydrothiopyran	80—81 (18)	1.4849	0.9141	50	88
61.	2-Butyl-tetrahydrothiopyran	85.5—86 (10)	1.4838	0.9086	30	88
62.	2-Isobutyl-tetrahydrothiopyran	79—80 (10)	1.4828	0.9063	31	88
63.	3-Butyl-tetrahydrothiopyran	218 (760)	1.4884	—	22	28
64.	2,2,6,6-Tetramethyl-tetrahydrothiopyran	65 (12)	1.4763	—	low	150, 151
65.	2,6,6-Trimethyl-2-ethyl-tetrahydrothiopyran	87 (13)	1.4849	—	26	127, 150, 151

TABLE 2 (contd.)

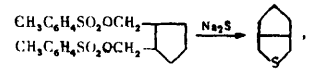
No.	Compound	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	Yield, %	Reference
66.	2,3-Dimethyl-6-isopropyl-tetrahydrothiopyran	86—89 (8)	1.4805	—	—	150
67.	2,6-Diphenyl-tetrahydrothiopyran	m.p. 98°	—	—	40	135
68.	6-Thiabicyclo[3,1,1]heptane	175 (775)	1.519 (in dibutyl sulphide)	—	low	129
69.	6-Thiabicyclo[3,2,1]octane	m.p. 174—175°	—	—	77	154
70.	1-Thiatetralin	m.p. 128—130°	—	—	85	42, 56, 139
71.	2-Thiatetralin	164.7 (760)	—	1.1328	59	46, 56
72.	*trans*-1-Thiadecalin	80—82 (2)	1.5210	—	—	7
73.	*cis*-2-Thiadecalin	122.5—123.25 (20)	1.53346	1.0350	83.5	55
74.	*trans*-2-Thiadecalin	115.5—116.5 (20)	1.52173	1.0058	86.5	55
75.	6-Methyl-1-thiatetralin	137 (12)	1.600	1.086	—	139
76.	6-Ethyl-1-thiatetralin	163—164 (23)	1.5845 (23°)	—	—	137
77.	6,8-Dimethyl-1-thiatetralin	146—147 (12)	1.594	1.075	—	139

Birch, Hunter, and McAllan prepared *cis*-4-thiatricyclo-[5,2,1,$0^{2,6}$]decane (yield 18%) and *cis*-4-thiatricyclo-[5,2,2,$0^{2,6}$]undecane (yield 47%) by the same method[155]:

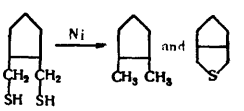


where n = 1 or 2.

Owen and Peto prepared the stereoisomeric 3-thiabicyclo[3,3,0]octanes¶ by the action of sodium sulphide on the *p*-toluenesulphonic acid esters of *cis*- and *trans*-1,2-di-(hydroxymethyl)cyclopentane:



and also showed that with Raney nickel *trans*-1,2-di(mercaptomethyl)cyclopentane produces 1,2-dimethylcyclopentane and *trans*-3-thiabicyclo[3,3,0]octane[160]:



Thus of the existing methods for the preparation of saturated cyclic sulphides the two most important are: reaction of α,ω-dihalides with potassium or sodium sulphide, and the catalytic conversion of tetrahydrofuran and tetrahydropyran homologues or α,ω-diols into the corresponding saturated cyclic sulphides by the action of hydrogen sulphide at elevated temperature.

Table 2 gives the physical properties and yields of the saturated cyclic sulphides of the thiophan and tetrahydrothiopyran series prepared up to 1960.

¶ It is interesting that cyclic sulphides of this type do not obey the Auwers-Skita rule[156—159].

II. SPECTRA OF SULPHIDES OF THE THIOPHAN AND THIACYCLOHEXANE SERIES

1. Ultra-Violet Spectra

Unlike ordinary alcohols and ethers, which are almost transparent in the spectral region attainable with quartz spectrographs and are therefore used as solvents, dialkyl sulphides have absorption bands in the long-wave region[161-164].

Fehnel and Carmack[165] studied a large number of ultra-violet spectra of dialkyl sulphides, and showed that they give a narrow absorption band near 2100 Å ($\log \epsilon \sim 3$); the intensity of absorption increases with branching of the alkyl radicals attached to the sulphur, and the maximum shifts towards the long-wave region (Table 3).

Up until 1954 no more than 20 ultra-violet spectra of alkyl sulphides had been recorded[166], including those of thiophan[18] and tetrahydrothiopyran[17]. Only very limited use can be made of electron absorption spectra for the identification of organic sulphur compounds in petroleum products. Thus according to Obolentsev and Lyubopytova's data[168,169] the ultra-violet spectra of 2-alkylthiophans (where alkyl = = C_3H_7, iso-C_4H_9, C_5H_{11}, iso-C_5H_{11}, or iso-C_6H_{13}) are almost identical with the spectra of the corresponding dialkyl sulphides; they differ only in having an inflection at 230–235 mμ, and have such similar intensities that the spectra practically coincide (Table 4).

The ultra-violet spectra of 2-phenylalkylthiophans differ from those of the 2-alkylthiophans. The absorption band of 2-phenylthiophan begins at about 310 mμ. The fine structure characteristic of aromatic hydrocarbons is not observed, and the intensity of the absorption is somewhat greater than in the alkylthiophans. The ultra-violet spectra of 2-phenylethyl- and 2-phenylpropyl-thiophan are practically identical.

TABLE 3. Ultra-violet spectra of alkyl sulphides (in ethanol).

Compound	Absorption band, mμ		Inflection, mμ	
	λ_{max}	ϵ_{max}	λ	ϵ
Dimethyl sulphide	210	1020	229	140
Diethyl sulphide	210	1800	229	140
Dibutyl sulphide	210	1200	229	145
Di-isopropyl sulphide	211	2100	—	—
Di-t-butyl sulphide	213	2600	—	—
Thiophan	210	1100	239	55
Tetrahydrothiopyran	210	1800	229	180

TABLE 4. Comparison of the extinction in the ultra-violet absorption spectra of thiophans.

Compound	Logarithm of the molecular extinction coefficient			
	225 mμ	230 mμ	235 mμ	245 mμ
Thiophan	2.56	2.12	1.87	1.60
2-Propylthiophan	2.47	2.02	1.96	1.63
2-Isobutylthiophan	2.54	2.05	1.79	1.58
2-(3-Methylbutyl)thiophan	2.51	2.03	1.81	1.61

It has been shown that the indirect determination of aliphatic sulphides in petroleum products from the absorption spectra of their iodine complexes[170-172] is better than potentiometric titration for determining sulphide sulphur[173,174].

2. Raman Spectra

Yur'ev, Tatevskii, and Gragerov have published data on the Raman spectra of thiophan and eight 2- and 3-alkylthiophans[175].

The characteristic frequency 690 cm^{-1} was found in all the spectra studied, and it was assigned to fully symmetrical vibrations of the thiophan ring. However, the Raman spectra of sulphides with an open chain of carbon atoms were also found to have intense frequencies in the region 600–700 cm^{-1},[176-179] assigned to valency vibrations of the C–S bond. This assignment was confirmed by a theoretical calculation of the frequencies of methyl mercaptan[180], and then of the simpler organic sulphides and disulphides[181-184].

A group of workers has shown that the frequency 690 cm^{-1} and a number of other frequencies in the region 600–740 cm^{-1} in the Raman spectra of cyclic sulphides must be related to the characteristic stretching vibrations of the C–S bonds[185-189].

A decisive interpretation of the frequencies in the Raman spectra of cyclic sulphides of the thiophan and tetrahydrothiopyran series became possible as a result of a detailed study of the cyclopentane molecule, which was chosen as a structural model of the thiophan molecule[190]; it was found that the cyclopentane ring is distorted and exists in several forms of almost the same energy, *i.e.* the distortion of the cyclopentane ring is indefinite in character[190].

On passing from cyclopentane to thiophan, *i.e.* exchanging a methylene group for a sulphur atom, the symmetry of the molecule should be largely destroyed. Since there is a large difference in mass between the sulphur atom and the methylene group, and the harmonic vibrations of the C–S bond are small compared with the vibrations of the C–C bond, the interaction of the C–S bond with the other bonds should decrease, and conditions should be such that a characteristic frequency appears for the C–S bond. At the same time, the vibrations of the ring in the thiophan molecule are apparently highly distorted, and their effect is so reduced that they are practically indiscernible in the spectra. Some workers consider that the Raman spectra cannot be used to identify such an important structural fragment as the thiophan ring[191].

The stretching vibrations of the C–S bonds in the Raman spectra of thiophans are in the region 600–700 cm^{-1}; for example, the spectra of 2,5-dimethylthiophan[189] and 2,3,5-trimethylthiophan[84] show three lines in this region. The 1450 cm^{-1} region apparently contains the deformation vibrations of the methylene and methyl groups of the thiophans; thus the frequency 1448 cm^{-1} in the spectrum of 2,5-dimethylthiophan corresponds to the frequency 1451 cm^{-1} in the spectrum of 2,3,5-trimethylthiophan.

The C–H stretching vibrations of the methylene and methyl groups appear at 2870–3174 cm^{-1}. The spectra of 2,5-dimethyl- and 2,3,5-trimethyl-thiophan, for example, show a splitting of the frequencies in this region, because of the effects of rotational isomerism and Fermi resonance[192,193].

It is difficult to utilise the results obtained in the study of the Raman spectra of saturated cyclic sulphides for

analytical purposes, because on passing from one homologue to another, many of the spectral lines change their frequency, and in most cases the spectra themselves are accompanied by a considerable background.

3. Infra-Red Spectra

Since Raman spectra are unsuitable for the identification of the ring of saturated cyclic sulphides, attempts have been made to use infra-red absorption spectra for this purpose. The C–S bonds of organic sulphides are very difficult to identify in the infra-red spectra, since the corresponding absorption bands are of very low intensity, and their position varies considerably[194].

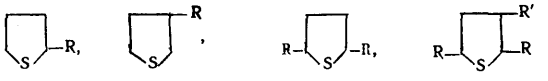
Many workers have considered the assignment of the C–S bands; for example, Thompson gives the frequency range 600–700 cm^{-1} for this group[195], while Colthup considers it absorbs in the range 675—760 cm^{-1}.[196] Sheppard[187] subdivides the region 600–700 cm^{-1} as follows:

	CH_3-S	685–705 cm^{-1};
Primary	RCH_2-S	630–660 cm^{-1};
Secondary	$RR'CH-S$	600–630 cm^{-1};
Tertiary	$RR'R''C-S$	570–600 cm^{-1}.

This division of the frequency interval is correct only for saturated open-chain sulphides.

The infra-red spectra of thiophan[18,51,190,197] and tetrahydrothiopyran[51,142,167,198] have been much studied. Thus Leonard and Figueras[142] have published the infra-red spectra of 2-methylthiophan, 2-methyltetrahydrothiopyran, and thiacycloheptane. Glazebrook and Saville[127] used the infra-red spectra of thiophan and tetrahydrothiopyran homologues for the analysis of mixtures of sulphides. The infra-red spectra of 2-propyl-, 2-butyl-, 2-isobutyl-, and 2-isopentyl-thiophan have also been recorded[63].

In investigating possible characteristic properties for analytical use in the spectra of thiophan homologues of the types:



Yur'ev, Rozantsev, and Egorov studied the infra-red spectra of the 2-alkylthiophans (R = C_2H_5, C_3H_7, C_4H_9), the 3-alkylthiophans (R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, iso-C_5H_{11}, C_6H_{13}), 2,5-dimethylthiophan and the 2,5-dimethyl-3-alkylthiophans (R = CH_3, R'= CH_3, C_2H_5, C_3H_7, C_4H_9, iso-C_4H_9, C_5H_{11}, iso-C_5H_{11}). For these compounds, the frequencies of the C–S bond vibrations are lower in the 2-alkylthiophans (715–730 cm^{-1}) than in the 3-alkylthiophans (730–750 cm^{-1}). The characteristic band corresponding to vibrations of the carbon skeleton of the thiophan molecule has a frequency of about 1260 cm^{-1} in the monoalkylthiophans and about 1250 cm^{-1} in the trialkylthiophans[199].

Yur'ev, Rozantsev, and Egorov have described the infra-red spectra of 2-methyl-, 3-methyl-, 3-phenyl-, 3-tolyl-, 2,5-dimethyl-3-phenyl-, and 2,5-dimethyl-3-benzyl-thiophans[200]. The infra-red spectra of various bicyclic and tricyclic sulphides have been published by Birch and his coworkers[26,55,56,109,129,155]. A comparative study of the infra-red spectra of various 2-alkyltetrahydrothiopyrans (where alkyl = CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9)[201] has shown the existence of a series of typical bands.

The infra-red spectra which have been obtained for a large number of thiophan and tetrahydrothiopyran homologues and derivatives can be used for the successful solution of specific problems of group analysis and identification of individual organic sulphur compounds present in petroleum.

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THE CHEMISTRY OF MAGNESYLAMINES†

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COMPOUNDS

Introduction 100

1. Reactions with halogeno-derivatives 101
2. Reactions with nitriles 102
3. Reactions with aldehydes, ketones, and quinones 102
4. Carboxylation 103
5. Reactions with acid chlorides and anhydrides, esters, and lactones 103
6. Condensation reactions 104
7. Use of magnesylamines for the synthesis of heterocycles 105
8. Other reactions 106

INTRODUCTION

Magnesylamines are derivatives of nitrogenous compounds in which the nitrogen is joined to magnesium subhalide (MgX). They were first prepared by Meunier[1] in 1903 by the reaction of primary and secondary amines with Grignard reagents:

$$RNH_2+R'MgX \longrightarrow RNHMgX+R'H,$$
$$R_2NH+R'MgX \longrightarrow R_2NMgX+R'H.$$

In primary amines magnesium subhalide may substitute both hydrogen atoms with the formation of dimagnesylamines[2]:

$$RNH_2+2R'MgX \longrightarrow RN(MgX)_2+2R'H$$

Unsubstituted magnesylamine may be prepared by the reaction of Grignard reagents with ammonia, ammonium chloride[3], and chloramine[4,5]:

$$RMgX+NH_3 \longrightarrow RH+H_2NMgX,$$
$$2RMgX+NH_4Cl \longrightarrow 2RH+MgClX+H_2NMgX,$$
$$RMgX+NH_2Cl \longrightarrow RCl+H_2NMgX.$$

† Aminomagnesium halides (Ed. of Translation).