



DESULPHURISATION WITH ACTIVATED METALS

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Nicholas Kowanko B.Sc.
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N.K.

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STATEMENT

This thesis contains no material previously submitted for a degree in any University, either by the author or by any other person, except when due reference is made in the text of the thesis.

Nicholas Kowanko.

1960.

PUBLICATIONS

Most of the work in this thesis has been published in the following papers:

1. Synthetic Applications of Activated Metal Catalysts.
Part III. Desulphurisation of Thiazoles with Raney nickel. J. Chem. Soc., 1957, 1652.
2. Synthetical Applications of Activated Metal Catalysts.
Part VI. Desulphurisations with Raney cobalt. J. Chem. Soc., 1959, 440.
3. Synthetical Application of Activated Metal Catalysts.
Part IX. A Comparison of the Desulphurising Abilities of Some Transition Metals. J. Chem. Soc., 1960, 1658.
4. Synthetical Applications of Activated Metal Catalysts.
Part X. The Desulphurisation of Thionaphtheno-(3,2-b)thionaphthen. J. Chem. Soc., 1960, 2969.

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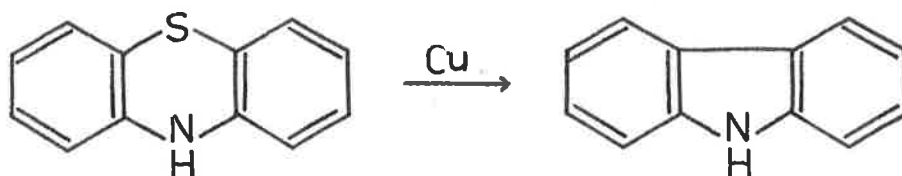
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CHAPTER I

INTRODUCTION

It has long been known that when some sulphur compounds are strongly heated with certain transition metals a reaction takes place leading to the sulphide of the metal and products which are generally free of sulphur. One of the first desulphurisations of this type was the conversion of phenothiazine to carbazole on heating with copper bronze.¹



In 1940 Bougault, Cattalain and Chabrier² showed that the well known hydrogenation catalyst, Raney nickel, can be used to desulphurise a variety of inorganic and organic sulphur compounds under relatively mild conditions. In all the compounds studied hydrogen was introduced at the sites of the sulphur, and double bonds, if present, were hydrogenated. The nickel was transformed to nickel sulphide, so that the reaction was non-catalytic in nature.



The elucidation of the structure of biotin, which was

published in 1942³ was based to a large extent on the desulphurisation of the material with Raney nickel. This work relied to a large extent on the first systematic study of the desulphurisation reaction, published by the same team in 1943,⁴ which may be summarised as follows:



Since then Raney nickel desulphurisation has been used in the determination of the structures of such products as, ω, ω' -bimethionine,⁵ penicillin,⁶ streptomycin,⁷ and oxytocin.⁸ Desulphurisation is now regarded as the method of choice for the degradation of natural or synthetic sulphur compounds.⁹

Early synthetic applications of desulphurisation were mainly concerned with the modification of groups in organic molecules. One of the first of these was a scheme devised by Wolfram and Karabinos¹⁰ for the reduction of carbonyl groups.



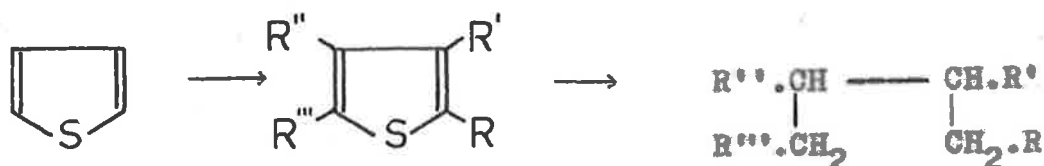
Such reactions have been used extensively, particularly in the steroid field, and in carbohydrate chemistry.¹¹ The reduction of acids to aldehydes¹² may be considered as an extension of this method.



Several other applications of desulphurisation to

synthesis have been made. For instance, quinones have been reduced to dihydro-aromatic compounds by conversion to the sulphuric ester of the leuco form, followed by desulphurisation.^{13,14} Phenanthridine has been prepared by desulphurisation of phenanthridinethione.¹⁵ The removal of thiol groups with Raney nickel has been extensively used, and Brown¹⁶ has described a preparation of Raney nickel which is particularly suitable for this purpose.

Desulphurisation of substituted thiophens constitutes a convenient method for the production of branched chain aliphatic acids, alcohols, ethers and hydrocarbons.¹⁷⁻²¹



Both the synthetic and analytical uses of Raney nickel have been recently reviewed.^{9,13,22}

Although the mechanism of desulphurisation is still largely unknown, several important observations have been made which shed some light on the nature of the process. For instance, Kenner, Lythgoe and Todd²³ suggested that hydrogenolysis with Raney nickel involved attack by hydrogen atoms, with the intermediate formation of radicals. Bonner showed unequivocally²⁴ that the hydrogen substituted at the sites of sulphur during desulphurisation is provided by the

Raney nickel, rather than by the concurrent dehydrogenation of ethanol solvent, as suggested by Wolfram and Karabincos.¹⁰ Also, the racemisation on desulphurisation of sulphides possessing an asymmetric centre adjacent to the sulphur atom provided strong evidence for the view that desulphurisation involves free radical intermediates.²⁵ Desulphurisation of the corresponding sulphones proceeded with inversion of configuration, so that a different mechanism was probably involved, possibly of the S_N2 type.²⁵ A similar mechanism was proposed for the Raney nickel induced cleavage of 2-arylethanol.²⁶

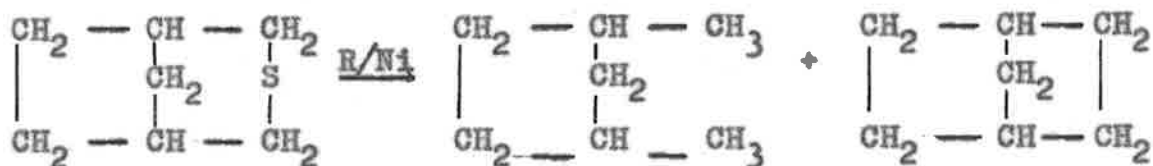
Hauptmann et al.^{27b,c,d} investigated the action of "hydrogen free" and "hydrogen poor" Raney nickel on aromatic thioesters, mercaptals and related compounds. Biaryls, aryl sulphides and stilbenes were formed, which prompted these authors also to propose a free radical mechanism for desulphurisation. The weakening of the C-S bond by the chemisorption of the sulphur atom (via its lone pair electrons) on the nickel was thought to permit detachment of the free radicals. Hauptmann's subsequent isolation of trimeric materials following desulphurisation^{27f} further supported a free radical mechanism. The same author established the intermolecular nature of the process by showing that mixed biaryls were formed after the desulphurisation of a mixture

of sulphides.^{27d} The following pathways were visualised for desulphurisation:



Accordingly, it was found that the yield of dimeric materials depended on the hydrogen content of the catalyst.^{27,28}

Badger and Sasse²⁸ observed a similar dimerisation following the desulphurisation of thiophens, and Birch and Dean²⁹ noticed the following cyclisation, which could only have occurred by a combination of free radicals:



The available evidence leaves little doubt that desulphurisation proceeds by the homolytic scission of the C-S bonds.

A further observation should be mentioned, namely, that desulphurisation appears to be facilitated by the presence of hydrogen on the metal.^{27a,f} However, biaryls may be formed from disulphides in excellent yield using "hydrogen free" nickel, provided that the temperature exceeds 220°. ^{27f} At lower temperatures sulphides are formed. ^{27f}

In 1957 Aller³⁰ found that Raney cobalt also effected

the desulphurisation of organic and inorganic compounds, and Hauptmann²⁷ observed that strongly degassed Raney copper, Raney cobalt and Raney iron desulphurised organic compounds at elevated temperatures, but less effectively than Raney nickel.

Raney³¹ treated a powdered alloy of nickel and silicon with aqueous alkali and obtained a residue of nickel with superior catalytic properties. Subsequent work³² revealed that nickel-aluminium alloys were more convenient. Nowadays Raney nickel is described³³ as "a catalyst which is prepared by the action of aqueous sodium hydroxide on a nickel-aluminium alloy".

Today Raney nickel is one of the most commonly used, and undoubtedly the most versatile, nickel catalyst. Some twenty or more different modifications of Raney nickel are known, each of which is claimed to be particularly suited to a special purpose. Common uses of Raney nickel include the hydrogenation of various classes of compounds,³³⁻³⁵ desulphurisation,^{9,13,22} dehalogenation,³⁶ the formation of heterocyclic biaryls,³⁷ N-alkylation of primary amines³⁸ and a variety of other reactions.

The preparations of some of the most commonly used Raney nickels (designated W1 - W7) have been summarised by Adkins and Billica.³⁹ Of these W5, W6, and W7 catalysts are prepared by adding powdered nickel-aluminium alloy

(50%, w/w) to ca. 30% aqueous sodium hydroxide solution at 50°, and digesting the mixture at that temperature for 50 min. W5 nickel is then washed free of alkali with distilled water in a glass cylinder. A considerable amount of hydrogen is lost from the catalyst during the washing, and it is therefore less 'active' than W6 or W7 nickel. W6 catalyst is similarly washed, but under a positive pressure of hydrogen, and is reputed to be the most active nickel hydrogenation catalyst known. W7 nickel is washed by decantation only, and therefore contains a considerable amount of alkali. Its activity in hydrogenation is at least as great as that of W6 nickel, but its range is limited somewhat by its high alkali and aluminium content.

The preparation of a hydrogen poor catalyst has been described by Badger and Sasse,^{37a,b} and employs a degassing technique (at 100°/12mm.). Hauptmann²⁷ has used Raney nickel almost free of hydrogen. Although many of the desulphurisations in the literature have been carried out with W1 and W2 Raney nickel, most of the present work has been performed with catalysts of the W5, W6, and W7 type, and with the degassed catalyst of Badger and Sasse (W7-J nickel).^{37b}

The high activity of Raney nickel towards hydrogenation has been linked with its highly defective crystal lattice,^{40,41}

with residual metallic aluminium,^{42,43} and with the presence of alumina,⁴⁴ but only the relationship between the hydrogen content and catalytic activity has been definitely established.^{45,46} It is found⁴⁶ that activity in hydrogenation falls off linearly with the hydrogen content of the catalyst. Desulphurisation with Raney nickel is not a catalytic process, and the nickel functions simply as a reagent. Nevertheless, the more active Raney nickel hydrogenation catalysts also appear to be more effective desulphurising agents.^{27a,f} It may be mentioned here that the use of the term 'catalyst' in conjunction with desulphurisation, both in this thesis and in the literature, is strictly indefensible, except on the grounds of habitual association of Raney metals with catalytic hydrogenation. However, as both catalytic hydrogenation and desulphurisation are thought to involve, as first step, the adsorption of the reactants on the metal surface,^{9,27b,g} the two processes are clearly related. Thus a study of adsorption phenomena such as poisoning in catalytic reactions⁴⁷ may assist in our understanding of desulphurisation, provided that we keep in mind that desulphurisation proceeds with the destruction of active sites by sulphide formation, while in catalysis the active sites are regenerated by desorption of the reaction products.

Raney nickel is a heterogeneous mixture, the properties

of which are governed by the method of preparation,³³ the length of storage,⁴⁸ and probably also by less tangible factors. This fact is exemplified by the diversity of the physical data for Raney nickel. Its composition, for instance, has been given⁴² as Al, 1-3; Fe, 1; Cu, 0.1; Co, 0.05; Mn, 0.04%, in addition to nickel, hydrogen and oxygen. Adkins and Billica³⁹ found only nickel and aluminium (11%) in W6 catalyst, while Ipatieff and Pines⁴⁴ quoted nickel (77%), alumina (21%), metallic aluminium (1.36%), and sodium aluminate (0.5%), also for W6 nickel. The latter values are in fair agreement with those of Smith et al.⁴⁶ and of Kokes and Emmett.⁴⁸

The particle size of Raney nickel has been given⁴⁹ as 40-80 Å, that is, about one tenth of the size of the particles (primary crystals) of reduced nickel catalysts, which are of the order of 400-1090 Å. The density of Raney nickel increases linearly with the amount of hydrogen removed,⁴⁸ and is surprisingly low (6.6-6.2 g./ml., after allowing for some 20% of alumina), suggesting a highly defective crystal structure.^{40,41,48}

Metallic nickel can exist in both hexagonal and face-centred cubic close packed structures.⁵⁰ Of these the hexagonal form is a little more stable at room temperature, but most methods of preparation lead to the cubic form. On

heating at 170° for several days the cubic form changes to hexagonal.^{50,51} Only face-centred cubic nickel is catalytically active, the hexagonal being completely inert.⁵¹ Both reduced nickel⁵¹ and Raney nickel⁴⁸ contain only the cubic lattice. This arrangement has two different inter-atomic spacings, namely 2.47 and 3.50 Å.⁵² It is found in experiments on oriented metal films that the 3.50 Å spacing is the more effective in the hydrogenation of ethylene,^{52,53} and this is in agreement with theoretical calculations.⁵²

Although the surface area of Raney nickel has been given as 100 m²./g. and more,⁵⁴ more recent calculations by Kokes and Emmett⁴⁸ give the value for W6 nickel as 63 m²./g. The area was unaltered by heating to 350°, and decreased by one quarter after heating to 500°. Smith, Chadwell and Kirelis⁴⁶ obtained a value of ca. 16.2 m²./g. by adsorption of palmitic acid, and another variety of Raney nickel has been reported⁵⁵ to have a surface area of 18.6-50 m²./g. The surface area of Raney nickel decreases linearly with the hydrogen content until some 70% of the hydrogen is removed, and then more rapidly.⁴⁶ When all the hydrogen has been removed the surface area is only ca. one fifth of its original value.

One of the distinguishing features of Raney nickel is its high hydrogen content. Freshly prepared catalyst of the W6 type may contain as much as 157 ml. of

hydrogen per g. of catalyst,⁴⁶ but on storing, particularly under water, excessive hydrogen is lost and a stable state is reached which contains 72-81 ml. of hydrogen per g.⁴⁸ It has been suggested that "a large portion of the hydrogen lost during ageing is that labile portion which is removed from the fresh catalyst by heating to 100-120°."⁴⁸ Some workers⁵⁶⁻⁵⁸ consider the hydrogen to be present in the form of a hydride, NiH_2 , or of a mixture of hydrides, but more recently Raney nickel has been regarded as a nickel promoted by adsorbed hydrogen.⁴⁶ The hydrogen is thought to be in the form of atoms attached to nickel in a metastable state. The hydrogen atoms are slowly desorbed on standing, and the rate of desorption can be accelerated by reducing the pressure or by raising the temperature. Hydrogen evolution becomes very rapid between 160-200°, ⁴⁸ and it is thought⁴⁸ that the highly exothermic combination of hydrogen atoms (liberated by the degassing) to form molecules may be responsible for the explosions which sometimes occur during degassing.^{27,46,37b} Smith, Chadwell and Kiralis⁴⁶ were also able to show that the catalytic activity of Raney nickel towards the hydrogenation of benzene was proportional to its hydrogen content. Freidlin et al.⁴⁵ have demonstrated that the hydrogen in Raney nickel is chemically heterogeneous and is thus not present as a hydride. They also showed that

part of the sorbed hydrogen enters into the composition of the active centres of the catalyst, and together with the nickel determines the catalytic activity, in agreement with the findings of Smith et al.⁴⁶

X-Ray analysis of Raney nickel led Freidlin et al.⁵⁹ to the following conclusions:

1. The physical structure of Raney nickel is not altered by the removal of hydrogen from the active centres. (This was supported by the finding that Raney nickel freed from hydrogen by treatment with hydroquinone could be completely restored by treatment with hydrogen.)
2. In the process of forming Raney nickel crystals, hydrogen entering into the composition of the active centres is distributed not at internodal points of the crystal (i.e. does not form a solid solution with nickel), but at the boundary surfaces of crystals forming a particle of Raney nickel powder (Fig. 1.1).⁵⁹

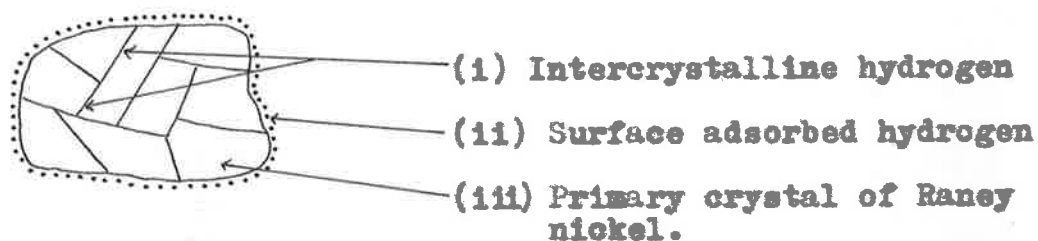


Fig. 1.1

In a recent paper Kokes and Emmett⁴⁸ concluded from an

extensive physico-chemical study of Raney nickel that "the hydrogen is held in the nickel in the form of substitutional replacement of nickel atoms in the lattice. It does not appear to be present as adsorbed hydrogen, or as dissolved hydrogen; neither does it appear to be formed by the reaction of residual aluminium during the process of heating the sample to remove hydrogen". Their evidence for these conclusions may be summarised as follows:

1. The low density of W6 Raney nickel suggests 30.4% lattice vacancies.
2. If each vacancy carries one hydrogen atom, 70 ml./g. can be accounted for. This agrees well with the 72-81 ml./g. found in 'stable' (aged) W6 catalyst.
3. The surface area ($63 \text{ m}^2/\text{g.}$) corresponds to a maximum of 8-10 ml. of physically adsorbed hydrogen per g. of catalyst. Only 20% of the surface of Raney nickel is actually nickel, the remainder being presumably alumina, so that a monolayer of hydrogen would only correspond to 1.5-2 ml./g.
4. Unlike all other cases of desorption of hydrogen from metal surfaces, which are endothermic, the desorption of hydrogen from Raney nickel is exothermic, so that adsorption is probably not a major factor in hydrogen attachment.
5. Ordinary solution of hydrogen in nickel only accounts for

0.01 ml./g., and supersaturated solutions are considered unlikely. Moreover, only about 50 ml./g., or about one half of the hydrogen content of Raney nickel can be replaced by treating Raney nickel degassed at 1200° with hydrogen at 400°/140 atm. This agrees with the finding that Raney nickel does not anneal completely on degassing, but about one half of the lattice vacancies remain.

6. Magnetic measurements suggest that each hydrogen is, on the average, contributing one electron to the nickel.

7. The maximum rate of hydrogen evolution from Raney nickel on heating occurs at 180-220°, that is, at the temperature (one third to one quarter of the m.p.) at which sintering and atom migration are expected to commence.

Comparatively little is known about other Raney transition metals, and only few physical properties have been recorded. The best known of these is Raney cobalt.^{30,34,40a,49,60}

The composition of one type of Raney cobalt has been given³⁰ as Al, 7.1; Si, 0.23; Fe, 7.3; Ni, less than 0.01; Mn, 0.15; NaOH, 0.48%, in addition to cobalt, hydrogen and oxygen. Its hydrogen content was reported to be 100-110 ml./g., and the surface area, estimated by the adsorption of stearic acid, was 15.8 m²./g.³⁰ Unlike Raney nickel, Raney cobalt

is not normally pyrophoric unless warmed;³⁰ but some samples prepared by the method of Billica and Adkins (W7)³⁹ have been found to be pyrophoric in the course of the present work.

Generally speaking, Raney cobalt exhibits properties which are very similar to those of a weak Raney nickel,^{30,34} except that the activity towards hydrogenation decreases more rapidly on ageing than in the case of nickel.³⁰ The only notable difference reported³⁰ was the failure of Raney cobalt to catalyse the isomerisation of allyl alcohol to propionaldehyde. Raney cobalt was also inferior to nickel in the catalysis of the Cannizzaro reaction.³⁰ The main application of Raney cobalt has been to the reduction of nitriles under pressure,^{34,35} and in the reduction of oximes. Although Reid and Schiller⁶¹ reported that the pressure hydrogenation of oximes stops at the imine stage, only amines were found by Reeve and Christian⁶² in a series of comparative hydrogenations using both Raney nickel and cobalt catalysts.

Like nickel, cobalt exists in face-centred cubic and hexagonal forms, but the shortest interatomic separations (2.51 \AA) are identical in both modifications.^{50,63} The cubic form is again more commonly encountered. The percentage d -character for cobalt has been calculated⁶⁴ as 39.5, compared with nickel (40.0), so that both metals should form

bonds of similar strength with chemisorbed substances.⁶⁵

Raney iron³³⁻³⁵ has found little application, although it has been reported to hydrogenate triple bonds selectively to double bonds at pressures of 55-75 atm., and temperatures of 100-135^o. Recently Johnston et al.⁶⁶ described a preparation of high purity Raney iron for magnetic studies. The composition of their material was estimated as total Fe, 86.3-97; metallic Fe, 81.3-93.7; total Al, 0.4-5.3; and total Na, 0-0.2%, depending on the method of storage. Iron is very readily oxidised in air⁶⁶ so that it is very difficult to obtain an iron catalyst with a 'clean' surface. Unlike nickel, cobalt and copper, iron crystallises in the body-centred cubic system^{50,65} exhibiting both 2.48 and 2.87 Å spacings.⁶⁵ The percentage d-character of iron has been given⁶⁴ as 39.7.

Raney copper^{34,35} has found a limited application in high pressure hydrogenations. It is considerably weaker than nickel, but no systematic study has been made. Copper crystallises with face-centred cubic symmetry, the shortest interatomic distance being 2.56 Å⁶³ or 2.59 Å.⁶⁶

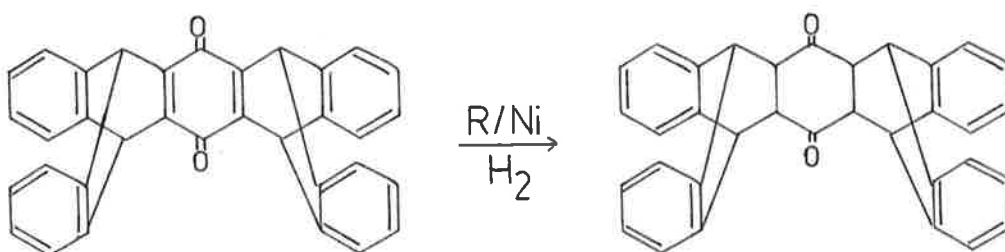
Sulphides and thiophen derivatives are notorious catalyst poisons in hydrogenation.⁴⁷ This property is common to most members of sub-group VIb and

group V. Maxted⁴⁷ has pointed out that all catalyst poisons possess lone pairs of electrons which enable their chemisorption on the metal surface. Magnetic susceptibility measurements⁴⁷ support the view that a covalent bond is formed by donation of a pair of electrons from the poison atom into the d-band of the metal. However, chemisorption may also occur when a molecule has empty valency orbitals.⁴⁷ For instance, in the chemisorption of hydrogen on nickel there is some evidence for the reverse electronic movement, leading to hydride ions, but this is not common.^{47,67}

It has already been pointed out that desulphurisation probably involves chemisorption of the sulphur atom on the metal as first step.^{9,27b,c} The chemisorption might be expected to depend on the geometry and energy of the lone pairs of the sulphur atom in the particular compound, as well as on other molecular geometry, and on the geometry of the nickel surface.

It may be mentioned in passing that the active sites of Raney nickel are not necessarily part of a crystal plane. The successful desulphurisation of derivatives of 1-methyl- and 1,8-dimethyldibenzothiophen⁶⁸ and of other compounds possessing sterically hindered sulphur atoms⁶⁹ strongly suggests that some of the active sites may protrude well above the bulk of the surface. The same conclusion may be

drawn from the work of Balandin and Klabunovski,⁷⁰ who were able to carry out the following hydrogenation over Raney nickel:



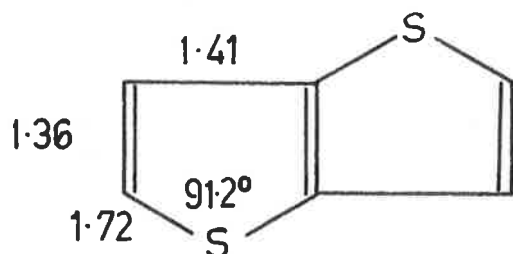
This requires a 'bump' on the catalyst surface at least 3.17 Å high and no more than 4.8 Å wide.

Sulphur has an electronic configuration K,L,(3s)², (3p_x)²,3p_y,3p_z in the ground state. The 3d orbitals, empty in the ground state, are of comparable energy with the 3p levels, and can therefore also enter into bond formation.^{71,72} The expansion of the sulphur outer shell by use of the d-orbitals is now adequately substantiated and has recently been reviewed.⁷²

Although the H-S-H angle in H₂S is 92.1°, suggesting almost pure p-orbital bonding, the observed asymmetry of the molecular electric field suggests admixture of ca. 15% of both s- and d-orbitals.^{71,73} Considerable hybridisation of orbitals can also be inferred from the variation of the bond angle in compounds containing sulphur linked to two

other elements. The dihedral angle of sulphur varies from $74-110^\circ$, depending, presumably, on the extent of admixture of s-, p-, and d-orbitals.⁷¹ Since s-, p-, and d-electrons are probably involved to a varying extent in the bonding of various sulphides, the geometry of the lone pairs is largely a matter of conjecture. However, the $(3p_x)^2$ pair, perpendicular to the S-C bond, and the non-directional $(3s)^2$ pair are probably available for chemisorption.

Thiophen is not suitable for analysis by X-ray diffraction,⁷⁵ but Schomaker and Pauling,⁷⁶ after assuming the values 1.35 and 1.44 Å for the 2,3 and 3,4 bonds respectively, found the C-S bond to be 1.74 Å, and the C-S-C angle to be 91° . The related thiophthen, however, has been analysed as follows:



It has been suggested that pd^2 hybridisation takes place in the thiophen sulphur atom.^{78,79} Two of the hybrid orbitals then have the correct energy and symmetry to conjugate with the p-orbitals of the carbon atoms. The third

orbital is mainly d in character and is unoccupied in the ground state.^{72,78} The $(3s)^2$ lone pair is presumably left largely unaltered. This is illustrated in Fig. 1.2,⁷² where the molecular plane is also a plane of antisymmetry.

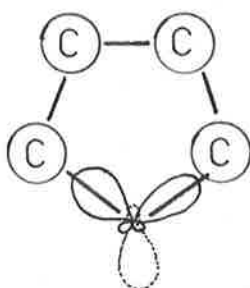


Fig. 1.2

Conventionally,⁴⁷ chemisorption of thiophen is expected to involve the non-directional $(3s)^2$ pair, which is donated to the nickel. Cilento⁸⁰ has suggested that perpendicular chemisorption of thiophen on nickel is possible by use of the vacant pd^2 hybrid orbital of the sulphur atom, the electrons being furnished by the 3d- band of nickel. This is supported by the work of Maxted,⁴⁷ who has pointed out that chemisorption can occur when a molecule has empty valency orbitals.

Lastly, it should be mentioned that the desulphurisation reaction has no analogy in oxygen chemistry.^{27E} Hauptmann^{27E} has observed, however, that the analogous selenium compounds are readily deselenized by Raney nickel to give the expected products.

CHAPTER II

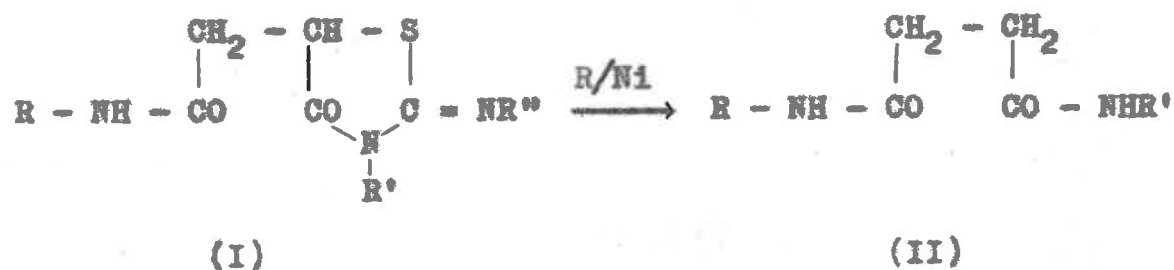
THE DESULPHURISATION OF THIAZOLES

INTRODUCTION:

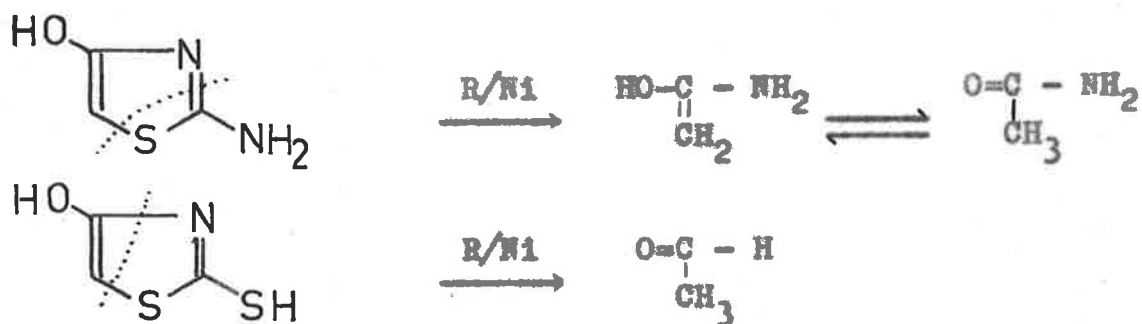
Although the thiazole ring system is comparatively well known,⁸¹ there have been only few attempts to study its behaviour towards activated metals such as Raney nickel. Cook, Heilbron and Levy⁸² succeeded only in removing the thiol group from 2-mercapto-4-phenyl-5-aminothiazole by treatment with Raney nickel; the 4-phenyl-5-aminothiazole formed was not further desulphurised under the conditions used. Moreover, Blomquist and Diguil⁸³ have claimed that both 2-mercapto-4-nitro-6-methylbenzothiazole and 2-mercapto-4-nitro-6-methoxybenzothiazole were unaltered by low-pressure hydrogenation using a large excess of Raney nickel. Both these findings suggest that the thiazole ring must be relatively resistant to desulphurisation. This is not surprising in view of the fact that the nitrogen atom of the heterocycle will probably compete with the sulphur atom for chemisorption on the nickel surface, thus hindering the reaction.⁴⁷

On the other hand, the desulphurisation of thiazolidines has been frequently observed. Marrian,⁸⁴ for instance,

reported the cleavage of thiazolidones of the type (I) to substituted succindiamides (II) in the presence of Raney nickel.



Nevertheless, some examples of the desulphurisation of the thiazole nucleus have been recorded, inter alia, by Hurd and Rudner.⁸⁵ In their experiments 2-amino-4-hydroxythiazole gave acetamide in high yield when treated with Raney nickel. However, a different mode of ring fission, leading to acetaldehyde, was observed by these workers in the case of 2-mercapto-4-hydroxythiazole.



Also, 2-amino-4-phenylthiazole was found to yield methylamine, acetophenone, and α -methylbenzylamine, while

Also, Hurd and Rudner⁸⁵ obtained a mixture of benzo-
thiazole, o-aminothiophenol and aniline from the desulphur-
isation of 2-mercaptobenzothiazole with Raney nickel in the
presence of ammonia. However, Ivanov and Ivanov⁸⁶ have
claimed that desulphurisation of this compound under neutral
conditions leads to benzothiazole only, and that a mixture
of aniline and N-methylaniline is formed in the presence of
alkali.

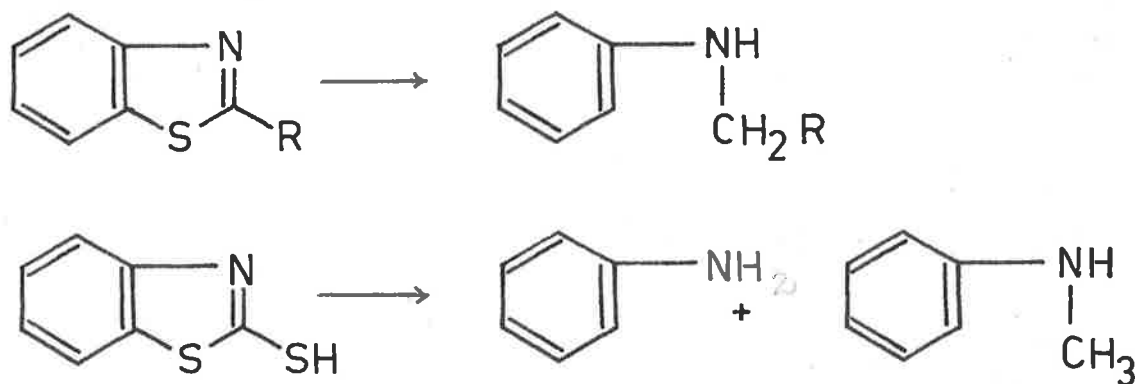
It will be seen that the existing experimental data on
the desulphurisation of thiazoles do not form a simple
pattern, and may at times appear to be contradictory. One
of the reasons for this diversity may be that different
preparations of Raney nickel were used by the various
experimenters. A more systematic investigation of the de-
sulphurisation of thiazoles was therefore undertaken.

Most of our work was carried out in methanol solvent
as this alcohol is known not to alkylate primary amines in
the presence of Raney nickel,³⁸ and as primary amines have
been reported among products of thiazole desulphurisation.^{85,86}
Several preparations of Raney nickel differing greatly in
alkalinity, and hydrogen content, were used. The resulting
primary and secondary bases were separated as their tosyl
derivatives, and the tertiary bases were removed by steam
distillation. All the products were identified by mixed

m.p. with authentic specimens.

RESULTS AND DISCUSSION:

Very hydrogen rich (neutral) W6³⁹ and (alkaline) W7³⁹ Raney nickel catalysts transformed both benzothiazole and 2-methylbenzothiazole to the corresponding secondary amines in excellent yield, and no primary amines were found. On the other hand, 2-mercaptobenzothiazole gave a mixture of N-methylaniline (67%) and aniline (19.5%) when desulphurised with W7 nickel.



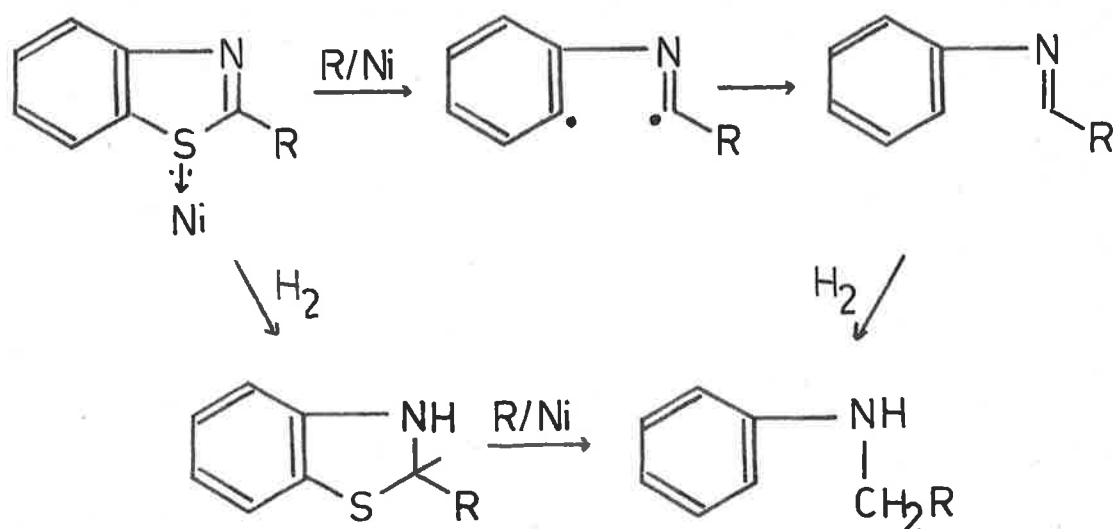
Hydrogen-poor (degassed) W7-J Raney nickel was used in an attempt to desulphurise benzothiazole in xylene solution. No desulphurisation occurred after refluxing for 12 hr., and most of the base was recovered unchanged. However, a small amount (0.2%) of dimeric material, identified as 2,2'-bibenzothiazolyl, was obtained. A similar catalyst, in methanol solvent, effected considerable desulphurisation of 2-mercaptobenzothiazole. Benzothiazole (35%) and N-methyl-

aniline (22%) were the main products; but aniline (7.2%) and bibenzothiazolyl (5.6%) were also formed.

A neutral catalyst of hydrogen content intermediate between the above catalysts (W5 Raney nickel)³⁹ gave the most diverse results. It converted 2-mercaptobenzothiazole to benzothiazole only, and no products of ring fission were found. Dimerisation occurred only to the extent of 0.1%. However, when a similar experiment was conducted in the presence of sodium hydroxide (just less than required to form the thiolate salt), no benzothiazole survived the reaction. The products were N-methylaniline (48%), aniline (17%), o-aminothiophenol (10%) (isolated as 2,2'-diaminodiphenyl disulphide), and bibenzothiazolyl (7%). When benzothiazole was refluxed with 10% methanolic sodium hydroxide, and then treated with W5 Raney nickel as above, the yield of aniline (43%) by far exceeded that of N-methylaniline (11%).

Although the above data suggest that both hydrogen content of the catalyst and basicity of the medium affect the course of desulphurisation of benzothiazoles, both neutral W6 and alkaline W7 catalysts gave identical products. Since the products were secondary amines, and since no loss of carbon atoms occurred, it is thought that the pathway in this reaction is comparable with the

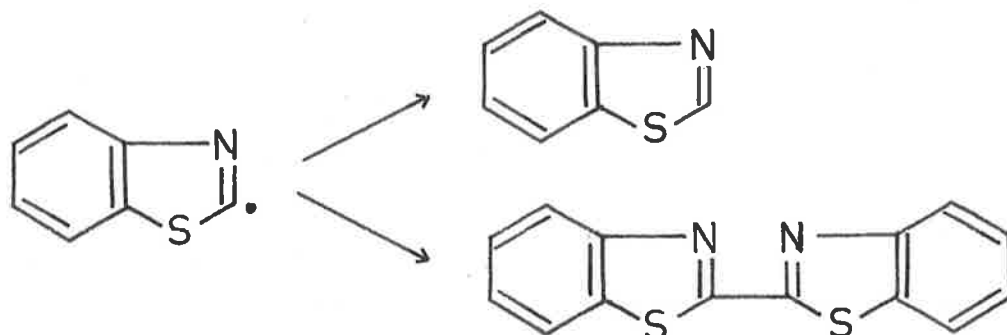
desulphurisation of thiophens with Raney nickel.⁹ Removal of sulphur probably leads to unsaturated intermediates, which are then hydrogenated.



The alternative pathway, involving hydrogenation prior to desulphurisation, is not invoked from an analogy with the desulphurisation of thiophen derivatives, which in all probability proceeds via unsaturated intermediates. It is thought that desulphurisation of benzothiazoles with W6 and W7 Raney nickel proceeds so rapidly that the side reactions introduced by the presence of alkali are virtually excluded. In the desulphurisation of 2-mercaptobenzothiazole with W7 nickel it is suggested that the nickel is partly poisoned by reaction with the thiol group. Desulphurisation of the ring

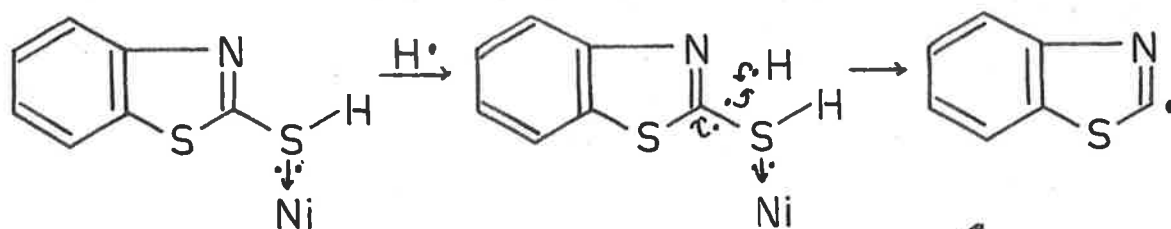
would then proceed sufficiently slowly to allow the competing reaction with alkali to take place, giving a mixture of aniline and N-methylaniline.

The great difference in the yield of dimeric material obtained with W7-J Raney nickel from benzothiazole and 2-mercaptobenzothiazole suggests that different mechanisms are involved in the formation of this compound from the two different starting materials. The similarity of thiazoles and pyridines is well known, so that dimerisation of benzothiazole by a mechanism suggested by Badger and Sasse^{37a} for pyridine derivatives is possible. The similarity of the two processes is supported by the fact that the yield of dimer obtained from benzothiazole (0.2%) is of the order predicted for a pyridine derivative of similar basicity.⁸⁷ On the other hand, the yield of bibenzothiazolyl obtained from 2-mercaptobenzothiazole (7%) is too high to have arisen in this manner, and it is suggested that the compound is here formed by the dimerisation of benzothiazolyl radicals.

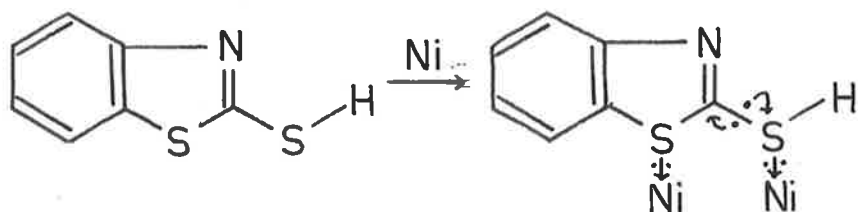


There are at least two feasible ways in which 2-mercaptobenzothiazole can lose its thiol group to give the radical. The first step would be chemisorption of the thiol sulphur atom on the metal surface. Chemisorption may be expected to take place in this way, rather than via the hetero-sulphur atom because the lone pair electrons of the latter would be expected to be less readily available for bond formation due to their participation in the aromatic system. Attack by a hydrogen atom on the chemisorbed sulphur atom (path A) would then lead to bond fission as shown.

A

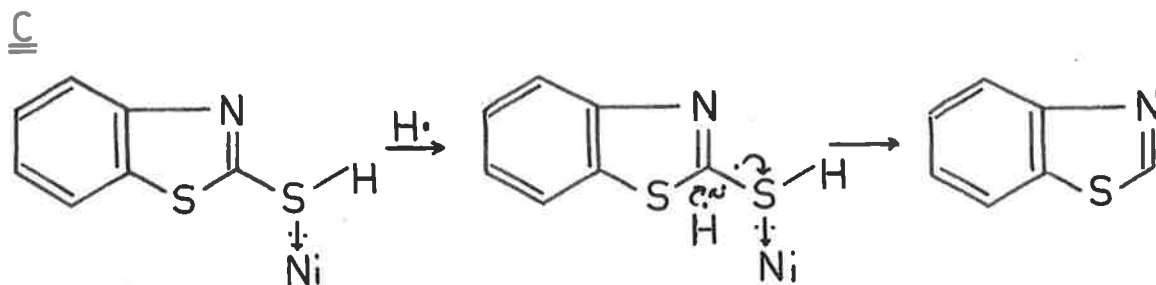


B



Alternatively (path B), chemisorption of both sulphur atoms on the metal surface may provide the necessary driving force for the homolytic bond fission, without the intervention of a hydrogen atom.

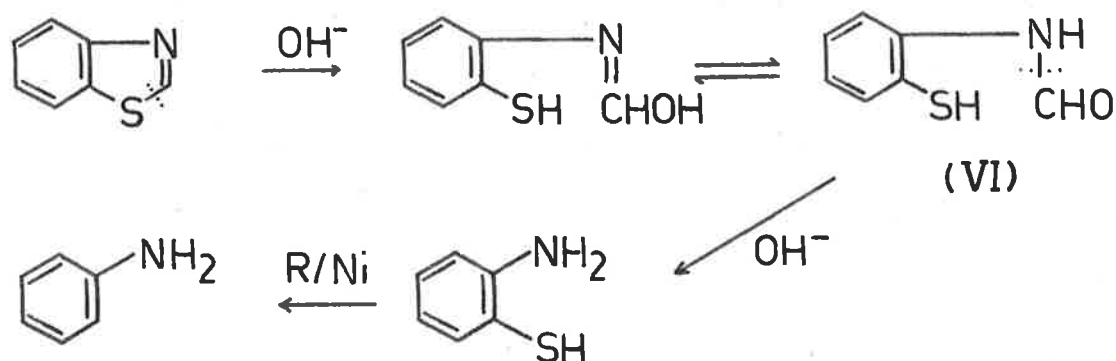
The benzothiazole formed in this reaction can arise by collision of a benzothiazolyl radical with a hydrogen atom, or directly, by attack of a hydrogen atom on the quaternary carbon atom C₍₂₎, followed by bond fission as shown in path C. Other products of the reaction, namely aniline and methylaniline, are almost certainly derived from benzothiazole.



The failure of W5 Raney nickel to attack the benzothiazole nucleus, although it removed the thiol group from 2-mercaptobenzothiazole, is in qualitative agreement with the results of Ivanov and Ivanov.⁸⁶ A possible explanation may be that the acidic mercapto group may interact with the nickel to give nickel ions. These are known to be powerful poisons for hydrogenations,⁴⁷ and may also prevent the

desulphurisation from proceeding further. Such poisoning would not be possible in an alkaline medium, and accordingly almost complete reaction was observed in the experiment conducted in the presence of sodium hydroxide.

Benzothiazole is known to be cleaved to *o*-aminothiophenol by alkali.⁸⁸ Desulphurisation of this would lead to aniline.



Although reduction of the formyl derivative (VI), and desulphurisation, may be expected to lead to *N*-methylaniline, formanilide was hydrolysed to aniline when refluxed with W5 Raney nickel under the same experimental conditions, and no secondary base could be found. It is therefore thought that *N*-methylaniline arises by a different mechanism, independent of alkali, and probably by the process postulated for W6 and W7 nickel.

The competing nature of the reactions leading to aniline and *N*-methylaniline was demonstrated by pre-treating

benzothiazole with dilute sodium hydroxide, and then adding W5 Raney nickel. Under these conditions the ratio of aniline to N-methylaniline was greatly increased.

Unlike benzothiazoles, mononuclear thiazoles could not be converted to the corresponding secondary amines with either W6 or W7 Raney nickel. Multiple ring fission took place, particularly with W7 nickel, and the reaction was found to be generally more complex. Results are summarised in Table 2.1.

Ammonia was readily evolved from all 2-aminothiazoles, and ammonia, rather than methylamine, was formed in the desulphurisation of 4-phenyl- and 2-amino-4-phenylthiazoles. However, methylamine was obtained when the products of desulphurisation were treated with hydrochloric acid during working up.

It was observed that all 4-phenylthiazoles gave α -methylbenzylamine as one product when treated with either catalyst. Acetophenone was also found in most experiments using W6 Raney nickel, but not with W7. 2-Amino-4-methyl-5-phenylthiazole gave the analogous products, α -methylphenethylamine and phenylacetone, with either catalyst, but only a small amount of the ketone was isolated when W7 catalyst was used.

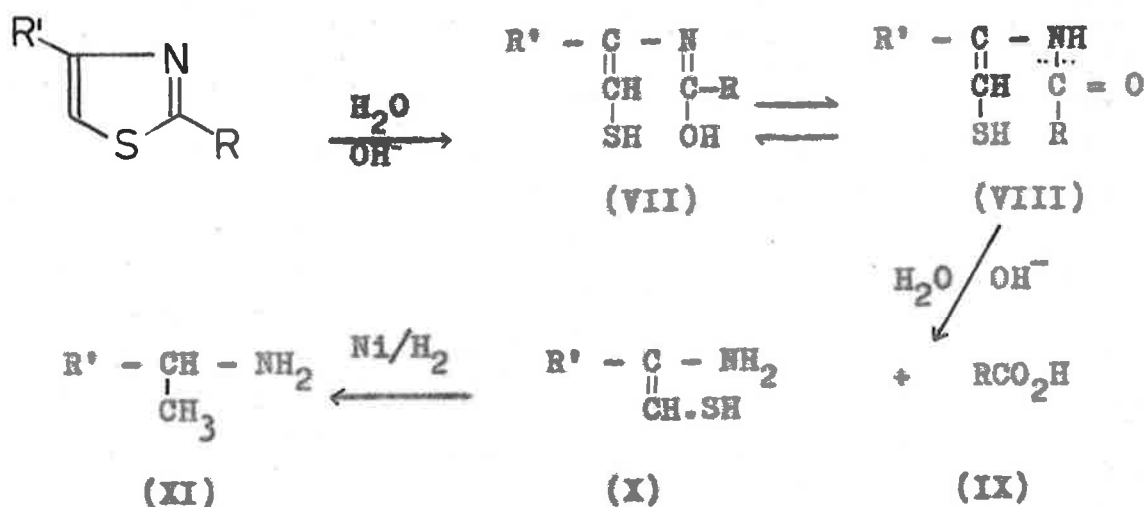
It is interesting to note that no acetophenone was

found after desulphurisation of 2,4-diphenylthiazole with W6 or W7 nickel. However, benzaldehyde and ammonia were formed during distillation of the basic fraction. Similarly, the desulphurisation of 2-(α -naphthyl)-4-phenylthiazole with W7 nickel gave 1-naphthaldehyde and ammonia. This reaction also produced a small amount of 1-methylnaphthalene.

It is evident from these results that the desulphurisation of simple thiazoles does not follow a simple pattern, and a series of competing or alternative reactions is possible. The actual path(s) followed depend on the thiazole used, and particularly on the alkalinity of the medium. Thus the formation of acetophenone is favoured by nearly neutral conditions, while α -methylbenzylamine is formed on either the neutral or alkaline nickel. It must be remembered, however, that the reaction mixture is basic even when W6 nickel is used by virtue of the thiazoles themselves, and, as the reaction proceeds, of the basic products.

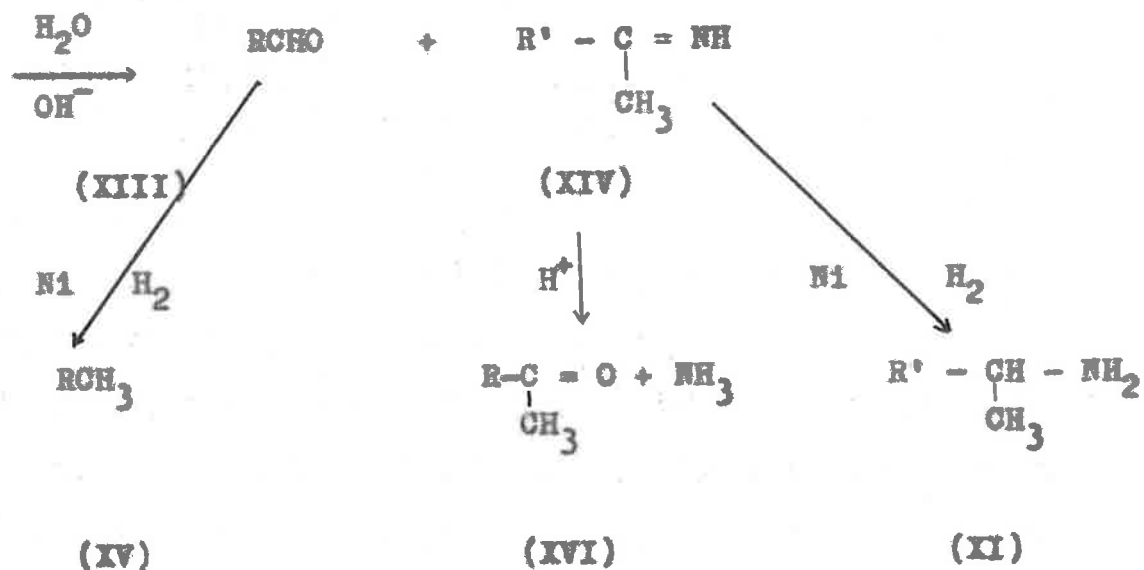
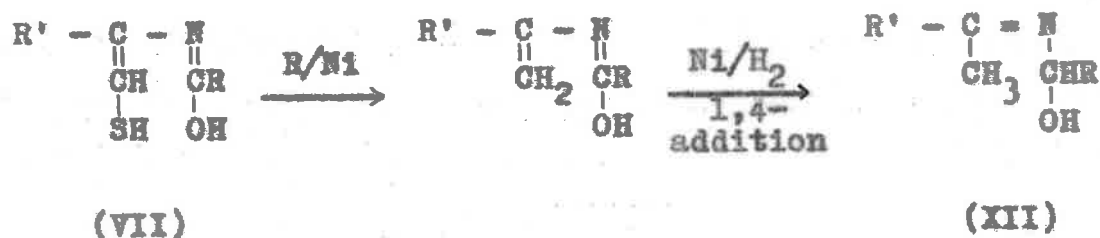
As thiazoles are labile to base, ring fission to the hydroxythiol (VII) should proceed readily. This could hydrolyse further to the acid (IX) and an amino-thiol (X), desulphurisation of which would lead to α -methylbenzylamine

(or α -methylphenethylamine) (XI), which was isolated in all experiments. No carboxylic acids (X) were found under the conditions used.

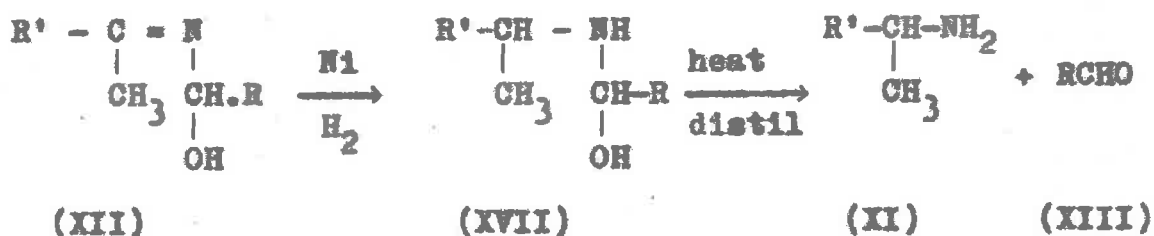


Alternatively, desulphurisation and partial hydrogenation of the thiol (VII) could lead to the intermediate (XII), which in turn could react in two ways, or survive the reaction. Basic conditions would favour its hydrolysis to an aldehyde (XIII) and a ketimine (XIV). These compounds could then take up hydrogen to give the observed amine (XI) and a hydrocarbon (XV). The 1-methylnaphthalene obtained from 2-(α -naphthyl)-4-phenylthiazole may well have arisen in this way. (The analogous methane and toluene expected from 2-unsubstituted- and 2-phenylthiazole respectively would not be detected under the experimental conditions used). Any residual ketimine (XIV) would hydrolyse to

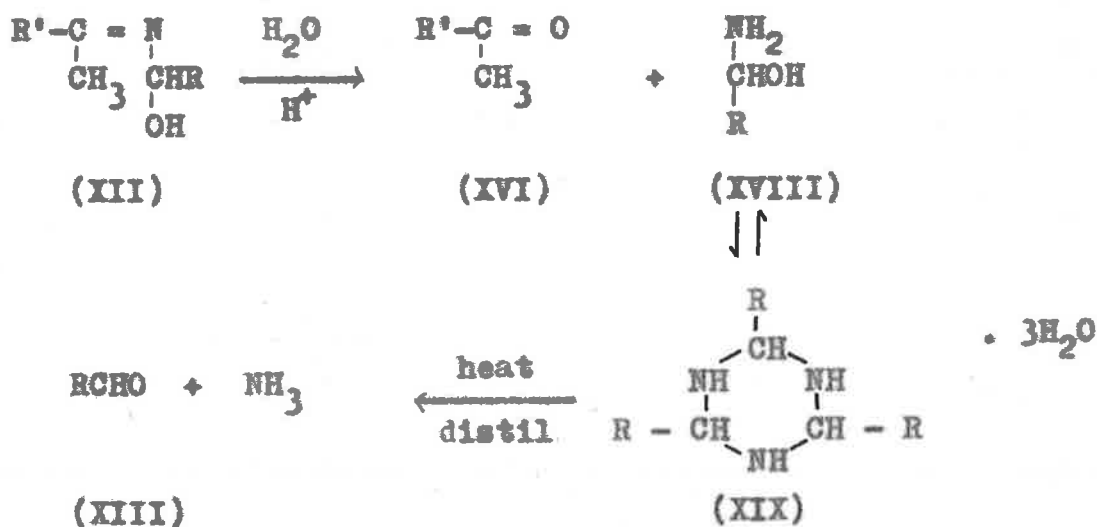
the ketone (XVI) (acetophenone or phenylacetone) and ammonia during working up with acid.



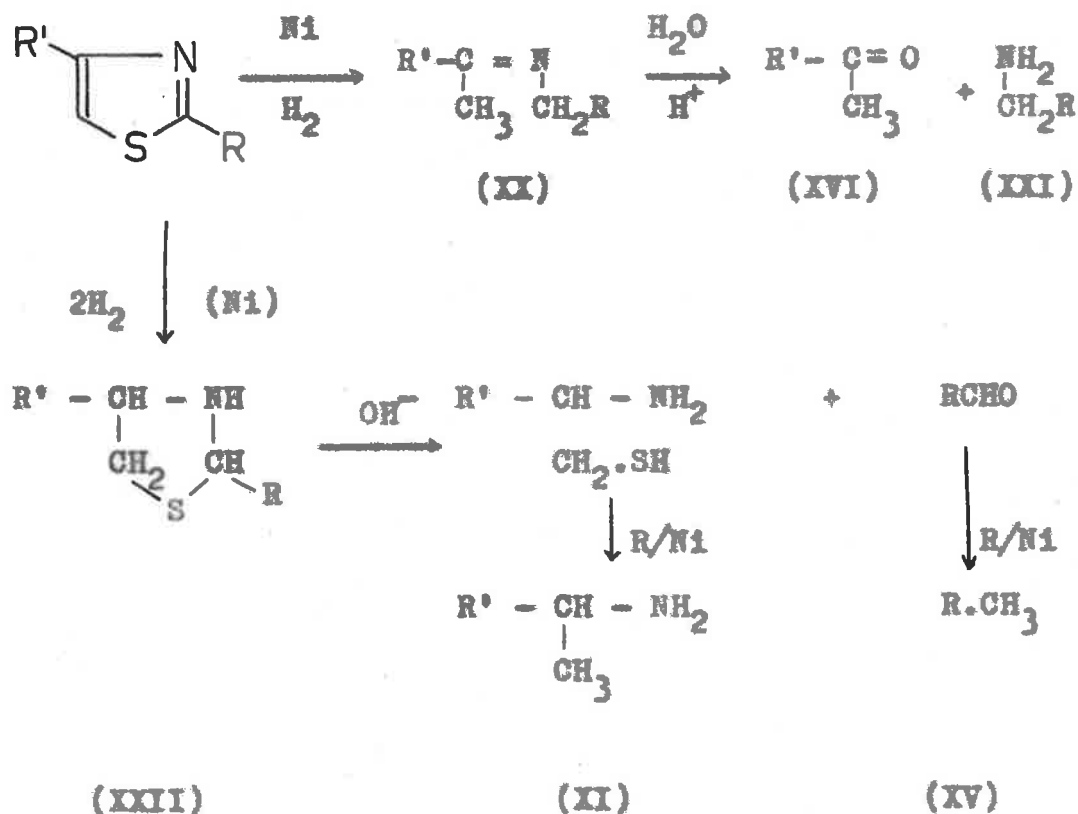
Under less basic conditions (as with 2,4-diphenyl- and 2-(α -naphthyl)-4-phenylthiazole) the intermediate (XII) may take up hydrogen to give the base (XVII) which will be expected to survive the reaction, but decompose on distillation to give the primary amine (XI) and aldehyde (XIII), as was indeed found in the above experiments.



If the intermediate (XII) survives the reaction, it would be expected to hydrolyse during working up to give the ketone (XVI) and an aldehyde ammonia (XVIII), which could acquire considerable stability in the trimeric form (XIX), but which would decompose on distillation to the aldehyde (XIII) and ammonia. Indeed, the properties of the unstable basic materials, which gave benzaldehyde or 1-naphthaldehyde and ammonia, are consistent with those of aldehyde ammonias, but no ketone (XVI) was found after desulphurisation of 2,4-diphenylthiazole in which a considerable amount of benzaldehyde was found.



As with benzothiazoles, it is suggested that direct desulphurisation (and partial hydrogenation) to the intermediate (XX) competes with alkaline ring fission (which gave VII). Acid hydrolysis of (XX) during working up would lead to ketones (XVI) and amines of the type (XXI). The acetophenone and methylamine formed from 4-phenylthiazole almost certainly arose in this way. It was possible to show that α -methylbenzylamine is not converted to acetophenone by Raney nickel, and the base was recovered unchanged after working up.



Finally, although the study of the desulphurization of thiophen derivatives suggests the contrary, the above data do not exclude the possibility of ring hydrogenation to a thiazolidine (XIII). Such compounds decompose very rapidly under alkaline conditions to mercaptamines and aldehydes, which would readily be converted to amines (XI) and hydrocarbons (IV) respectively in the presence of Raney nickel.

EXPERIMENTAL

Desulphurisation of Benzothiazoles

Preparation of Raney metals.- Commercial sodium hydroxide flakes and B.D.H. Raney nickel alloy (containing 50% Ni w/w) were used. W5, W6 and W7 catalysts were prepared by the method of Billica and Adkins,³⁹ except that the final washings were carried out with methanol instead of ethanol, and the centrifugation was omitted. W7-J Raney nickel was prepared according to the method of Badger and Sasse.^{37a} All catalysts were freshly prepared before use in each experiment.

Desulphurisation of 2-Mercaptobenzothiazole.-

(1) With W5 Raney nickel. A mixture of 2-mercaptobenzothiazole (10 g.), in methanol (250 ml.), and W5 Raney nickel (from 65 g. of alloy) was refluxed for 8 hr. The reaction mixture was filtered hot, the metal washed with hot methanol, and the combined filtrates evaporated on the water bath. To the residue was added a small amount of material obtained by dissolution of the nickel in dilute hydrochloric acid, basification, steam distillation, and extraction of the steam distillate with ether, followed by removal of the dried solvent. The combined oil was distilled to give

benzothiazole (4.41 g., 54.5%), b.p. 230°. The picrate formed yellow needles, m.p. 169.5-170°

Found : C, 43.2; H, 2.5; N, 15.5.

Calc. for $C_{13}H_8O_7N_4S$: C, 42.9; H, 2.2; N, 15.4%.

The residue after distillation was recrystallised from xylene. 2,2'-Bibenzothiazolyl (10 mg.) formed plates, m.p. 297.5-298°, alone or mixed with a specimen prepared by an improved method of Zubarovski,⁸⁹ who, however, gives m.p. 306-308°

Found : C, 62.7; H, 3.2; N, 10.2.

Calc. for $C_{14}H_8N_2S_2$: C, 62.7; H, 3.0; N, 10.4%.

(ii) As above, in the presence of sodium hydroxide.- In a similar experiment, sodium hydroxide (2 g.) was added to the reaction mixture at the beginning of the reaction. Concentration of the methanolic extracts left a tarry residue which was diluted with water (50 ml.) and extracted with ether. When kept in air the aqueous (alkaline) phase deposited 2,2'-diaminodiphenyl disulphide (0.75 g., 10.1%) as yellow plates, m.p. and mixed m.p. 93-4°

Found : C, 58.0; H, 4.7; N, 11.4; S, 26.4.

Calc. for $C_{12}H_{12}N_2S_2$: C, 58.1; H, 4.8; N, 11.3; S, 25.8%.

The dihydrochloride of this base crystallised from concentrated hydrochloric acid as needles, m.p. 210-211°

Found : C, 40.3; H, 5.2.

Calc. for $C_{12}H_{18}O_2N_2S_2Cl_2$: C, 40.5; H, 5.1%.

The recorded⁹⁰ m.p. of this salt (112-114°) seems to be in error. The oil obtained by evaporation of the etherial layer was subjected to a Hinsberg separation using toluene-*p*-sulphonyl chloride (9 g.) and 10% aqueous sodium hydroxide. This gave 2,2'-bibenzothiazolyl (0.55 g., 6.9%), *N*-methyl-toluene-*p*-sulphonanilide (4.1 g., 47.5%), and toluene-*p*-sulphonanilide (1.5 g., 16.5%), all identified by comparison with authentic specimens.

(iii) With W7-J Raney nickel.- 2-Mercaptobenzothiazole (12 g.) in methanol (150 ml.) was refluxed with W7-J Raney nickel (from 125 g. of alloy) for 29 hr. Extraction of the nickel with methanol and with benzene, and concentration to small volume gave 2,2'-bibenzothiazolyl (0.52 g., 5.6%), m.p. and mixed m.p. 295-298°. The residual oil was subjected to a Hinsberg separation with toluene-*p*-sulphonyl chloride and aqueous sodium hydroxide, and gave benzothiazole (3.44 g., 35.1%), b.p. 230° (picrate, m.p. 169°); *N*-methyl-toluene-*p*-sulphonanilide (3.60 g., 22%); and toluene-*p*-sulphonanilide (1.23 g., 7.2%), all identified as above.

(iv) With W7 Raney nickel.- A mixture of 2-mercaptobenzothiazole (5.0 g.), W7 Raney nickel (from 65 g. of alloy),

and methanol (200 ml.) was refluxed for 3 hr. Working up using excess tosyl chloride gave a mixture of tosyl-N-methylaniline (5.04 g., 67%), and ditosylaniline (2.34 g., 19.5%), separated by fractional recrystallisation from ethanol. Both products were identified by comparison with authentic specimens. No other products were found.

Desulphurisation of benzothiazole.-

(i) With W7 Raney nickel. A mixture of benzothiazole (6 g.), methanol (250 ml.), and W7 Raney nickel (from 65 g. of alloy) was refluxed for 3 hr. Filtration, thorough extraction with methanol, followed by attempted Hinsberg separation as usual gave N-methyltoluene-p-sulphonanilide (8.4 g., 84%) as sole product.

(ii) With W6 Raney nickel. When W6 catalyst was used in a similar experiment, the same product was obtained in 87% yield. No other products were found.

(iii) With W7-J Raney nickel. A solution of benzothiazole (10 g.) in sulphur-free xylene (35 ml.) was added to W7-J Raney nickel (from 65 g. of alloy) by the method of Badger and Sasse,^{37a} and the mixture refluxed for 12 hr. Distillation of the product gave unchanged benzothiazole (8.4 g.), identified as the picrate, and a residue. After repeated recrystallisation from xylene this gave 2,2'-bibenzothiazolyl(0.02 g.), m.p. and mixed m.p. 298°.

(iv) With W5 Raney nickel, after pre-treatment with 10% methanolic sodium hydroxide. A mixture of benzothiazole (10 g.), sodium hydroxide (15 g.), and methanol (150 ml.) was refluxed for 2.5 hr. W5 Raney nickel (from 65 g. of alloy) in methanol (50 ml.) was then added and the mixture refluxed for 8 hr. Hinsberg separation of the product gave N-methyltoluene-p-sulphonanilide (1.23 g., 7.25%) and toluene-p-sulphonanilide (4.69 g., 29.5%). Some dark red nickel-organic compound was also formed but this was not investigated.

Desulphurisation of 2-Methylbenzothiazole.-

(i) With W7 Raney nickel. 2-Methylbenzothiazole (5 g.), W7 Raney nickel (from 65 g. of alloy), and methanol (250 ml.) were refluxed for 3 hr. The reaction mixture was filtered, the catalyst washed thoroughly with hot methanol, and the combined extracts acidified with dilute hydrochloric acid, and evaporated. The residue was made strongly alkaline and treated with toluene-p-sulphonyl chloride. No primary or tertiary base could be detected, and N-ethyltoluene-p-sulphonanilide (8.2 g., 80%), m.p. and mixed m.p. 86° was isolated as sole product.

(ii) With W6 Raney nickel. When a similar experiment was carried out using W6 Raney nickel, the same product (8.35 g., 82%) was isolated. No side products could be found.

Action of W5 Raney nickel on formanilide.- A solution of formanilide (7.2 g.) in methanol (220 ml.) was refluxed with W5 Raney nickel (from 65 g. of alloy) for 8 hr. Working up as for benzothiazoles gave toluene-*p*-sulphonanilide (6.3 g., 43%), and a small amount of an oil which smelt like phenylisocyanide. No derivative of N-methyl-aniline could be found.

2,2'-Diaminodiphenyl disulphide.- Was prepared from benzothiazole by ring fission with alkali and aerial oxidation of the intermediate thiophenol according to the method of Gardner.⁸⁸

2,2'-Bibenzothiazolyl.- The following procedure was found to give better yields than that described by Zubarowski.⁸⁹ 2,2'-Diaminodiphenyl disulphide (1 g.) was heated with glycollic acid (1.025 g.) in a sealed tube at 340° for 13 hr. After extraction of the product with ethanol and with petroleum ether, repeated recrystallisation of the residue from xylene (charcoal), and sublimation at 200°/30 mm., 2,2'-bibenzothiazolyl formed plates m.p. 298° (0.80 g., 86.5%).

Synthesis of simple thiazoles

4-Phenylthiazole.- This thiazole was prepared by the condensation of thioformamide⁹¹ and phenacyl bromide by

the method of Wiley, England and Behr.⁹²

2,4-Diphenylthiazole.- 2,4-Diphenylthiazole was prepared from thiobenzamide⁹³ and phenacyl bromide according to the method of Hubacher.⁹⁴ The crude thiazole was purified by chromatography on alumina in benzene/light petroleum (2:1) to give colourless prisms, m.p. 93-94° (lit. m.p. 92-93°).

2-Amino-4-phenylthiazole.- This was obtained by the condensation of thiourea with phenacyl bromide by the method of Traumann.⁹⁵

2- α -Naphthyl-4-phenylthiazole.- A solution of 1-naphthonitrile (30 g.) and dimethylamine (2 ml.) in ethanol (200 ml.) was cooled to -10° and saturated with hydrogen sulphide, quickly transferred to an autoclave, and heated at 80-90° for 4 hr. After evaporation the residue was extracted with ether, and the extract washed with dilute hydrochloric acid and with water, dried and evaporated. The resulting crude 1-thionaphthamide (9 g.) was heated with phenacyl bromide (9.6 g.), sodium acetate (3.85 g.), and ethanol (45 ml.) on the steam bath until the solvent evaporated. Water was added, the mixture extracted with ether, the ether dried and evaporated. After chromatography on alumina in light petroleum, and crystallisation from light petroleum, 2- α -naphthyl-4-phenylthiazole (11.0 g., 19.5%) formed plates, m.p. 88°

Found: C, 79.5; H, 4.5; N, 4.5.

$C_{19}H_{13}NS$ requires C, 79.4; H, 4.5; N, 4.9%.

2-Amino-4-methyl-5-phenylthiazole.- Benzyl methyl ketone⁹⁶ (70 g., 0.52 M), thiourea (78 g., 1.04 M), and iodine (133 g., 0.52 M) were heated on the steam bath for 8 hr. (Compare similar condensations by King and Hlavecek.⁹⁷) The mixture was then extracted with ether, the residue dissolved in boiling water and treated with charcoal. The filtrate was basified with potassium carbonate, and the product purified by crystallisation from ethanol and from benzene. 2-Amino-4-methyl-5-phenylthiazole (21 g., 21%) was obtained as plates, m.p. 165°

Found: C, 63.4; H, 5.2.

$C_{10}H_{10}N_2S$ requires C, 63.2; H, 5.3%.

The picrate crystallised from ethanol in yellow needles, m.p. 248°

Found: C, 45.9; H, 3.2; N, 16.5.

$C_{16}H_{13}O_7N_5S$ requires C, 45.8; H, 3.1; N, 16.7%.

Desulphurisation of simple thiazoles

Desulphurisation of 4-phenylthiazole.-

(1) With W7 Raney nickel. A mixture of 4-phenylthiazole (10 g.), W7 Raney nickel (from 65 g. of alloy),

and methanol (250 ml.) was refluxed for 3 hr. Ammonia (or methylamine) was liberated during the reaction. This was detected with litmus paper and Nessler's reagent. The reaction mixture was filtered hot and the catalyst washed thoroughly with boiling methanol. Combined filtrate and washings were acidified with dilute hydrochloric acid (100 ml.), and the solvent was evaporated on the water bath. Basification of the dark red residue with 20% aqueous sodium hydroxide, followed by extraction with ether, and distillation of the dried extracts, gave α -methylbenzylamine, b.p. 190-195°, (2.3 g.), identified as the oxalate, m.p. 235-236° (lit., m.p. 238°)

Found: C, 65.0; H, 7.2; N, 8.2.

Calc. for $C_{18}H_{24}O_4N_2$: C, 65.1; H, 7.2; N, 8.4%.

A higher-boiling fraction was found to be unchanged 4-phenylthiazole (1.3 g.), m.p. 44° (picrate, m.p. and mixed m.p. 163°).

(11) With W6 Raney nickel. When 4-phenylthiazole (8 g.) was similarly desulphurised with W6 nickel (from 65 g. of alloy) by refluxing in methanol (250 ml.) for 3 hr., evaporation of the acidified methanolic extracts yielded a dark red residue. Extraction with ether and subsequent evaporation of the dried etherial solution, gave acetophenone (0.75 g.), identified as the 2,4-dinitrophenylhydrazone,

m.p. and mixed m.p. 240° . Basification of the aqueous phase, followed by ether extraction, evaporation of the dried solvent, and distillation of the residue, gave α -methylbenzylamine (1.95 g.), b.p. 195° , identified as the oxalate, m.p. and mixed m.p. 235° , and unchanged 4-phenylthiazole (1.55 g.), identified as the picrate.

(iii) Formation of methylamine. In another experiment using 4-phenylthiazole (5 g.), W6 Raney nickel (from 65 g. of alloy), and methanol (250 ml.) a slow stream of nitrogen was passed through the reaction mixture during the time of reflux (3 hr.), and the outcoming gases passed through dilute hydrochloric acid. Evaporation of the hydrochloric acid did not yield any methylamine hydrochloride or ammonium chloride, and no methylamine could be detected when the exit gases were passed through a 0.5% alcoholic solution of 1-chloro-2,4-dinitrobenzene for 30 min. (in the middle of the reaction). Filtration, extraction, and evaporation of the acidified methanolic extracts, followed by ether extraction as usual, gave acetophenone (0.46 g.), identified as the 2,4-dinitrophenylhydrazone. The aqueous phase was basified and warmed, the liberated methylamine being identified by passing the gas into a solution of 1-chloro-2,4-dinitrobenzene. The cooled basic solution was then extracted with ether, the ether layer dried and distilled to give α -methylbenzylamine

(1.73 g.), identified as the oxalate.

Desulphurisation of 2-amino-4-phenylthiazole.-

(i) With W7 Raney nickel. 2-Amino-4-phenylthiazole (10 g.) was desulphurised in methanol solution (250 ml.) by refluxing with W7 Raney nickel (from 65 g. of alloy) for 3 hr. Working up as described for 4-phenylthiazole (i) gave α -methylbenzylamine (4.03 g.), identified as the oxalate, (m.p. and mixed m.p. 235°); chloroplatinate, m.p. $215-216^{\circ}$ (decomp.) (lit., m.p. $213-214^{\circ}$ (decomp.)). Ammonia was liberated during the reaction.

(ii) With W7 Raney nickel in a stream of nitrogen. The experiment was repeated with a slow stream of nitrogen passing through the reaction mixture, and into dilute hydrochloric acid solution. Evaporation of the acid at the completion of the reaction gave a colourless crystalline residue (4 g.) which sublimed without melting. Basification with concentrated sodium hydroxide solution liberated a volatile base which consisted mainly of ammonia, but a trace of methylamine could be detected with 1-chloro-2,4-dinitrobenzene. Working up of the reaction mixture in the usual way gave α -methylbenzylamine (3.3 g.), identified as above.

(iii) With W6 Raney nickel. A mixture of 2-amino-4-phenylthiazole (10 g.), W6 Raney nickel (from 65 g. of alloy), and methanol (250 ml.) was refluxed for 3 hr.

Ammonia was evolved vigorously at the beginning of the reaction, but evolution virtually stopped after 2.5 hr. Filtration, extraction, and evaporation of the acidified methanolic extracts gave a partly solid mass which was filtered off and washed with ether. Recrystallisation of the solid from dilute hydrochloric acid gave 2-amino-4-phenylthiazole hydrochloride (4 g.), m.p. and mixed m.p. 204°. The ethereal solution gave acetophenone (1.50 g.), identified as the 2,4-dinitrophenylhydrazone. Basification of the aqueous phase gave ammonia and α -methylbenzylamine (2.15 g.), b.p. 190°, identified as the oxalate, m.p. and mixed m.p. 235°.

Desulphurisation of 2,4-diphenylthiazole.-

(1) With W7 Raney nickel. A mixture of 2,4-diphenylthiazole (10 g.), W7 Raney nickel (from 65 g. of alloy), and methanol (250 ml.) was refluxed for 3 hr., filtered and extracted in the usual way. Anhydrous oxalic acid (5 g.) was added and the methanolic extracts evaporated. It was not possible to obtain α -methylbenzylamine oxalate in this way, the only crystalline product being hydrated oxalic acid (7 g.), m.p. 120°. The combined products were basified, extracted with ether, and the ether dried and distilled to give benzaldehyde (1.65 g.), identified as the 2,4-dinitrophenylhydrazone, and α -methylbenzylamine (1.05 g.),

identified as the oxalate.

(ii) With W6 Raney nickel. Desulphurisation of 2,4-diphenylthiazole (9 g.) with W6 catalyst by the method described for 4-phenylthiazole (ii) gave a product which was separated into basic and non-basic fractions. Recrystallisation of the "non-basic" fraction from benzene-hexane gave unchanged 2,4-diphenylthiazole (2.35 g.), identified by comparison with an authentic specimen. The basic fraction was distilled, to give α -methylbenzylamine (0.95 g.), b.p. 195° , identified as the oxalate, m.p. 235° , and another fraction which decomposed at ca. 250° with evolution of ammonia. From this fraction benzaldehyde (2.53 g.) was obtained and identified as the 2,4-dinitrophenylhydrazone.

Desulphurisation of 2-amino-4-methyl-5-phenylthiazole.-

(i) With W7 Raney nickel. A solution of this thiazole (8 g.) in methanol (250 ml.) was desulphurised by refluxing with W7 Raney nickel (from 65 g. of alloy) for 3 hr. The mixture was filtered and extracted with methanol, and the residue, after evaporation of the acidified solvent, separated into neutral and basic fractions. The neutral fraction (0.25 g.) was identified as phenylacetone, giving a 2,4-dinitrophenylhydrazone, orange needles, m.p. 155° (lit., m.p. $155-156^{\circ}$), and a semicarbazone, needles, m.p.

195° (lit., m.p. 195-198°). Distillation of the basic fraction gave α -methylphenethylamine (1.175 g.), b.p. 200-202° (lit., b.p. 203°)

Found : C, 80.25; H, 9.95; N, 10.2.

Calc. for $C_9H_{13}N$: C, 80.0; H, 9.6; N, 10.4%.

The chloroplatinate crystallised from dilute hydrochloric acid in golden-yellow needles, decomp. ca. 220°. The analytical sample was dried over sodium hydroxide and phosphoric oxide in vacuo.

Found: C, 31.9; H, 4.4; N, 4.05; Cl, 30.7; Residue, 27.9.

Calc. for $C_{18}H_{28}N_2Cl_6Pt$:

C, 31.8; H, 4.1; N, 4.1; Cl, 31.3; Pt, 28.7%.

Distillation of the high-boiling fraction gave unchanged 2-amino-4-methyl-5-phenylthiazole (0.85 g.), identified as the picrate, m.p. and mixed m.p. 248°.

(11) With W6 Raney nickel. Desulphurisation of 2-amino-4-methyl-5-phenylthiazole (10 g.) was carried out with W6 Raney nickel as above. Ammonia was evolved during the reaction. The residue, after removal of the acidified solvent, deposited a crystalline hydrochloride which was separated and basified to give unchanged 2-amino-4-methyl-5-phenylthiazole (2.77 g.), identified as the picrate. The liquid product was separated into neutral and basic fractions. The neutral fraction (0.75 g.) was found to be phenylacetone,

giving a 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 155°. Distillation of the basic fraction gave α -methylphenethylamine (1.80 g.), b.p. 200-203°; identified as the chloroplatinate. Recrystallisation of the residue gave unchanged base (2.55 g.), identified as the picrate.

Desulphurisation of 2- α -naphthyl-4-phenylthiazole.-

A mixture of the thiazole (10 g.), W7 Raney nickel (from 65 g. of alloy) and methanol (250 ml.) was refluxed for 3 hr. The reaction mixture was filtered and the nickel extracted with boiling methanol (3 x 200 ml.). Combined extracts and filtrate were acidified with dilute hydrochloric acid (100 ml.) and distilled from the water bath. Addition of excess picric acid to the distillate, followed by concentration, gave 1-methylnaphthalene picrate (1.8 g.), m.p. and mixed m.p. 142°. The residue from the desulphurisation was separated into basic and non-basic fractions in the usual way. The non-basic fraction on removal of ether, deposited unchanged 2- α -naphthyl-4-phenylthiazole (2.15 g.), identified by comparison with an authentic specimen. Distillation of the remainder of the neutral fraction gave acetophenone (0.38 g.), identified as the 2,4-dinitrophenylhydrazone. The basic fraction was distilled to give α -methylbenzylamine (0.85 g.), b.p. ca. 190°; identified as the oxalate, m.p. 235°, and a viscous oil (2.05 g.), b.p.

260-280°. This material was not completely soluble in hydrochloric acid, but gave a chloroplatinate and a 2,4-dinitrophenylhydrazone. Separation into neutral and basic components gave 1-naphthaldehyde (2.0 g.), identified as its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 255°. Ammonia was the only basic component found.

The action of Raney nickel on α -methylbenzylamine.-

The base (4 g.) was dissolved in methanol (250 ml.), added to freshly prepared W7 Raney nickel (from 65 g. of alloy), and the mixture refluxed and worked up as in the case of the thiazoles. No ammonia or methylamine could be detected when a slow stream of nitrogen was passed through the reaction mixture and into hydrochloric acid. An attempt was made to separate the reaction mixture into basic and non-basic components, but no acetophenone or other neutral component could be found. Working up of the basic fraction gave unchanged α -methylbenzylamine (2.9 g., 72.5%).





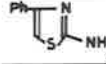


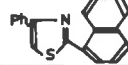
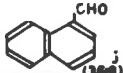
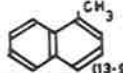
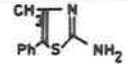
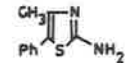
The results of these desulphurisations have been summarised in Table 2.1.

Table 2.1

- (a) All experiments were carried out in refluxing methanol (250 ml.). Reaction time was 3 hr. throughout.
- (b) All products were identified by direct comparison with authentic or analysed specimens.
- (c) 30 g. of Raney nickel were used in each experiment.

TABLE 2.1

DESULPHURISATION OF SIMPLE THIAZOLES^(a)
 PRODUCTS^(b)

COMPOUND	WEIGHT USED (g)	R / Ni ^(c)	% RECOVERED	$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	$\text{Ph}-\overset{\text{NH}_2}{\text{CH}}-\text{CH}_3$	NH ₃	OTHER PRODUCTS
	10	W7	13	—	30.8%	—	—
	5	W6	—	12.3	4.6	—	CH ₃ -NH ₂ AFTER HCl TREATMENT
	8	W6	20	12.5	32.7	—	TRACE CH ₃ NH ₂
	10	W7	—	—	59.4	+	
	10	W6	33	22	31.6	+	CH ₃ NH ₂ AFTER HCl
	10	W7	—	—	20.7	—	Ph . CHO (36.9)
	9	W6	26.7	—	28.8	—	Ph . CHO (63); NH ₃ (LATER)
	10	W7	22	9.1	16.8	—	 (2.9)  (13.9) NH ₃ (LATER)
	8	W7	11.3	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph} \cdot \text{CH}_2$ (4.6)	$\text{CH}_3-\overset{\text{NH}_2}{\text{CH}}-\text{Ph} \cdot \text{CH}_2$ (20.8)	+	
	10	W6	52	10.6	25.3	+	

55

CHAPTER III

Desulphurisations with Raney cobalt

The use of Raney nickel in desulphurisation has been extensively investigated,^{9,13,22} but Raney cobalt has not been systematically studied. Aller described the preparation of a very active Raney cobalt hydrogenation catalyst.^{30a} In the process of studying its general properties he observed^{30b} that this Raney cobalt desulphurised methyl thioglycollate to methyl acetate at room temperature. The general conclusions from this work were that Raney cobalt shows properties which are very similar to those of Raney nickel, but that cobalt generally exhibits a lower activity. Hauptmann^{27g,98} used degassed Raney cobalt to desulphurise organo-sulphur compounds at elevated temperatures. In these reactions also Raney cobalt behaved similarly to Raney nickel, but showed a lower activity.

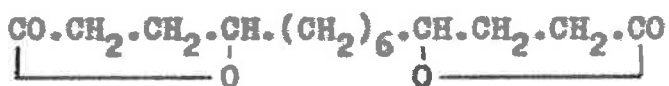
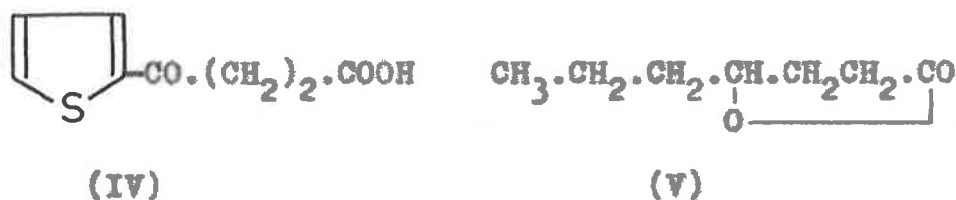
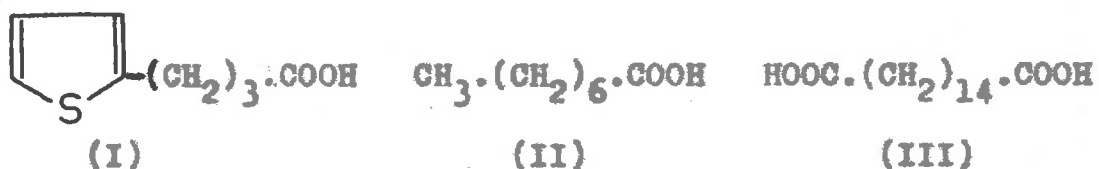
A metal less active than nickel might have advantages in some cases, especially if it could effect desulphurisation without the complete reduction of all unsaturated groups. Raney cobalt seems to be promising in this respect as it is known to be a weak hydrogenation catalyst.^{30,61,62}

This chapter records the results of a systematic study of Raney cobalt in desulphurisation. It will be shown that Raney cobalt generally leads to the same products as Raney nickel, but that it has a lesser activity. Attention will also be drawn to some difference between the two desulphurising agents.

The desulphurisation of thiophen carboxylic acids with Raney cobalt proceeded to give the same products as were obtained with Raney nickel.^{17,28} Thus thiophen-2-carboxylic acid gave *n*-valeric acid, and δ -2-thienylbutyric acid (I) was desulphurised to *n*-octanoic acid (II). In addition the reaction produced some dimeric product (hexadecan-1,16-dicarboxylic acid (III)). In the case of γ -2-thienylbutyric acid, in agreement with the results obtained with nickel,²⁸ it was found that the proportion of dimeric product increased with the concentration of the reaction mixture. Such a result is, of course, expected if the dimeric product results from a recombination of free radicals.²⁸

Desulphurisation of β -2-thienylpropionic acid (IV) resulted in some simultaneous reduction of the keto group, for 4-hydroxyoctanoic acid lactone (V) and 4,13-dihydroxyhexadecane-1,16-dioic acid dilactone (VI) were obtained in addition to 4-oxo-octanoic acid (VII) and 4,13-dioxo-

hexadecane-1,16-dioic acid (VIII). Although all these products have been obtained by Raney nickel desulphurisation of this acid,^{28,99} they are not normally formed under the same experimental conditions. In this respect cobalt seems to be less selective than nickel.



(VI)



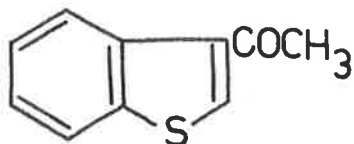
(VII)



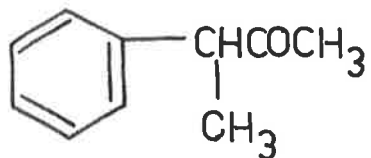
(VIII)

Thiophen ketones were also desulphurised with Raney cobalt to give the same products as were obtained with nickel.^{17,28} For instance, 2-benzoylthiophen yielded

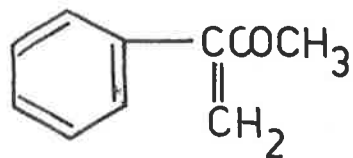
valerophenone, and 3-acetylthionaphthen (IX) gave 3-phenyl-2-butanone (X). However, the desulphurisation of 2-benzoylthiophen with W7 Raney cobalt gave no dimeric product (1,8-dibenzoyloctane), but a considerable amount of this material was isolated when "Aller" Raney cobalt was used. This result is surprising, for the desulphurisation of 2-acetylthiophen with W7 cobalt produced some 2,11-dodecanedione, in addition to the expected 2-hexanone. The desulphurisation of 3-acetylthionaphthen also gave no dimeric product, but this is in agreement with the result of desulphurisation with Raney nickel.²⁸ It was hoped that desulphurisation of 3-acetylthionaphthen could be effected without simultaneous reduction to yield 3-phenylbut-3-en-2-one (XI). However, this material could not be detected in the product, although specially searched for, using infrared spectroscopy. (Also, no olefin was found when desulphurisation was effected with copper-poisoned nickel.)



(IX)



(X)



(XI)

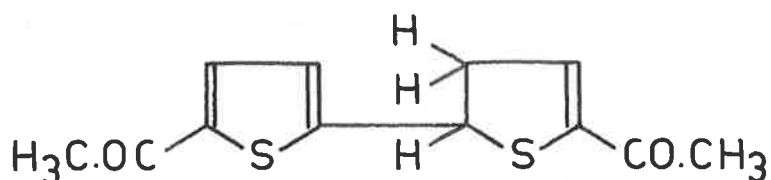
Although the products obtained with cobalt are generally similar to those obtained with nickel, on the

basis of the extent of desulphurisation under similar conditions, W7 Raney cobalt is much less effective than W7 Raney nickel. In the desulphurisation of 3-acetylthionaphthen, for instance, Raney cobalt was about one sixth as active as Raney nickel.²⁸ The ratio of monomeric product to dimeric product also differed with the two metals. For example, in the desulphurisation of 2-benzoylthiophen with "Aller" Raney cobalt the ratio of dibenzoyloctane to valerophenone was 1 : 7.3. With W7 Raney nickel, however, a ratio of 1 : 18.6 was found, that is, less than half the number of dimerisations for the number of molecules attacked.

In the thiophen series the formation of dimeric products probably occurs by recombination of the free radical intermediates arising from desulphurisation.^{9,28} However, it is always possible that dimerisation to derivatives of 2,2'-bithienyl may precede desulphurisation.⁹ No bithienyls have been observed in the desulphurisation of thiophen derivatives, but their presence has not been rigorously excluded.

When 2-acetylthiophen was treated with Raney cobalt under conditions favourable to the formation of dimers²⁸ the expected products (2-hexanone and dodecanedione) were obtained. A small quantity of an alcohol resulting from the reduction of the keto group (2-hexanol) was probably also present. Closer examination of the dimeric fraction led to the

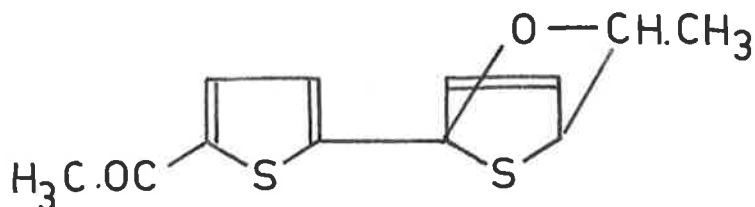
isolation of a very small quantity of an unknown compound "R", which contained oxygen and sulphur. "R" was not 5,5'-diacetyl-2,2'-bithienyl, although analysis suggested a similar composition. The compound had only one carbonyl band in the infrared (5.94μ), and its ultraviolet absorption spectrum was nearly superimposable on that of 2-acetylthiophen if a molecular weight of 252 was assumed. (The molecular weight of diacetylbithienyl is 250.) On the basis of this evidence the compound "R" was tentatively formulated as a dihydrobithienyl derivative (XII).



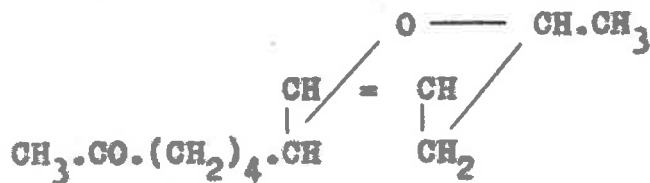
(XII)

In a similar desulphurisation when the method of working up was modified the yield of "R" was nearly one third of the dimeric fraction, and further experiments were directed at the elucidation of its structure. The molecular weight (Rast) of "R" was found to be 235 ± 30 , in agreement with structure (XII) ($M = 252$). A compound possessing such a structure may be expected to be dehydrogenated easily to give diacetylbithienyl. However,

"R" was recovered unchanged after refluxing with chloranil in xylene solution for 4 hr. The spectroscopic and analytical data for "R" can also be accommodated by structure (XIII)*. In addition, this structure accounts for the stability of the material towards dehydrogenation.



(XIII)



(XIV)

An attempt was made to desulphurise "R" with Raney nickel. Considerable reduction of the carbonyl group(s) occurred and the infrared spectrum of the product showed little resemblance to that of dodecanedione. The small quantity used did not permit the identification of the product of desulphurisation.

Reduction of the carbonyl groups could be avoided

* The author is indebted to Dr. J.M. Cornforth, F.R.S. for suggesting structure (XIII).

when the desulphurisation of "R" was carried out with deactivated Raney nickel, but the product had two carbonyl bands corresponding to free and conjugated carbonyl groups in roughly equal amount. However, the infrared spectrum did not contain an Ar.C-H band at 6.65μ , and the product was therefore probably not a mixture of desulphurised and undesulphurised material. Accordingly, there was little change in the infrared spectrum upon sublimation of the product of desulphurisation. Although the structure of this material is not known, it is thought that it is not dodecanedione.

The results of the desulphurisation of "R" are not in agreement with structure (XIII), since the product had two carbonyl bands, but are compatible with structure (XII) if the isolated double bond survived desulphurisation as in (XIV).

Although no definite structure can be proposed for "R" at this stage, the evidence is consistent with the view that this compound is a derivative of bithienyl such as (XII).

The effect of W7 Raney cobalt on thiazoles was found to be similar to that of a rather weak Raney nickel. Some deamination of 2-amino-4-phenylthiazole occurred, and acetophenone was isolated. With 2-mercaptobenzothiazole the thiol group was removed, but no product resulting from the de-

sulphurisation of the benzothiazole ring system could be detected. Accordingly, benzothiazole was recovered unchanged after treatment with W7 Raney cobalt.

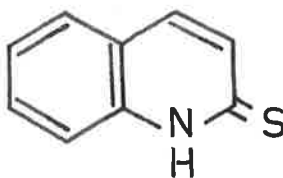
Phenanthridone (XV) is readily converted to phenanthridinethione, and the desulphurisation of this product with commercial Raney nickel offers a useful route to phenanthridine.¹⁵ With more active Raney nickel, however, the reaction is complicated by the fact that reduction to dihydrophenanthridine generally occurs,⁹⁸ necessitating a further dehydrogenation step. With W7 Raney cobalt, however, it has been found that the desulphurisation proceeds smoothly to give phenanthridine in high yield.

2-Quinolone is also readily converted to thioquinolone (XVI) (2-mercaptoquinoline), but the desulphurisation of this compound with Raney cobalt gave a variety of products. The main constituents were quinoline (68%) and 2,2'-bi-quinolyl (13.5%), but 2-hydroxyquinoline (2-quinolone) and the hitherto unknown di-2-quinolyl sulphide were also formed in small amounts. A remarkably stable cobalt complex was also isolated. This has tentatively been formulated as tris-(2-mercaptoquinolyl) cobalt on the basis of the results of elementary analysis and hydrolysis with strong acid. Some properties of this material have been listed in the experimental section.

Acridinethione (9-thioacridone) (XVII) was very resistant to desulphurisation with Raney cobalt, and some of the thione was recovered unchanged. However, a small amount of acridine was isolated, as well as a considerable amount of 9,9'-biacridyl. The reaction also produced a mixture of three other bases (detected by paper chromatography), but separation or identification of these compounds could not be achieved. It is thought that these bases are probably isomeric biacridyls.



(XV)



(XVI)



(XVII)



(XVIII)

Desulphurisation of imidazolidinethione (XVIII) with Raney cobalt did not yield imidazolidine, but gave ethylenediamine, presumably by hydrolysis of the parent base.

Some N,N'-diformylethylenediamine was also isolated. The yield of this material was higher than could have arisen by trans-formylation of the intermediate monoformyl derivative (derived by the hydrolysis of imidazolidine). It seemed therefore likely that the formylation of ethylenediamine resulted from the action of cobalt on the methanol solvent. Such a process would represent a specific property of Raney cobalt, for Raney nickel does not formylate primary amines in methanol.^{38c} However, when ethylenediamine was refluxed with W7 cobalt in methanol under the conditions of the experiment no formylated products were found.

EXPERIMENTAL

Preparation of Raney cobalt.-

W7 Raney cobalt was prepared from cobalt-aluminium alloy (Lights; 30% Co, 70% Al) by the same method as for W7 nickel³⁹ except that the metal was washed ten times by decantation with water and twice with methanol. The final centrifugation was omitted.

"Aller" Raney cobalt was prepared at 15-20° by the method of Aller.³⁰

Desulphurisation of thiophen-2-carboxylic acid.-

To a solution of the acid (5.0 g.) in aqueous sodium carbonate (100 ml., 10%) was added W7 Raney cobalt (from 65 g. of alloy), and the mixture stirred at 80-90° for 2 hr. The metal was filtered off and washed with hot sodium carbonate solution to give, after acidification, unchanged thiophen-2-carboxylic acid (3.75 g.), m.p. and mixed m.p. 126-127°. Extraction of the mother liquors with ether, and removal of the dried solvent gave valeric acid, identified and weighed as the p-bromobenzylisothiuronium salt (3.3 g., corresponding to 0.97 g. of valeric acid, m.p. 162°).

Desulphurisation of γ -2-thienylbutyric acid.-

(1) In high dilution. A mixture of γ -2-thienylbutyric

acid (8.0 g.), W7 Raney cobalt (from 125 g. of alloy), and 10% aqueous sodium carbonate (to make a total volume of 900 ml.) was stirred on the water bath for 1.75 hr. The metal was filtered off, washed well with hot sodium carbonate solution, the combined filtrates acidified and extracted thoroughly with ether. Distillation of the residue after removal of solvent gave :

- (a) n-octanoic acid (2.57 g.), b.p. 72-73°/0.05 mm.;
- (b) γ -2-thienylbutyric acid (4.90 g.), b.p. 104°/0.05 mm.; and
- (c) a residue (0.2 g.).

The residue was extracted with sodium carbonate solution, the extract treated with charcoal and acidified to give a brown material. Recrystallisation from ether and from concentrated nitric acid gave impure hexadecane-1,16-dicarboxylic acid (ca. 8 mg.), identified by comparison of its infrared spectrum with that of the authentic acid.

(11) In high concentration. γ -2-Thienylbutyric acid (30 g.) was dissolved in the minimum amount of 5% sodium carbonate solution, and freshly prepared W7 Raney cobalt (from 250 g. of alloy) added. The mixture (300 ml.) was heated on the water bath for 5 hr. and then dissolved in hydrochloric acid. The solution was extracted continuously with ether for 18 hr., the ether dried and distilled off

and the residue distilled to give :

- (a) forerun (mainly n-octanoic acid) (1.68 g.), b.p. 60-80°/0.1 mm.;
- (b) n-octanoic acid (6.52 g.), b.p. 80°/0.1 mm.;
- (c) γ -2-thienylbutyric acid (18.9 g.), b.p. 115°/0.1 mm.; and
- (d) a residue (1.2 g.).

Fraction (d) was extracted with sodium carbonate solution, the extract treated with charcoal and acidified. Recrystallisation from ether gave a product (0.175 g.) which was further purified by recrystallisation from concentrated nitric acid (6 x) to yield hexadecane-1,16-dicarboxylic acid as plates, m.p. and mixed m.p. 123-124°.

Desulphurisation of β -2-thienylpropionic acid.-

A stirred mixture of β -2-thienylpropionic acid (7 g.), W7 Raney cobalt (from 250 g. of alloy), and aqueous sodium carbonate (7%) (to make the total volume to 300 ml.) was heated on the steam bath for 5 hr. The cobalt was extracted with sodium carbonate solution and the combined filtrates were acidified. On cooling, 4,13-dioxohexadecanedioic acid (0.27 g.), m.p. and mixed m.p. 152-153°, separated. Concentration of the mother liquors from 1000 ml. to 500 ml. and cooling gave β -2-thienylpropionic acid (1.415 g.), m.p. and mixed m.p. 119-120°. The mother liquors were extracted with ether, the ether evaporated, and the residue distilled.

Four fractions were collected :

- (a) 4-hydroxyoctanolactone (0.89 g.), b.p. 114-118°/22 mm.,
 n_D^{24} 1.4456 (lit. n_D^{19} 1.4451);
- (b) oil, b.p. 152-166°/22 mm. (0.62 g.);
- (c) oil, b.p. 180°/22 mm. (0.54 g.); and
- (d) a residue (0.5 g.).

Recrystallisation of fractions (b) and (c) from light petroleum gave 4-oxo-octanoic acid, m.p. and mixed m.p. 50-52°. The residue (d) was separated into acidic and neutral components. The acidic part was a small amount of brown tar which contained sulphur, and was thus probably derived from the thiophen acid by pyrolysis. Repeated recrystallisation of the neutral component from benzene - light petroleum gave impure 4,13-dihydroxyhexadecane-1,16-dioic acid dilactone (3.7 mg.), m.p. 76-78° (lit. m.p. 86-88°), identified by its infrared spectrum.

Desulphurisation of 2-benzoylthiophen.-

(1) With W7 Raney cobalt. A mixture of 2-benzoylthiophen (30 g.), W7 Raney cobalt (from 125 g. of alloy), and methanol (to make the total volume 200 ml.) was refluxed for 5 hr. Soxhlet extraction of the mixture with methanol, followed by removal of the solvent using an efficient fractioning column, and distillation of the residue gave two fractions:

- (a) *n*-valerophenone (1.84 g.), b.p. 80°/0.05 mm., identified as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 152-153°;
- (b) 2-benzoylthiophen (24.75 g.), b.p. 100-102°/0.05 mm.; and a small amount of tarry residue which did not contain 1,8-dibenzoyloctane.

(ii) With "Aller" Raney cobalt.³⁰ A similar desulphurisation was carried out, except that "Aller" Raney cobalt was used instead of the W7 catalyst. Distillation of the product gave :

- (a) *n*-valerophenone (2.2 g.), b.p. 80-100°/0.04 mm., identified as the 2,4-dinitrophenylhydrazone;
- (b) 2-benzoylthiophen (25.5 g.), b.p. 110-120°/0.04 mm.; and
- (c) a residue (0.5 g.) which on recrystallisation from ethanol gave 1,8-dibenzoyloctane (30 mg.), m.p. and mixed m.p. 92-93°.

Desulphurisation of 3-acetylthionaphthen.-

(1) With W7 Raney cobalt. 3-Acetylthionaphthen (30 g.) was refluxed with W7 Raney cobalt (from 125 g. of alloy) in methanol (to make the total volume 200 ml.) for 5 hr. The mixture was filtered and the cobalt extracted continuously with methanol for 24 hr. Combined filtrate and extracts were distilled slowly using a 60 cm. heat-compensated

fractionating column packed with single-turn glass helices, in order to remove methanol. The residue was taken up in ether, dried and distilled to give :

- (a) forerun (4.44 g.), b.p. below $96^{\circ}/0.1$ mm.;
- (b) 3-acetylthionaphthen (24.16 g.), b.p. $96-102^{\circ}/0.1$ mm.; and
- (c) a small amount of residue.

Redistillation of fraction (a) gave 3-phenyl-2-butanone (1.4 g.), b.p. $110-112^{\circ}/24$ mm., identified as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. $171-172^{\circ}$; and 3-acetylthionaphthen (3.04 g.), b.p. ca. $250^{\circ}/24$ mm.

Examination of the infrared spectrum of this sample of 3-phenyl-2-butanone for presence of unsaturated intermediates showed only a slight contamination with 3-acetylthionaphthen. No olefin absorption was noted. Samples of 3-phenyl-2-butanone similarly prepared with Raney nickel by Dr. Sasse²⁸ also contained this impurity but no olefinic absorption was found.

(11) With copper-poisoned nickel.¹⁰⁰ W7 Raney nickel (12 g.) was stirred on the water bath with a solution of cupric acetate (1.2 g.) in methanol (100 ml.) for 20 min. and washed three times by decantation with methanol. The resulting catalyst was added to 3-acetylthionaphthen (3.0 g.) in methanol (50 ml.) and the mixture refluxed on the water bath for 22 hr. The reaction mixture was filtered

hot, extracted repeatedly with boiling methanol and the extracts distilled from the water bath. The concentrated extracts (20 ml.) on cooling deposited unchanged 3-acetylthionaphthen (0.645 g.). The filtrate was taken up in ether, the ether dried with magnesium sulphate and distilled to give two fractions :

- (a) 3-phenyl-2-butanone (0.476 g.), b.p. ca. 100°/24 mm.; and
- (b) 3-acetylthionaphthen (0.180 g.), b.p. ca. 105°/0.01 mm.

The 3-phenyl-2-butanone was examined by infrared spectroscopy for the presence of olefins but none could be detected.

Desulphurisation of 2-acetylthiophen.-

(i) A mixture of 2-acetylthiophen (30 g.), and W7 Raney cobalt (prepared from 125 g. of alloy) was made up to 200 ml. with methanol and refluxed for 5 hr. The cobalt was filtered off, extracted continuously with methanol for 20 hr., the filtrate and extracts combined and distilled to remove methanol. Distillation of the residue under reduced pressure gave three fractions :

- (a) 2-hexanone (2.77 g.), b.p. 60°/30 mm., identified as the 2,4-dinitrophenylhydrazone;
- (b) 2-acetylthiophen (26.3 g.), b.p. 102°/20 mm., identified as the 2,4-dinitrophenylhydrazone;
- (c) an oil (0.5 g.), b.p. 80-90°/0.5 mm.

Redistillation of fraction (c), followed by repeated

recrystallisation from light petroleum (b.p. below 40°) in solid carbon dioxide gave 2,11-dodecanedione (10 mg.), m.p. and mixed m.p. $54-56^{\circ}$.

(ii) A mixture of 2-acetylthiophen (60 g.), W7 Raney cobalt (prepared from 250 g. of alloy), and methanol (to make the total volume 250 ml.) was refluxed for 24 hr.

Working up as before gave the following fractions :

(a) a fore-run (1.0 g.), b.p. $100^{\circ}/22$ mm., which did not contain ketones (probably 2-hexanol);

(b) 2-acetylthiophen (50.75 g.), b.p. $104-105^{\circ}/22$ mm., identified as above;

(c) an oil (0.996 g.), b.p. $90-120^{\circ}/0.03$ mm.; and

(d) a small amount of solid removed from the neck of the flask. Fraction (c) was extracted with light petroleum (b.p. below 40°) and the extracts purified by chromatography on alumina in the same solvent, followed by recrystallisation using solid carbon dioxide to give 2,11-dodecanedione (0.96 g.), m.p. and mixed m.p. $54-56^{\circ}$

(identity confirmed by infrared spectra). The petroleum-insoluble part of fraction (c) was found to be identical with fraction (d) by mixed m.p. and comparison of the infrared spectra. Recrystallisation of the combined materials from benzene - light petroleum gave a compound "R" (30 mg.) as needles, m.p. $88.5-89^{\circ}$

Found: C, 58.1; H, 4.75; S, 24.3; O, 12.4%.

Its infrared spectrum (Fig. 3.1) showed one carbonyl band at 5.94μ (suggesting a CO.C=O system) and possibly a weak isolated CH_2 band at 6.90μ , in addition to the strong band at 6.99μ , ascribed to acetyl CH_2 . The spectrum had little similarity to that of 5,5'-diacetyl-2,2'-bithienyl, except for the C=O absorption which appeared at 5.98μ . The carbonyl band of 2-acetylthiophen was at 5.975μ .

The ultraviolet absorption spectrum of "R" in ethanol gave two maxima at 261 and $284 \text{ m}\mu$ (shown in Fig. 3.2, assuming molecular weight 252). This spectrum also differed significantly from that of 5,5'-diacetyl-2,2'-bithienyl (Fig. 3.2); λ_{max} (log ϵ in parentheses): 262 (3.54), 282 (3.44), 345 (infl.) (4.35), 370 (4.40) and $425 \text{ m}\mu$ (infl.) (2.75). The spectra of some related thiophen derivatives are given in Figs. 3.3 and 3.4.¹⁰¹

(iii) Experiment (ii) was repeated, except that the total volume was 200 ml. instead of 250 ml. The cold reaction mixture was filtered directly into the thimble of a hot Soxhlet and extracted with methanol for 20 hr. and with a second batch of that solvent for 48 hr. The first extract was black, but became red on cooling and standing in a stoppered flask overnight. The combined extracts were distilled from the water bath to give a

distillate A and a residue B. Careful fractionation of distillate A gave 2-hexanone, identified and weighed as the 2,4-dinitrophenylhydrazone (5.6 g., corresponding to 2.0 g. of 2-hexanone). 2-Hexanol was detected by gas-liquid chromatography of the liquors obtained after removal of 2-hexanone as the 2,4-dinitrophenylhydrazone. Residue B was taken up in ether, dried and distilled to give 2-acetylthiophen (50.0 g.), b.p. $96^{\circ}/12$ mm. and 2,11-dodecanedione (0.930 g.), b.p. $140-160^{\circ}/\text{ca. } 0.5$ mm. (bath temp. 240°). A tarry residue C (2.015 g.) was left after distillation. Chromatography of the residue C on alumina in benzene - hexane gave a forerun of yellow, viscous tar (1.6 g.), which darkened on standing, and substance "R" (0.380 g.), identical in all respects with the material obtained in (11).

"R" could not be dehydrogenated with chloranil and was recovered unchanged after refluxing for 4 hr. in xylene. Rast molecular weight determination was found to be 235 ± 30 .

A sample of "R" was desulphurised with W7 Raney nickel in ethanol. The product (purified by sublimation) showed free and hydrogen bonded O-H absorption at 2.75 and 3.0μ , but had only weak carbonyl absorption at 5.85μ , suggesting that extensive reduction of carbonyl groups had taken place.

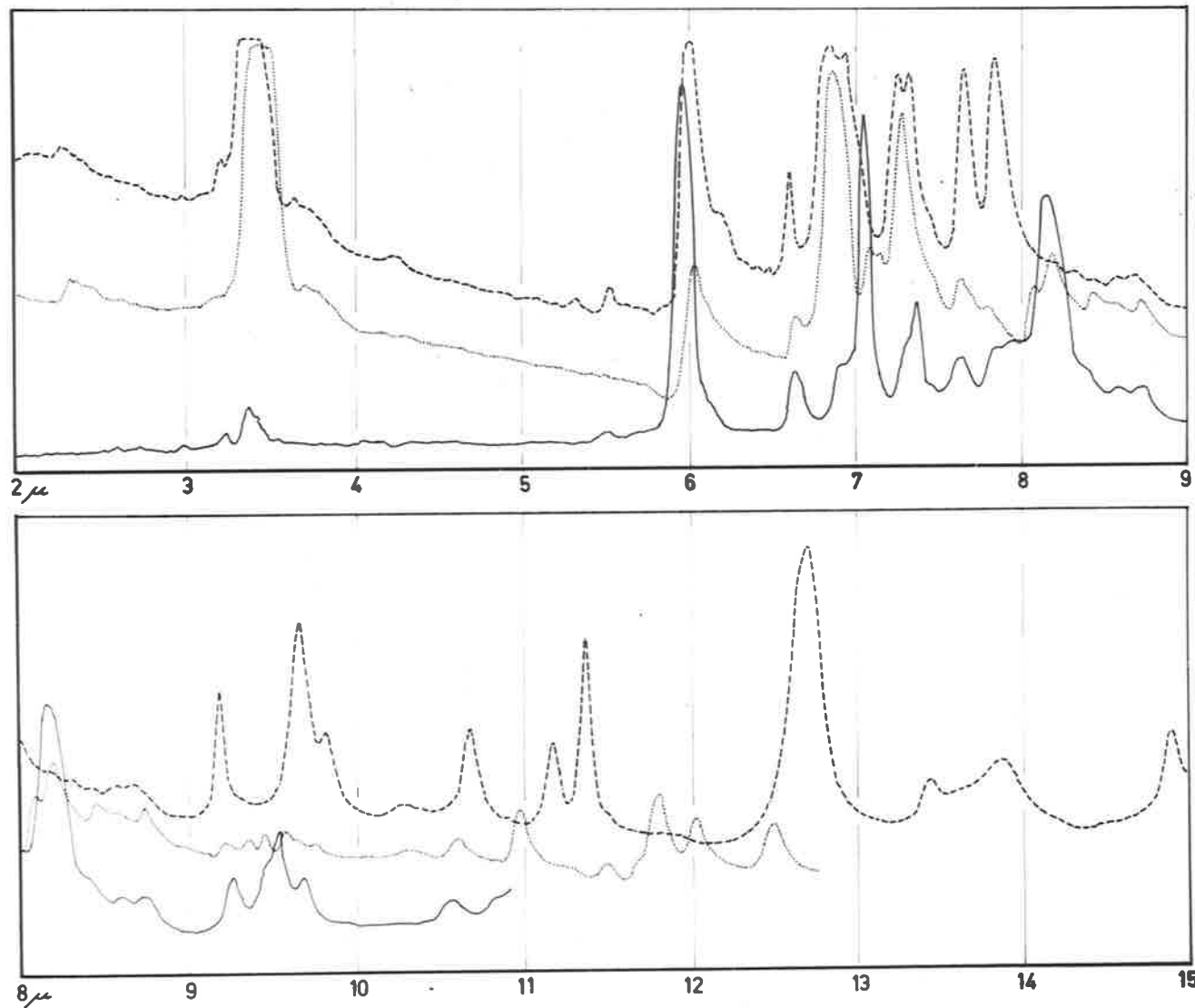


Figure 3.1, — Unknown in CCl_4 ,
 — Unknown in nujol, --- 5,5'-diacetyl-2,2'-bithienyl in nujol.

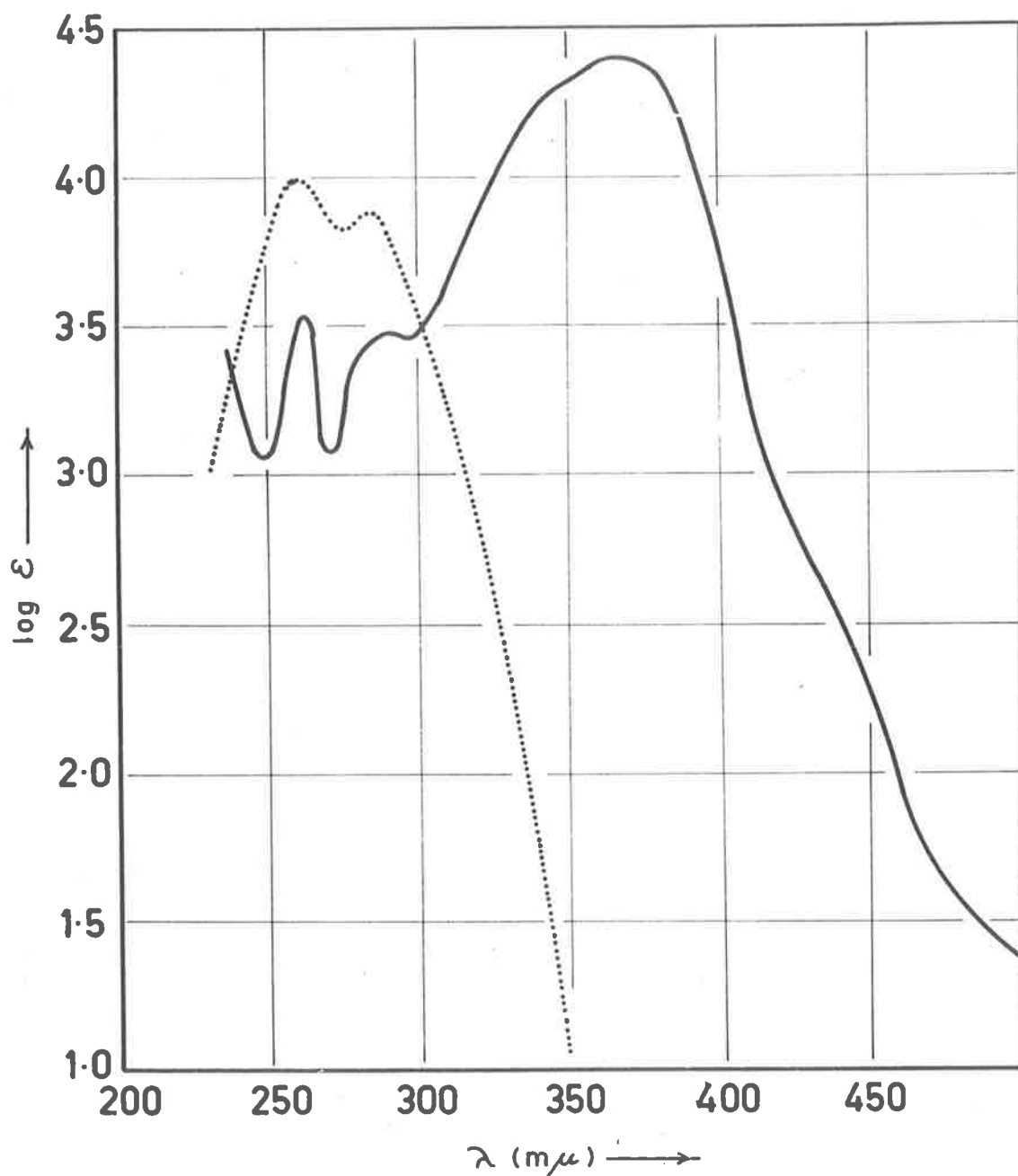


Figure. 3.2. — $\text{CH}_3.\text{CO}.\text{SS}.\text{CO}.\text{CH}_3$.

..... Unknown, spectra in ethanol.

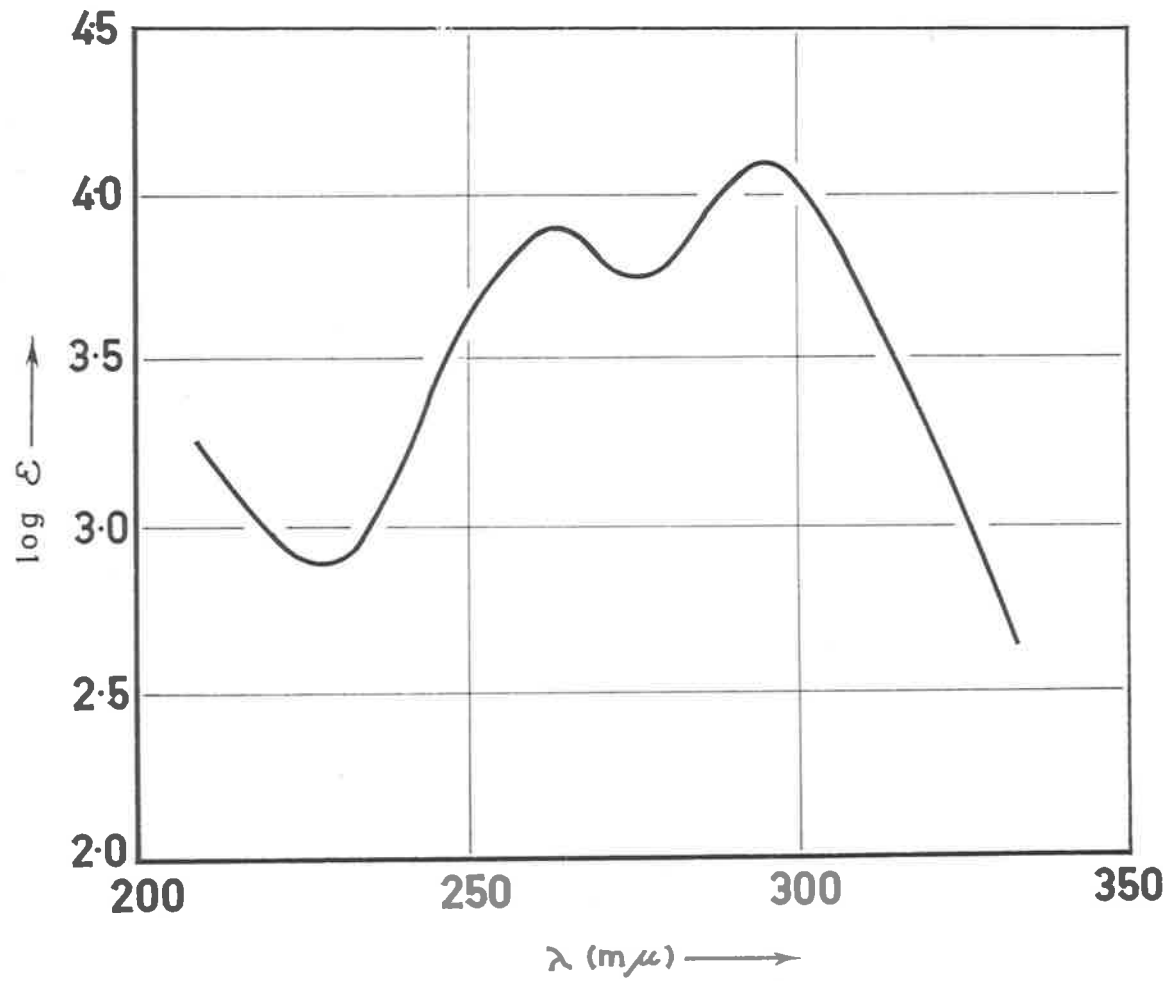
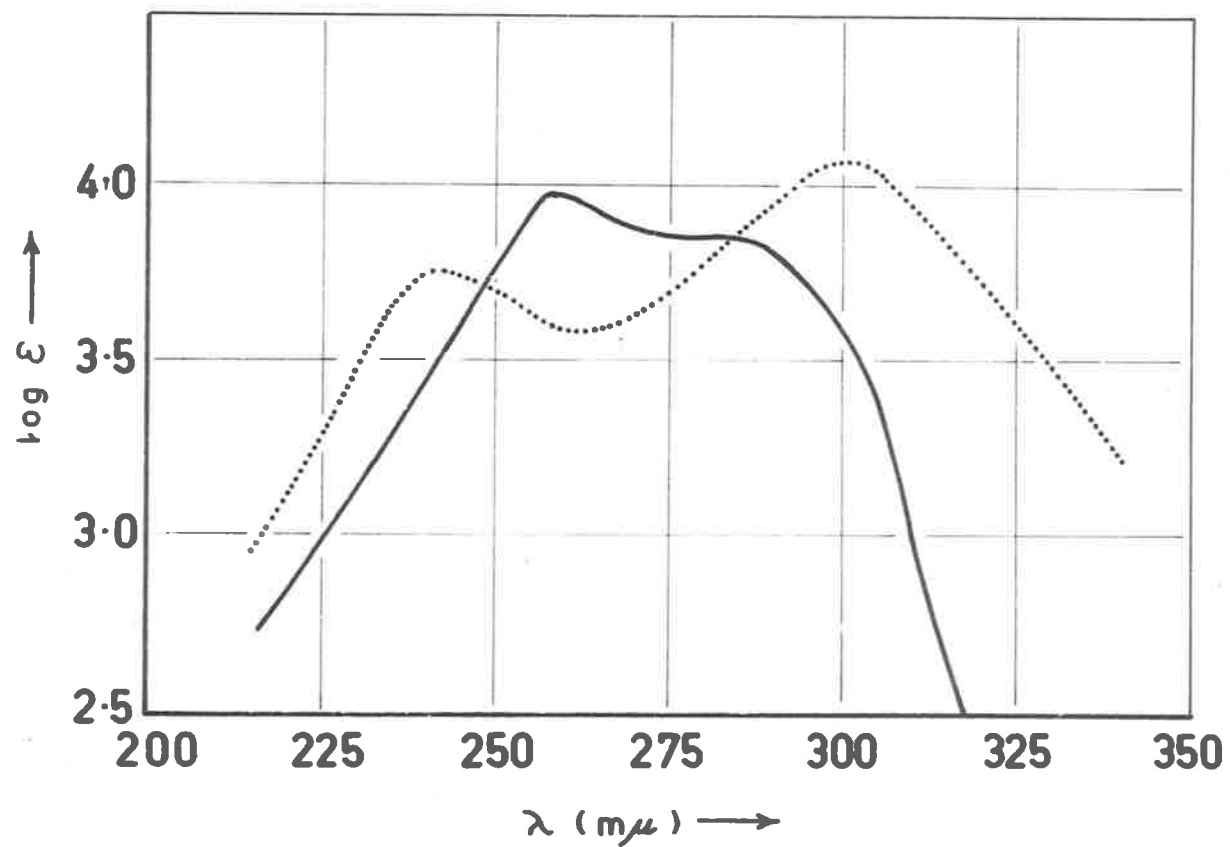


Figure 3.3. 2-acetyl-5-methylthiophen.



Figure, 3.4. — 2-acetylthiophen.
..... 2,2'-bithienyl.

The material could not be identified.

In another desulphurisation the Raney nickel was deactivated and freed from water and ethanol by azeotropic distillation with benzene prior to the addition of "R". The product of this desulphurisation showed no O-H absorption but had two carbonyl bands of nearly equal intensities at 5.85 and 5.98 μ . (The carbonyl absorption of 2,11-dodecanedione is at 5.83 μ .) Sublimation of the product did not lead to a significant change in the infrared spectrum except that the intensity of the band at 5.98 μ was slightly increased.

Desulphurisation of thiazoles.-

(i) 2-Amino-4-phenylthiazole. A mixture of the thiazole (5 g.), W7 Raney cobalt (from 65 g. of alloy) and methanol (250 ml.) was refluxed in a slow stream of nitrogen for 4 hr. The exit gases were passed into dilute hydrochloric acid, subsequent evaporation of which gave ammonium chloride (0.15 g.). The reaction mixture was filtered, the metal washed with hot methanol, the combined extracts acidified and evaporated. Separation of the residue into basic and non-basic components gave unchanged 2-amino-4-phenylthiazole (4.4 g.) and acetophenone (0.55 g.), identified as the 2,4-dinitrophenylhydrazones.

(ii) Benzothiazole. When a solution of benzothiazole

(10 g.) in methanol (250 ml.) was refluxed with W7 cobalt catalyst for 3.5 hr. and the mixture extracted in the usual way and subjected to Hinsberg separation, only unchanged benzothiazole (6.08 g.) was isolated. No primary or secondary amine could be found.

(iii) 2-Mercaptobenzothiazole. 2-Mercaptobenzothiazole (10 g.) was refluxed in methanol solution (250 ml.) with W7 Raney cobalt (from 65 g. of alloy) for 4.5 hr. The reaction mixture was filtered hot and the metal extracted with boiling solvent. The combined extracts were acidified with dilute hydrochloric acid (100 ml.) and concentrated by distillation. On cooling 2-mercaptobenzothiazole (3.0 g.) was deposited and the liquors were treated with tosyl chloride and aqueous alkali. Steam distillation gave benzothiazole (2.74 g.), identified as the picrate but no primary or secondary amine could be detected.

Desulphurisation of phenanthridinethione.⁻¹⁵

(i) In dimethylformamide-ethanol. A mixture of phenanthridinethione (1.0 g.), W7 Raney cobalt (ca. 5 g.), dimethylformamide (10 ml.) and ethanol (10 ml.) was refluxed for 1.5 hr. The mixture was filtered hot, the cobalt washed with hot solvent and the combined filtrates evaporated on the water bath in vacuo. After one recrystallisation from acetone - water the phenanthridine

(0.61 g., 72%) had m.p. 105-106°, undepressed by admixture to an authentic sample.

(ii) In pyridine. In a similar desulphurisation, pyridine (20 ml.) was used as solvent and the mixture worked up as before. The residue, after evaporation, was taken up in the minimum amount of dimethylformamide and acidified with hydrochloric acid to give unchanged phenanthridinethione (0.168 g.), m.p. ca. 260°.

Basification of the remainder with ammonia gave impure phenanthridine (0.68 g.), m.p. 88-106°, which could not be purified by repeated recrystallisation from acetone - water and therefore probably contained dihydrophenanthridine as impurity. Chromatography on alumina in benzene-hexane gave pure phenanthridine, m.p. 105-106°.

Desulphurisation of 2-mercaptoquinoline.-

When a mixture of 2-mercaptoquinoline (3.0 g.), W7 Raney cobalt (from 30 g. of alloy) and methanol (60 ml.) was refluxed for 5 hr., much brown solid was formed. The mixture was filtered hot and the solids washed with hot methanol. Evaporation of the combined filtrates yielded 2,2'-biquinolyl (0.026 g.), m.p. and mixed m.p. 193-194°, and quinoline, identified and weighed as the picrate (4.10 g.), m.p. and mixed m.p. 203°. The solids were further extracted with hot dimethylformamide in a Soxhlet

for 12 hr. and the extract concentrated to 10 ml. Cooling and filtration gave a brown solid (A) and a filtrate (B). Solid (A) was extracted with 1:1 hydrochloric acid. Neutralisation of the extract gave 2-hydroxyquinoline (0.036 g.), m.p. and mixed m.p. 199°, and quinoline, identified and weighed as the picrate (0.43 g.). No cobalt ions were found in the acid extract. The acid insoluble portion of solid (A) was recrystallised from dimethylformamide to give tris-(2-mercaptoquinoline)cobalt(?) (0.455 g.) as shiny black needles

Found: C, 60.3; H, 3.4; N, 7.4; S, 18.0; Co, 11.8.

$C_{27}H_6N_3S_3Co$ requires: C, 60.1; H, 3.4; N, 7.8;
S, 17.8; Co, 10.9%.

Dilution of filtrate (B) with water (100 ml.) gave a yellow material (0.34 g.) which was chromatographed on alumina in benzene - hexane. The products were 2,2'-biquinolyyl (0.295 g.), m.p. and mixed m.p. 193° (also red complex with cuprous ions), and di-2-quinolyyl sulphide (0.045 g.), m.p. 188° (from light petroleum, b.p. 100-120°)

Found: C, 75.3; H, 4.4; N, 9.25; S, 11.1.

$C_{18}H_{12}N_2S$ requires: C, 75.0; H, 4.2; N, 9.7; S, 11.1%.

Its m.p. was not depressed by admixture with a specimen prepared by fusing 2-chloroquinoline with sodium sulphide

for 20 hr.

Reactions of tris-(2-mercaptoquinoline)cobalt (?).

Dilute hydrochloric acid had no effect on the material. Boiling concentrated hydrochloric acid produced a green coloration which was discharged on dilution with disappearance of free cobalt ions. However, the "complex" could be hydrolysed by heating with concentrated hydrochloric acid in a sealed tube at 140-160° for 40 min. Basification of the hydrolysis mixture, followed by ether extraction (20 x) gave di-2-quinolyl sulphide (identified by paper chromatography in butanol/HCl/water). Extraction of the neutral component of the hydrolysis mixture yielded 2-mercaptoquinoline as main product. Cobalt ions were detected in the hydrolysate. In another hydrolysis a partial solution of the "complex" in hot concentrated hydrochloric acid was poured into concentrated sodium hydroxide solution. Most of the "complex" was re-formed but 2-mercaptoquinoline and di-2-quinolyl sulphide could be isolated by ether extraction and compared with authentic specimens.

Concentrated sulphuric acid dissolved the "complex" on warming but it was precipitated unchanged on dilution. Sodium fusion (twice) did not detect nitrogen, although sulphur was readily detected. This suggests a strong

N-Co bond.

Summary of yields.

2-Mercaptoquinoline (3.0 g.) was desulphurised with W7 cobalt (from 30 g. of alloy) to give:

- (a) quinoline (1.63 g., 68%), isolated as the picrate;
- (b) 2,2'-biquinolyl (0.321 g., 13.5%);
- (c) 2-hydroxyquinoline (0.036 g.);
- (d) di-2-quinolyl sulphide (0.045 g.); and
- (e) tris-(2-mercaptoquinolyl)cobalt (?) (0.455 g.).

Desulphurisation of thioacridone (acridinethione).

(1) In dimethylformamide - ethanol. A mixture of thioacridone (3 g.), dimethylformamide (30 ml.), ethanol (30 ml.) and W7 Raney cobalt (from 30 g. of alloy) was refluxed for 13 hr. The catalyst was filtered off, washed with hot dimethylformamide and with boiling ethanol, the combined filtrates evaporated, and the residue extracted with boiling 0.5N sodium hydroxide solution (2 x 250 ml.). The extracts on cooling and saturation with carbon dioxide gave unchanged thioacridone (0.92 g.). Continuous extraction of the alkali-insoluble portion with light petroleum (b.p. 65-69°) for 2 hr. and evaporation of the solvent, gave acridine (identified as the picrate (0.10 g.), m.p. and mixed m.p. 261-262°). The petroleum-insoluble fraction

(0.85 g.), m.p. ca. 364°, did not contain any acridone as it failed to form a p-(diethylamino)phenyl derivative and showed no N-H, O-H or C=O bands in the infrared (Nujol). Extraction of this fraction with chlorobenzene, and chromatography of the extract on alumina in chlorobenzene gave 9,9'-biacrydyl (0.43 g.), m.p. and mixed m.p. 393°; identical R_F values when chromatographed on paper in butanol/HCl/water. Chromatography of the chlorobenzene-insoluble residue on paper in the above system showed the presence of trace amounts of acridine and thioacridone, and four bases, one of which (trace) was 9,9'-biacrydyl. That thioacridone was present only in trace quantities was confirmed by sodium fusion which detected nitrogen but no sulphur. After three recrystallisations from chlorobenzene this fraction gave only three spots on paper but sublimation and further fractional crystallisation from all available solvent systems failed to resolve the mixture. All components dissolved in concentrated hydrochloric acid but the residue, after extraction with dilute hydrochloric acid and recrystallisation from chlorobenzene, gave m.p. 210°. (One isomer of tetrahydrobiacrydyl has m.p. 214°).

(ii) In methanol. In another experiment, a mixture of thioacridone (3 g.), W7 Raney cobalt (from 30 g. of alloy), and methanol (50 ml.) was refluxed for 5 hr. Working up as

in the preceding experiment gave unchanged thioacridone (2.14 g.), and acridine picrate (0.24 g.). The dimeric fraction (0.37 g.) was identical in all respects with that obtained previously. 9,9'-Biacridyl (0.19 g.) was isolated from this mixture and identified as above.

Desulphurisation of imidazolidinethione.-

A mixture of imidazolidinethione (10 g.), W7 Raney cobalt (from 125 g. of alloy), and methanol (to make the total volume up to 250 ml.) was refluxed for 5 hr. The cobalt was filtered off, washed repeatedly with methanol, and the combined filtrates concentrated to 75 ml. Cooling gave imidazolidinethione (3.02 g.), m.p. and mixed m.p. 197-198°. Evaporation and distillation of the mother liquors gave ethylenediamine, b.p. ca. 100°, identified and weighed as the picrate (6.0 g.), m.p. and mixed m.p. 231-233°. More starting material (1.61 g.) was recovered from the residue by treatment with a little methanol. Distillation of the remainder yielded a yellow, viscous oil (3.28 g.), b.p. 190°/0.01 mm., which partly solidified. Trituration with ethanol, followed by recrystallisation from ethanol and from ethyl acetate gave N,N'-diformylethylenediamine (2.68 g.), m.p. 109-110°, undepressed by admixture with a specimen prepared by formylation of ethylenediamine

Found: C, 41.7; H, 7.1; N, 23.9; O, 27.5.

$C_4H_8O_2N_2$ requires: C, 41.4; H, 6.9; N, 24.1; O, 27.6%.

Alcoholic picric acid converted the formyl derivative into ethylenediamine picrate, m.p. and mixed m.p. 231-233^o, while hydrolysis with hydrochloric acid (1:1), followed by evaporation gave a hygroscopic hydrochloride (precipitate with silver nitrate; with ammonium picrate the hydrochloride yielded a precipitate of ethylenediamine picrate). The infrared spectrum of the diformyl derivative showed N-H and carbonyl bands in the region of amides.

Attempted formylation of ethylenediamine with W7 Raney cobalt and methanol. A mixture of W7 Raney cobalt (from 65 g. of alloy), methanol (150 ml.) and ethylenediamine (5.0 g.) was refluxed for 5 hr. Working up as in the previous experiment gave unchanged ethylenediamine (4.23 g., 84.6%), identified as the picrate, m.p. and mixed m.p. 232-234^o. No formyl or diformyl derivative was found.

Preparation of starting materials.-

β -2-Thienylpropionic acid and γ -2-thienylbutyric acid were prepared by the method of Badger, Rodda, and Sasse.¹⁷

5,5'-Diacetyl-2,2'-bithienyl was prepared in three steps according to the method of Wynberg and Logothesis.^{21a}

2-Hydroxyquinoline, (2-quinolone, carbostyryl) was obtained by adaption of the method of Einhorn and Lauch,¹⁰² using sodium hypochlorite solution instead of bleaching powder extract.

2-Chloroquinoline was prepared from 2-hydroxyquinoline by refluxing with a mixture of phosphorus oxychloride and phosphorus pentachloride by the general method of Rowlett, Jr. and Lutz.¹⁰³

2-Mercaptoquinoline (thiocarbostyryl) was obtained from 2-quinolone by treatment with phosphorus pentasulphide according to Rees.¹⁰⁴

9-Thioacridone was prepared from acridine and sulphur in a sealed tube by the method of Albert.¹⁰⁵

9-Chloroacridine was obtained from 9-thioacridone by treatment with phosphorus oxychloride according to Albert.¹⁰⁵

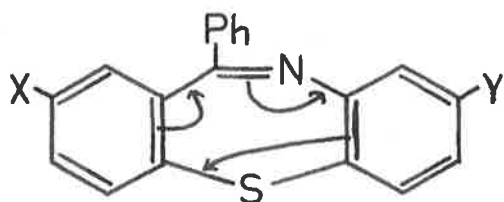
9,9'-Biacridyl. This compound was prepared by the method of Lehstedt and Hundertmark.¹⁰⁶

Di-2-quinolyl sulphide. A mixture of hydrated sodium sulphide (10 g.) and 2-chloroquinoline (1.0 g.) was fused together for 20 hr., poured into water and allowed to stand. The precipitated oil was extracted with ether, the ether dried and removed, and the residue chromatographed on

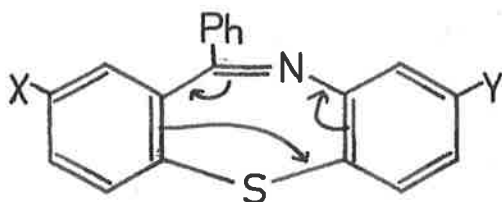
alumina. Elution with benzene-hexane gave unchanged 2-chloroquinoline (0.9 g.), and elution with benzene gave di-2-quinolyl sulphide (10 mg.), m.p. 188°, picrate m.p. 197° (ethanol). Two yellow bands which moved slowly in benzene were not eluted.

Recently Loudon et al. have used this method of desulphurisation (the so-called "extrusion of sulphur") as a synthetic approach to derivatives of phenanthrene¹¹¹ and of phenanthridine.¹¹² Dibenzothiepins and dibenzothiazepines were strongly heated with copper bronze in a high boiling solvent to give the required desulphurised product. Under similar conditions polycyclic thiazepines led to polycyclic aza-hydrocarbons.¹¹³

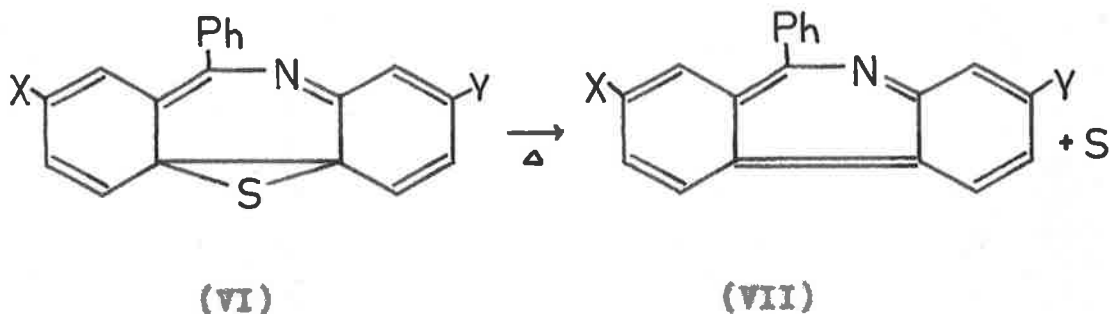
Galt and Loudon¹¹⁴ studied the effect of substituents on the extrusion of sulphur from dibenzothiazepines in an attempt to elucidate the mechanism of the reaction. They concluded that two types of electron shift probably occurred, represented by (IV) and (V), leading in both cases to the ethylene sulphide (VI). The latter compounds are known to split out a sulphur atom readily, forming olefins (VII).



(IV)



(V)



It must be noted that all the examples of the extrusion of sulphur with copper and with zinc involve ring contraction, and are generally accompanied by aromatisation. Although copper sulphide is reported to be formed during the reaction,^{1,107,108} there is considerable evidence to support the view that the sulphur atom is extruded in the free state and reacts subsequently.¹¹⁵ For instance, sulphur may be extruded from certain compounds by heat alone,^{115,a,b,d,e} in the absence of copper. It appears therefore, that the extrusion of sulphur is largely dependent on the overall molecular structure of the sulphur compound, and that the transition metal (copper) only plays a subsidiary part. This is in contrast with Raney nickel desulphurisation, which seems to be essentially an interaction of the sulphur atom with the activated metal, and is largely independent of the remainder of the molecule.^{4,9,13,22,27.}

The application of Raney nickel to desulphurisation has already been mentioned in Chapter I. A distinction must be

drawn, however, between two processes, both of which are commonly referred to as "desulphurisation with Raney nickel". The more common process involves the use of a Raney nickel rich in hydrogen at temperatures ranging from room temperature to ca. 100°. This reaction seems to be largely hydrogenolytic in nature and leads to sulphur-free compounds possessing the carbon skeleton of the sulphur compound.^{9,13,22} The other process involves the use of strongly degassed nickel at elevated temperatures (ca. 220°), and has been used principally by Hauptmann et al.²⁷ This reaction does not take place at low temperatures, but at elevated temperatures it leads to scission of the C-S bonds and a subsequent recombination of the fragments.²⁷ The conversion of disulphides to sulphides is common in this type of desulphurisation.²⁷ Hauptmann, Walter and Marino^{27f} have suggested that this high temperature reaction involves a topochemical interaction of the nickel with the sulphur atom.

It is thus possible to distinguish three processes which may lead to the desulphurisation of (that is, loss of sulphur from) an organic sulphur compound: (1) the extrusion of sulphur from cyclic sulphides, generally in the presence of copper; (2) hydrogenolysis of C-S bonds

with hydrogen rich Raney nickel; and (3) topochemical desulphurisation with degassed Raney nickel.

Raney cobalt has been found by Aller^{30b} to effect hydrogenolytic desulphurisation, and Hauptmann^{27g} observed that degassed Raney cobalt also effected appreciable desulphurisation at high temperatures, and a number of desulphurisations with Raney cobalt have been described by Sasse.^{98b} All these authors noted that Raney cobalt was less effective in desulphurisation than Raney nickel, in agreement with the results described in Chapter III. Hauptmann also used degassed Raney iron and Raney copper in desulphurisations at high temperatures, but found that they were even less effective than nickel or cobalt.^{27g}

In the present work several attempts were made to desulphurise di-1-naphthyl sulphide with finely divided metals not of the Raney type. A mixture of the sulphide and the metal was fused at 200° for 4 hr., the organic material then being extracted with solvent and worked up. Under these conditions copper bronze, zinc dust, reduced iron and reduced nickel gave no desulphurised products, but a very small amount of naphthalene was obtained from the experiment using precipitated silver. No desulphurisation of di-1-naphthyl sulphide occurred with copper bronze in refluxing ethyl benzoate, or in diethyl

phthalate at 300° under nitrogen. These results are shown in Table 4.1.

It is interesting that Loudon et al.¹¹⁰⁻¹¹⁴ obtained complete extrusion of sulphur from dibenzothiepins and dibenzothiazepines under these conditions. No ring contraction or aromatisation is possible in the case of di-1-naphthyl sulphide, and the failure to obtain sulphur-free material in these experiments is thus in complete agreement with the mechanism postulated by Galt and Loudon¹¹⁴ for extrusion.

Moreover, the experiments were carried out in the absence of hydrogen, and at a high temperature, so that topochemical desulphurisation might have been expected to take place. As no loss of sulphur occurred, it must be assumed that conditions other than these have to be met before topochemical desulphurisation can occur.

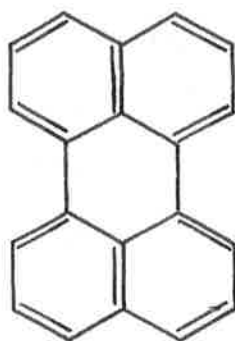
The metals used by Hauptmann²⁷ were prepared by the Raney method, or by reduction, and were strongly degassed at a high temperature under reduced pressure immediately before use. It has already been mentioned that Raney nickel probably contains some 30% lattice vacancies which are normally filled and stabilised by hydrogen.⁴⁸ Removal of this hydrogen from the metal probably leaves a

relatively porous and mobile lattice and a clean surface.

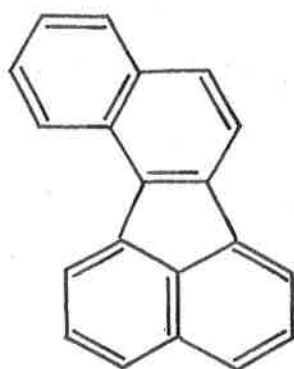
Desulphurisation must clearly take place on or near the metal surface,^{9,13} which will soon become covered with a layer of sulphide. At ca. 200° considerable mobility is possible within the defective lattice,^{116,117} and metal atoms can diffuse through the sulphide layer to re-form a reactive surface and continue the reaction.^{116,117} The presence of impurities is known to create lattice defects in crystals and it is thought that Raney metals are promoted towards topochemical desulphurisation in this way. The failure to observe topochemical desulphurisation in our experiments is consistent with the postulate that lattice vacancies, and a 'clean' (or reactive) metal surface are essential for topochemical desulphurisation.

It should be noted that when commercial copper bronze was activated with iodine in acetone¹¹⁸ prior to use, desulphurisation to naphthalene occurred to the extent of some 3% at 290°, and zinc dust effected about 5% of desulphurisation of di-1-naphthyl sulphide to give naphthalene, perylene (VIII) and benzo(j)fluoranthene (IX) when the reaction temperature was raised to 400°. The 'activation' with iodine probably exposes a clean copper surface, while the higher temperature probably increases

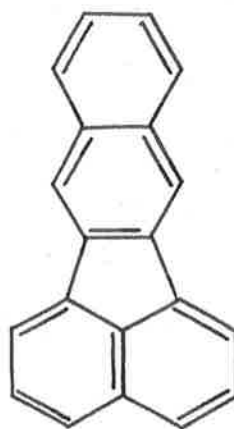
mobility within the zinc lattice, and may also assist in the fission of C-S bonds.



(VIII)



(IX)



(X)

The available Raney metals were found to be much more effective in promoting desulphurisation than the corresponding 'inactive' metals (see Table 4.2). Freshly prepared W7 Raney nickel in boiling methanol completely desulphurised di-1-naphthyl sulphide to naphthalene, and some hydrogenation to tetralin also occurred. It has already been mentioned that Raney nickel contains a large volume of hydrogen, so that the hydrogenation is clearly a secondary effect, for naphthalene was hydrogenated to tetralin under the same experimental conditions. On the other hand, an aged W7 Raney nickel gave only naphthalene and a trace of 1,1'-binaphthyl. Degassed (W7-J) Raney nickel was inactive as a desulphurising agent in boiling

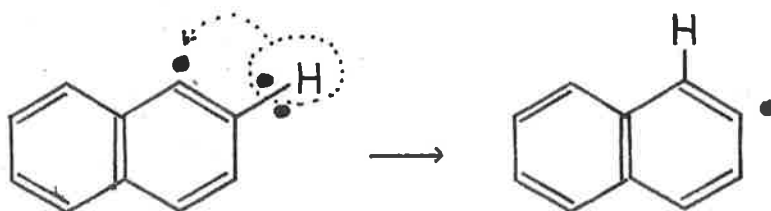
methanol. However, when this hydrogen poor Raney nickel was used at a higher temperature (in refluxing xylene and in diethyl phthalate at 220°), extensive desulphurisation occurred giving mixtures of naphthalene and 1,1'-binaphthyl, together with small amounts of 2,2'-binaphthyl, perylene, benzo(j)fluoranthene and benzo(k)fluoranthene (X).

The formation of 1,1'-binaphthyl and of the other condensed hydrocarbons is consistent with the view that desulphurisation gives naphthyl radicals which then react with hydrogen (to give naphthalene) or with similar radicals (to give the dimeric and condensed products). Catalytic cyclodehydrogenation of 1,1'-binaphthyl at the temperature of the reaction would then give the perylene (VIII) and benzo(j)fluoranthene (IX) observed.

The formation of small amounts of 2,2'-binaphthyl with W7-J Raney nickel is surprising. The isomerisation of 1,1'- to 2,2'-binaphthyl at high temperatures (490°) over platinum - alumina catalyst has been described,¹¹⁹ but no isomerisation occurred under the conditions of the present experiments. The hydrocarbon must therefore be formed by the combination of 2-naphthyl radicals. These radicals could arise in two ways: (a) from 2-naphthyl sulphide impurity; this is possible as commercial 1-bromonaphthalene,



which was used in the synthesis of the sulphide, commonly contains a small amount of the 2-isomer; (b) by migration of a hydrogen atom from the 2- to the 1- position of the 1-naphthyl radical:



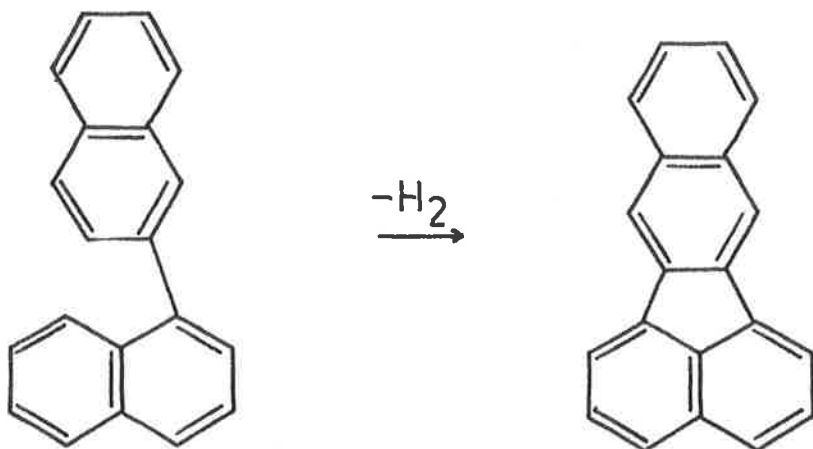
Reactions of this type are known. For instance, when 1-methylnaphthalene is heated, a small amount of the 2-isomer is formed.¹²⁰

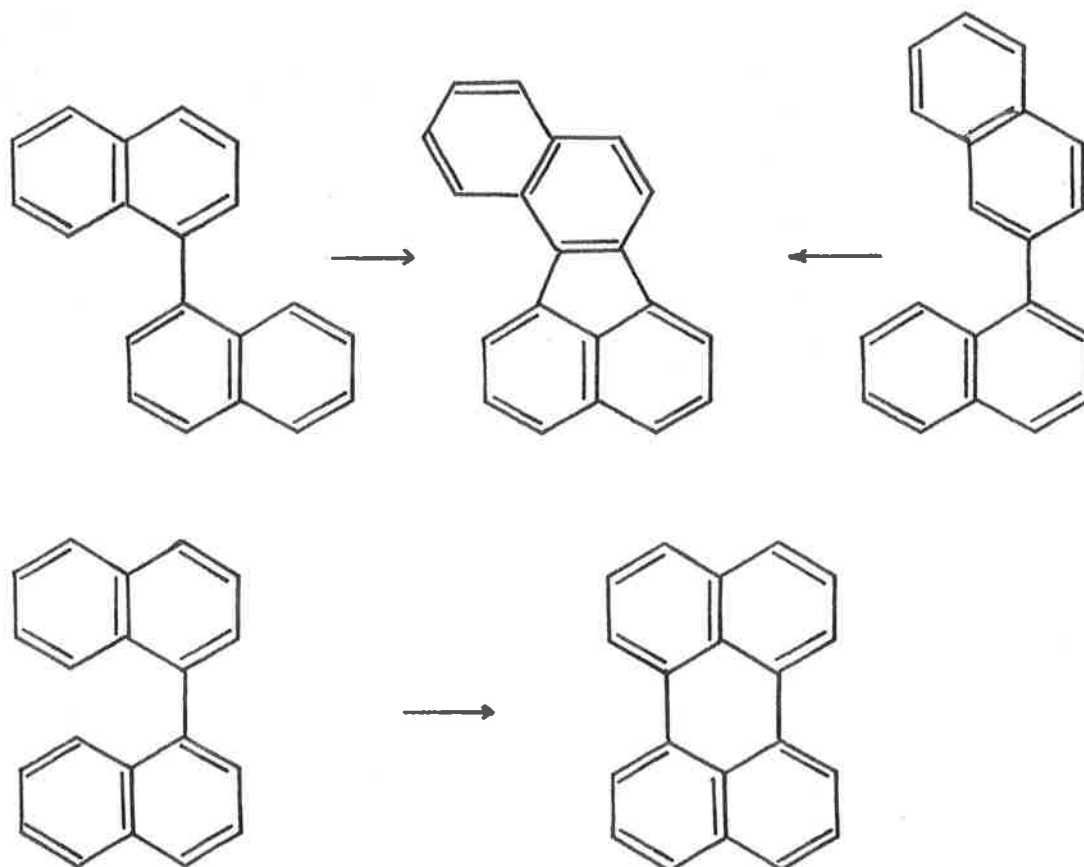
In the desulphurisation with W7-J Raney nickel at 220° the ratio of dimerisation to hydrogenation of 1-naphthyl radicals (from Table 4.2) was 19.8 : 69, or 2 : 7 very nearly. It is not unreasonable to assume that this course of reaction will also apply to 2-naphthyl radicals. As the yield of 2,2'-binaphthyl was 0.8%, the minimum amount of 2-naphthyl radicals must have been $0.8 + \frac{0.8 \times 7}{2} \% = 3.6\%$. This estimate ignores the fact that the collision of 2-naphthyl radicals with 1-naphthyl radicals is much more likely than with each other, since the latter are in excess. (It will be remembered that Hauptmann has demonstrated^{27d} the intermolecular nature of

desulphurisation by the formation of mixed biaryls.)

Clearly then, the amount of 2-naphthyl sulphide impurity should have been in excess of 3.6%. The rigorous purification of the starting material and its homogeneity on paper tends to exclude the possibility of this amount of impurity, and it is therefore suggested that rearrangement of 1-naphthyl radicals occurs according to (b).

No 1,2'-binaphthyl was detected, but this substance can undergo catalytic cyclodehydrogenation to benzo(k)fluoranthene and benzo(j)fluoranthene,¹¹⁹ both of which were found. Benzo(j)fluoranthene could also be formed by cyclodehydrogenation of 1,1'-binaphthyl, as an alternative to the formation of perylene.





Desulphurisation of di-1-naphthyl sulphide with W7 Raney cobalt gave only 4.5% of naphthalene, showing that cobalt is much weaker than nickel in effecting desulphurisation. It is also interesting to note that prolonged Soxhlet extraction was necessary in order to remove most of the unchanged sulphide from the cobalt. This suggests that adsorption of the sulphur compound on the metal had

occurred, but had not been accompanied by C-S hydrogenolysis. Raney cobalt is known to contain appreciable quantities of hydrogen,³⁰ and it may be inferred that this hydrogen is held within the particle, rather than on the surface, and is therefore not available for reaction.

When the reaction temperature was raised to 220° in diethyl phthalate, naphthalene was formed in 97% yield, and only small amounts of 1,1'-binaphthyl and of condensed products were obtained. It is thought that at the higher temperature, hydrogen moves from the interior of the metal to the surface, and hydrogenolysis of the C-S bonds is made possible. The low yield of binaphthyl suggests that topochemical desulphurisation had occurred to a small extent only. This may be due to the high concentration of hydrogen on the cobalt surface at 220°, but is more probably an illustration of Hauptmann's finding that cobalt is less active in topochemical desulphurisation than nickel.

The yield of desulphurised products obtained with Raney copper and with Raney iron was also increased by a rise in the reaction temperature. These metals were almost inactive in boiling methanol, but effected 4-40% of desulphurisation when the reaction temperature was raised to 220°; however, Raney tungsten was inactive even at 200°.

Hydrogen was found to be important in the desulphurisation of di-1-naphthyl sulphide with Raney copper and Raney iron. Reactions were carried out in an atmosphere of nitrogen or hydrogen, and with both metals the presence of external hydrogen led to an increase in the yield of desulphurised products. A hydrogen atmosphere may be expected to increase and maintain the concentration of surface adsorbed hydrogen, and may therefore enhance hydrogenolysis.

The influence of surface hydrogen on hydrogenolytic desulphurisation can also be inferred from a comparison of the experiments, in methanol, with W7 and W7-J Raney nickel. No desulphurisation occurred with the degassed metal, but it took place readily with the hydrogen rich nickel. It must be remembered that the degassing of Raney nickel results in a decrease of the surface area, so that W7 and W7-J nickels are not strictly comparable. Nevertheless, as the decrease in the surface area due to degassing must be less than one fourth of the total,⁴⁸ the observed difference in the reactivity of the two nickels is too great to be attributed to this effect alone.

The over-all results obtained with the Raney metals suggest that desulphurisation is facilitated by a rise in temperature and by the presence of hydrogen on the metal

surface. Hydrogenolytic desulphurisation appears to be the preferred process, although a considerable extent of topo-chemical desulphurisation is postulated with W7-J nickel at elevated temperatures. The order of reactivity of the metals appears to be nickel > cobalt > copper > iron and tungsten.

The desulphurising abilities of Raney copper, iron and tungsten were small in these experiments, and several reactions were carried out under more favourable conditions to establish more accurately the order of reactivity of these metals.

Dihexyl sulphide was used in these experiments. The Raney metals were prepared under hydrogen, and the desulphurisations were effected at 220° in a stream of that gas. Under these conditions Raney nickel, cobalt and iron effected complete desulphurisation, but copper gave only 22% of n-hexane. It is also noteworthy that Raney tungsten (which did not react with di-1-naphthyl sulphide at 200°) reacted to an appreciable extent with dihexyl sulphide; and even nickel obtained by reduction of the oxide in hydrogen showed some activity (see Table 4.3).

No dodecane was detected in any experiment, but this is not surprising as the reactions were carried out in a hydrogen atmosphere, and the reduction of the intermediate hexyl radicals would be greatly facilitated. Moreover, it

is known that alkyl radicals readily disproportionate to alkane and alkene.^{27g,121,122} The latter would be readily hydrogenated under the conditions used.

These results suggest that Raney iron is more reactive in desulphurisation than Raney copper, in contrast with the results obtained with di-1-naphthyl sulphide. Raney iron is known to be oxidised by water at high temperatures.⁶⁶ In the experiments with Raney iron in diethyl phthalate, methanol and water were removed from the metal by direct distillation, and Raney iron was therefore exposed for a considerable time to water at a high temperature. However, in the experiments using dihexyl sulphide the metals were dried by azeotropic distillation with toluene, below 65°, and oxidation was probably largely avoided. It is therefore suggested that the true order of reactivity of the metals is Ni > Co > Fe > Cu > W.

EXPERIMENTAL

Di-1-naphthyl sulphide.-

This material was prepared from 1-naphthylmagnesium bromide and thionyl chloride by Courtot and Paivar's method,¹²³ except that the intermediate sulphoxide was not isolated. After repeated recrystallisation from ethanol, chromatography on alumina in light petroleum, and further recrystallisation, di-1-naphthyl sulphide formed colourless needles, m.p. 110°

Found: C, 84.1; H, 5.0; S, 11.4.

Calc. for $C_{20}H_{14}S$: C, 83.9, H, 4.9; S, 11.2%.

Desulphurisation with "inactive" metals.-

Several attempts were made to desulphurise di-1-naphthyl sulphide with "inactive" preparations of copper, zinc, iron, silver and nickel. Copper bronze, zinc dust and reduced iron powder were commercial products (B.D.H.). The silver catalyst was prepared by precipitation from silver chloride with zinc dust in aqueous suspension according to Vanino.¹²⁴ Reduced nickel was obtained by heating commercial nickel oxide powder in a stream of hydrogen at 500°.

General procedure.-

Di-1-naphthyl sulphide (2.000 g.) was fused with the metal

(5 g. of nickel or an equivalent amount of another metal) for 4 hr. The melt was then extracted with benzene - hexane using a Soxhlet extractor. A drop of the extract was examined by chromatography on partially acetylated paper according to Spotswood,¹²⁵ and the remainder was chromatographed on alumina. The products were further purified by recrystallisation and identified by mixed m.p. wherever possible. Mother liquors from all crystallisations were examined by paper chromatography as a routine. Perylene and benzo(j)fluoranthene were identified by their R_f values on partially acetylated paper and by their ultraviolet absorption spectra.¹²⁶ (Authentic specimens were always run on the same chromatogram.)

It was found that copper bronze, zinc dust, iron and nickel gave no naphthalene or binaphthyl, and 91-99% of the sulphide was recovered unchanged. However, 0.1% and 3.14% of naphthalene were obtained with silver and with copper activated with iodine in acetone¹¹⁸ respectively. Most reactions produced trace amounts of fluorescent (presumably polycyclic) compounds which could not be isolated or identified. No desulphurisation occurred when the sulphide was heated with commercial copper bronze in refluxing ethyl benzoate solvent, or in diethyl phthalate at 300°. However,

heating the sulphide at 400° with zinc dust for 1 hr. gave a mixture from which di-1-naphthyl sulphide (87.5%) and naphthalene (4%) were isolated, together with small amounts of perylene and benzo(j)fluoranthene. The reaction also gave an unknown substance "BG" in low yield. "BG" was free of sulphur and formed yellow flat needles, micro m.p. $298-300^{\circ}$ (from glacial acetic acid, and from benzene - ethanol). Its infrared spectrum showed the absence of O-H and C=O groups. The material was homogeneous on acetylated paper with R_f a little higher than that of perylene. The fluorescence spectrum (Fig. 4.1) (λ_{\max} , 450, 475, 510 (?) $m\mu$) was very similar to perylene (λ_{\max} , 431, 457, 490 $m\mu$), but shifted to longer wavelengths. The ultraviolet absorption spectrum (Fig. 4.2) was also of the perylene type, but again shifted to longer wavelengths: (λ_{\max} , 221, 248, 256, 266, 371, 395, 416, 442 $m\mu$). The results of these desulphurations are summarised in Table 4.1.

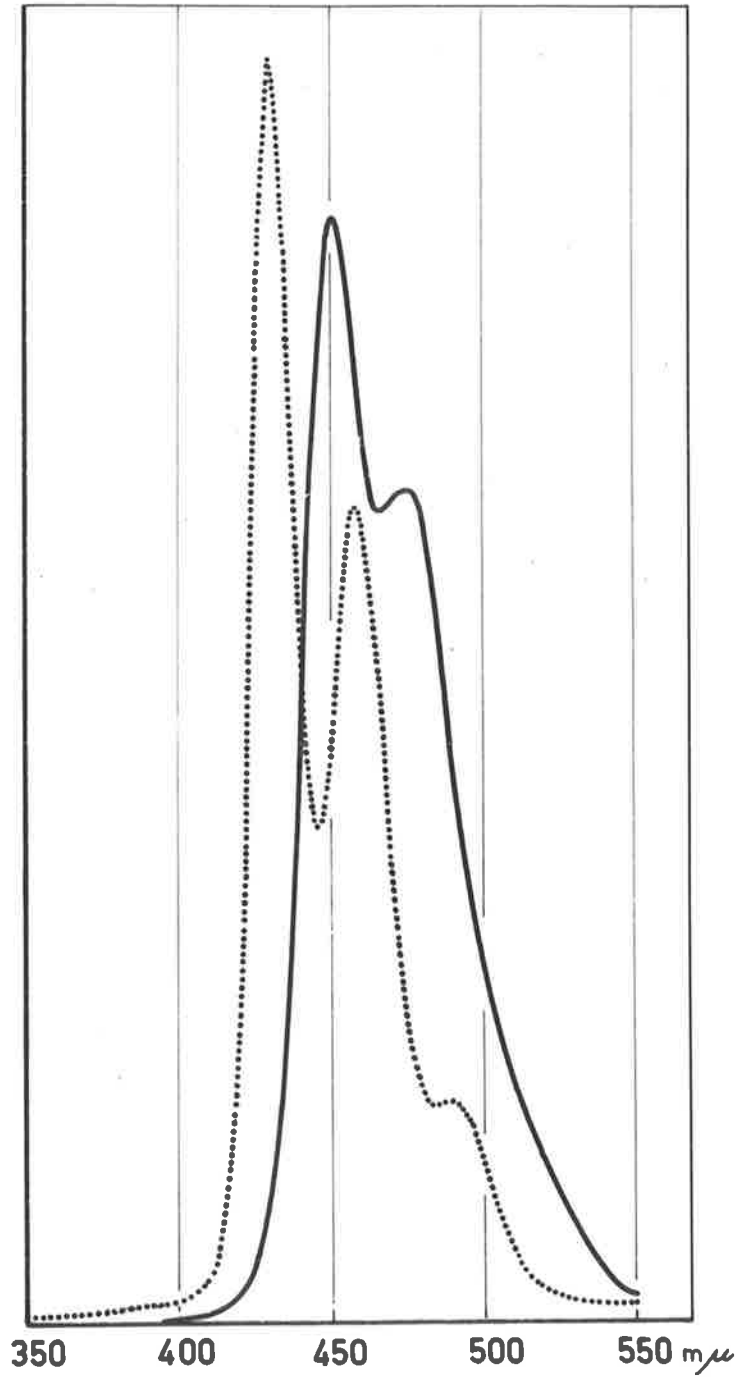


Figure 4.1.

— Unknown BG.
..... Perylene in alcohol.

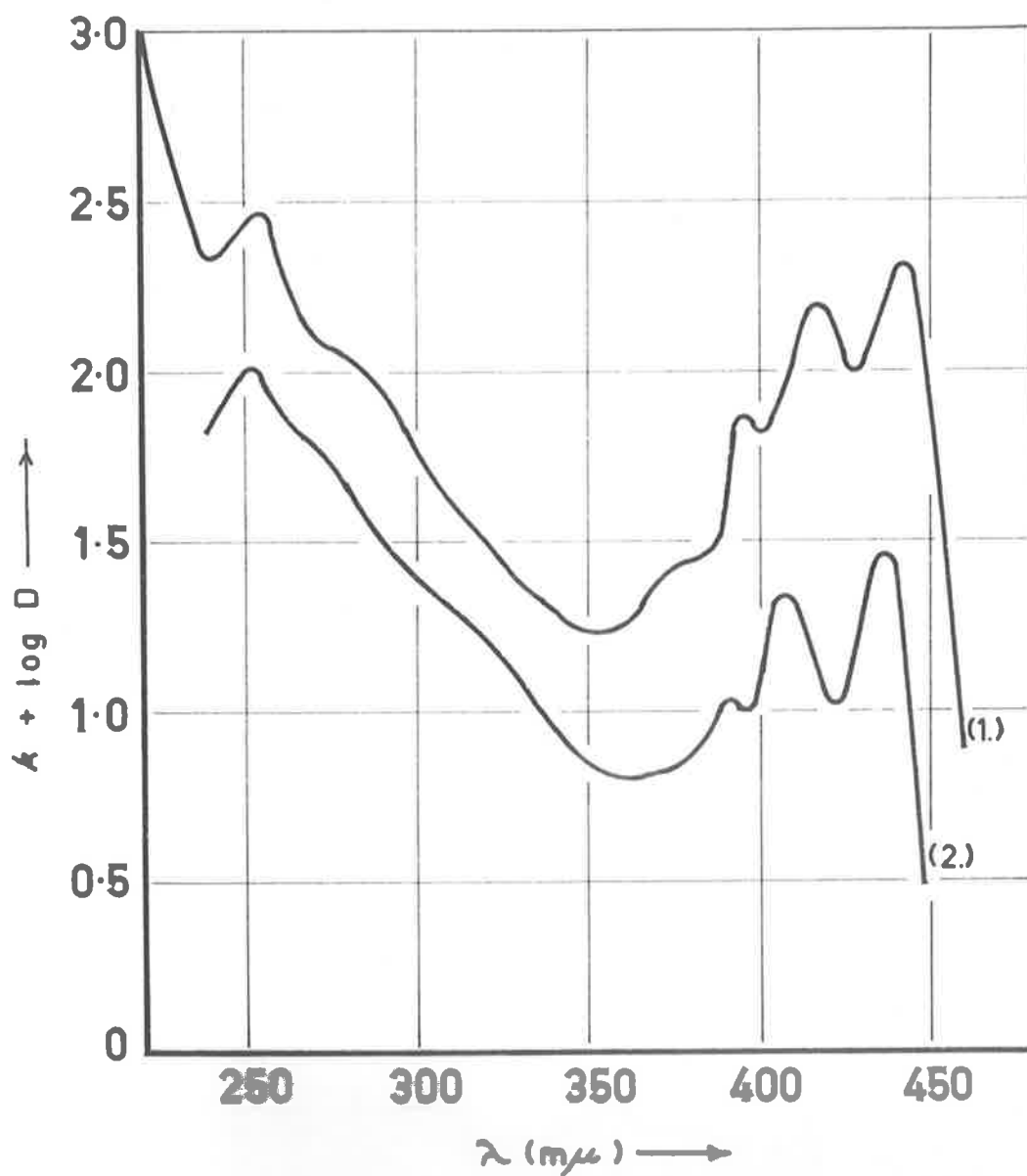


Figure. 4.2. (1) Unknown BG in ethanol.
(2) Perylene in ethanol.

TABLE 4.1

Metal	Solvent	Temp.	% recovd.	% Naphth- alene	Others
Cu bronze	-	200 ^o	99	-	-
Cu/I ₂	-	290	87.8	3.14	-
Cu bronze	Ph.COOEt	212	87.1	-	-
Cu bronze	D.E.P. ^a	300/N ₂	83.4	-	-
Fe (red.)	-	200	97.4	-	-
Zn dust	-	200	93.3	-	-
Zn dust	-	400	87.5	3.95	0.92 ^{b,c}
Ag	-	200	91	0.1	-
Ni (red.)	-	200	92.4	-	-

a. D.E.P. represents diethyl phthalate.

b. A mixture of perylene and benzo(j)fluoranthene was obtained, but was not separated.

c. An unidentified hydrocarbon was also obtained.

Desulphurisation of di-1-naphthyl sulphide with
Raney metals

Raney metals.-

W7 Raney nickel was prepared by the method of Billica and Adkins.³⁹ Aged W7 Raney nickel had been kept for 3 months

under methanol at room temperature. W7-J Raney nickel was prepared by the method of Badger and Sasse.³⁷ W7 Raney cobalt was obtained from 30-70 cobalt - aluminium alloy (Lights) by the procedure used for W7 nickel.³⁹ Raney iron was prepared from 50-50 iron - aluminium alloy (Fluka) by the method of Johnston et al.,⁶⁶ except that hydrogen or nitrogen was used instead of argon to supply the inert atmosphere, and the metal was washed with methanol instead of pyridine. Raney copper was similarly prepared from 50-50 copper - aluminium alloy (Fluka), and W7 copper was prepared by the method used for W7 nickel.³⁹ Raney tungsten was prepared from 30-70 tungsten - aluminium alloy using the procedure for nickel.³⁹ The alloy was kindly supplied by Dr. W.H.F. Sasse, who prepared it by igniting a mixture of tungsten trioxide and aluminium bronze.

Desulphurisations with Raney nickel.-

(1) Freshly prepared W7 Raney nickel (5 g.) was added to a hot solution of di-1-naphthyl sulphide (2 g.) in methanol (400 ml.), and the mixture refluxed for 4 hr. Filtration and extraction of the catalyst with methanol, followed by removal of the solvent by distillation, using an efficient fractionating column, gave a mixture of naphthalene and tetralin. This was not separated, but the components were identified by gas-liquid chromatography.

(ii) When an excess of W7 Raney nickel (30 g.) was refluxed with the sulphide (2 g.) in methanol (150 ml.) for 4 hr., the product was tetralin (1.435 g., 74%), identified by its b.p., infrared spectrum, and retention time in a gas-liquid chromatogram. No other products were found.

In another experiment, carried out under the above conditions, naphthalene (2 g.) was found to be completely hydrogenated to tetralin.

(iii) A mixture of aged W7 Raney nickel (5 g.), di-1-naphthyl sulphide (2 g.) and methanol (250 ml.) was refluxed for 4 hr., cooled, and extracted continuously with methanol in a Soxhlet for 8 hr. Concentration of the extracts to 10 ml. and cooling gave naphthalene (1.413 g.), m.p. and mixed m.p. 80° . Further concentration to 5 ml. and dilution with water (1 ml.) gave a mixture, m.p. $76-78^{\circ}$, which was sublimed at $100^{\circ}/12$ mm. to give pure naphthalene (0.166 g.) and a residue. This was recrystallised from light petroleum to give a colourless, microcrystalline material (0.029 g., 1.6%), m.p. 140° . The m.p. rose to 150° on admixture of this material with 1,1'-binaphthyl, m.p. 140° , but both samples had identical infrared spectra. The peculiar m.p. behaviour of 1,1'-binaphthyl has been noted previously in the literature.¹²⁷ The total yield of

naphthalene was 1.579 g., 88.5%.

(iv) Freshly degassed W7-J Raney nickel (5 g.) was refluxed with di-1-naphthyl sulphide (2 g.) in methanol (25 ml.) for 22 hr. Working up gave unchanged sulphide (1.998 g., 99.9%); a trace of perylene (less than 1 mg.) was isolated by chromatography of the product on alumina, and was identified by its fluorescence spectrum and R_f on acetylated paper.

(v) A mixture of W7-J Raney nickel (5 g.), di-1-naphthyl sulphide (2 g.) and xylene (5 ml.) was refluxed gently at ca. 140° for 4.5 hr. The mixture was extracted continuously in a Soxhlet with benzene for 8 hr., the solvents removed in vacuo and the residue chromatographed on a column of alumina in light petroleum, and light petroleum - benzene. All fractions were examined by chromatography on acetylated paper and like fractions were combined. The products, after recrystallisation, were naphthalene (1.096 g., 61.3%), m.p. and mixed m.p. 80° ; 1,1'-binaphthyl (0.272 g., 15.2%), identified by R_f , mixed m.p. and infrared spectrum; 2,2'-binaphthyl (0.008 g., 0.45%), identified by R_f value, mixed m.p. ($183.5-184^\circ$), and ultraviolet absorption spectrum; a trace of unchanged di-1-naphthyl sulphide (ca. 0.2%), identified by mixed m.p.;

perylene (0.2%), identified by paper chromatography, fluorescence spectrum and ultraviolet absorption spectrum¹²⁶ (λ_{max} 245, 251, 287, 366, 387, 406, 434 m μ); and a trace of benzo(j)fluoreanthene, identified by its R_f value and ultraviolet absorption spectrum¹²⁶ (λ_{max} 226, 242, 281, 292, 308, 318, 332, 349, 365, 376, 383 m μ). Several unidentified fluorescent compounds were also present in small amounts.

(vi) In a similar experiment a mixture of W7-J Raney nickel (5 g.), di-1-naphthyl sulphide (2 g.) and diethyl phthalate solvent (5 ml.) was heated at 220° for 4 hr. Saponification and working up gave the following products (identified as in (v) above): naphthalene (1.232 g., 69%); 1,1'-binaphthyl (0.355 g., 19.8%); 2,2'-binaphthyl (0.015 g., 0.8%); perylene and benzo(j)fluoranthene (total 0.006 g., 0.3%); and benzo(k)fluoranthene (0.004 g., 0.2%), identified by its ultraviolet absorption spectrum¹²⁶ (λ_{max} 240, 269, 282, 296, 308, 361, 380, 400 m μ). No sulphide was recovered. Resinous, highly fluorescent materials were also present in small amounts, but these could not be identified.

Desulphurisations with W7 Raney cobalt.-

(i) A mixture of W7 Raney cobalt (5 g.), di-1-naphthyl sulphide (2 g.) and methanol (25 ml.) was refluxed for 4 hr. Soxhlet extraction for 5 hr. with methanol gave naphthalene

(0.081 g., 4.5%), m.p. and mixed m.p. 80° , and unchanged di-1-naphthyl sulphide (0.39 g.), identified by mixed m.p. Prolonged extraction was necessary in order to remove more sulphur compound. After 4 days the extraction was discontinued, although probably incomplete. A total of 1.737 g., 86.5% of sulphide was recovered.

(11) In another desulphurisation W7 Raney cobalt (5 g.) was heated with di-1-naphthyl sulphide (2 g.) in diethyl phthalate (4 ml.) at 220° in a slow stream of nitrogen for 15 hr. Working up in the usual way gave naphthalene (1.738 g., 97%), m.p. and mixed m.p. 80° , 1,1'-binaphthyl (0.013 g., 0.73%), m.p. 150° , mixed m.p. 155° , identified by its infrared spectrum. Traces of perylene and of benzo(j)fluoranthene were also detected. Very small amounts of other fluorescent materials were picked up in the paper chromatograms, but could not be identified.

Desulphurisations with Raney copper.-

(1) W7 Raney copper (5.4 g.) was added to a solution of di-1-naphthyl sulphide (2 g.) in methanol (25 ml.) and the mixture refluxed for 4 hr. Working up gave naphthalene (0.025 g., 1.4%), m.p. and mixed m.p. 80° ; unchanged sulphide (1.678 g., 83.9%), m.p. $108-110^{\circ}$; and a mixture which was examined by paper chromatography. No perylene or benzo-

fluoranthenes were present, but the nature of the fluorescence of the main spot suggested that both 1,1'-binaphthyl and di-1-naphthyl sulphide were present. It must be noted that 1,1'-binaphthyl and di-1-naphthyl sulphide could not be separated to any appreciable extent by using papers of high or low acetyl content,¹²⁵ or by varying the solvent systems. Both materials exhibited a similar violet fluorescence under a mercury vapour lamp, but when viewed under a "Chromatalite" the sulphide appeared as a dark spot, while the hydrocarbon remained violet. The above chromatogram was run under optimum conditions for the resolution of these compounds (medium degree of acetylation; ethanol : toluene : water 17 : 4 : 1), and the spot obtained showed different fluorescence at its top and bottom edge, suggesting the presence of both biaryl and sulphide. The mixture was therefore chromatographed on a column of partially acetylated cellulose powder in ethanol : toluene : water (17:4:1) according to Spotswood¹²⁸ in the hope of obtaining samples of the pure components. No clear separation was effected, but two materials, m.p. 106-108° and m.p. 126° were obtained. Although these results suggest that 1,1'-binaphthyl is formed in this reaction, the evidence is not conclusive.

(ii) Raney copper was prepared under nitrogen by the method of Johnston.⁶⁶ A mixture of the metal (5.4 g.), di-1-naphthyl sulphide (2 g.) and diethyl phthalate (4 ml.) was heated in a slow stream of nitrogen at 220° for 4 hr. Working up gave naphthalene (0.399 g., 22.3%), identified by mixed m.p., and impure sulphide (1.493 g.), m.p. ca. 105°. Recrystallisation from ethanol gave pure di-1-naphthyl sulphide (1.114 g.), m.p. and mixed m.p. 108-110°, homogeneous on paper in the sense of (i) above. Evaporation of the mother liquors gave a material, m.p. 101-106°, which appeared from paper chromatograms to be a mixture of 1,1'-binaphthyl and di-1-naphthyl sulphide. Traces of perylene and of benzo(j)fluoranthene were also detected by paper chromatography. The mixture was chromatographed very carefully on a long column of alumina in petroleum ether (b.p. 40-60°). The first fraction, after two sublimations on a microscope slide, showed a micro m.p. 155-160° (lit. 159°). Its ultra-violet absorption spectrum was identical with that of 1,1'-binaphthyl. Subsequent fractions had m.p. 95-98°, and were thus presumably mixtures.

(iii) In a similar experiment the Raney copper was prepared under hydrogen, and the reaction was carried out as in (ii) above, but in a slow stream of that gas. The

products were naphthalene (0.782 g., 43.7%), m.p. and mixed m.p. 80° ; impure starting material (0.591 g., 29.5%), m.p. ca. 105° ; perylene (0.1%); and a trace of benzo(j)fluoranthene.


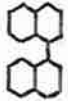

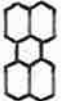
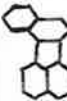

Desulphurisations with Raney iron.-

(i) Raney iron (5 g.) was prepared under hydrogen by the method of Johnston⁶⁶ and refluxed with a solution of di-1-naphthyl sulphide (1 g.) in methanol (25 ml.) for 24 hr. Considerable aerial oxidation of the metal occurred during the reaction. Working up gave unchanged sulphide (0.889 g., 88.9%) and a sample of impure starting material, which was estimated to contain ca. 0.004 g. of 1,1'-binaphthyl. A sample of the pure biaryl was isolated from this material by repeated sublimation and was identified by its ultra-violet absorption spectrum.

(ii) Raney iron (5 g., prepared under nitrogen) was heated with di-1-naphthyl sulphide (2 g.) in diethyl phthalate (4 ml.) at 220° in a slow stream of nitrogen for 4 hr. Working up gave naphthalene (0.076 g., 4.25%) and impure di-1-naphthyl sulphide (1.663 g., 82.1%), which was shown to contain 1,1'-binaphthyl.

(iii) In a similar experiment in which the metal was prepared under hydrogen, and the reaction carried out in a slow stream of that gas, the products were naphthalene

TABLE 4.2.
Desulphurisation with Raney Metals.

Catalyst	Solvent	Temp.	Catalyst Sulphide = W/W	% recovered							Time (hrs.)
W7 Ni	CH ₃ OH	64°	5:2	-	Mixture of naphthalene and tetralin only						4
W7 Ni	CH ₃ OH	64°	30:2	-	tetralin only (74%)						4
W7 Ni (aged)	CH ₃ OH	64°	5:2	-	88.5	1.6	-	-	-	-	4
W7-J Ni	CH ₃ OH	64°	5:2	99.9	-	-	-	trace	-	-	22
W7-J Ni	xylene	140°	5:2	abt. 0.2	61.3	15.2	0.4	0.2	trace	-	4.5
W7-J Ni	D.E.P. ¹	220°	5:2	-	69	19.8	0.8	0.3		abt. 0.2	4
W7 Co	CH ₃ OH	64°	5:2	86.8	4.5	-	-	-	-	-	4
W7 Co/N ₂	D.E.P.	220°	5:2	-	97	0.75	-	trace	trace	-	15
W7 Cu	CH ₃ OH	64°	5.4 : 2	83.9	1.4	?	-	-	-	-	4
R/Cu/N ₂	D.E.P.	220°	5.4 : 2	74.6	22.3	present	-	trace	trace	-	4
R/Cu/H ₂	D.E.P.	220°	5.4 : 2	29.5	43.7	-	-	abt. 0.1	trace	-	4
R/Fe	CH ₃ OH	64°	5:2	88.9	-	abt. 0.2	-	-	-	-	24
R/Fe/N ₂	D.E.P.	220°	5:2	82.1	4.25	present	-	-	-	-	4
R/Fe/H ₂	D.E.P.	220°	5:2	48.7	32	present	-	trace	trace	-	4
R/W	-	200°	1:0.15	95	-	-	-	-	-	-	4

1. D.E.P. is diethylphthalate (about 4-5 c.c. used).

2. Volume of methanol about 25 c.c.

(0.537 g., 32%), m.p. and mixed m.p. 80° , and impure sulphide (0.974 g., 48.7%), m.p. $100-105^{\circ}$. The latter was shown to contain traces of 1,1'-binaphthyl, perylene and benzo(j)fluoranthene.

Desulphurisation with Raney tungsten.-

Raney tungsten (1 g.) was mixed with di-1-naphthyl sulphide (0.150 g.) and the mixture heated at 200° for 4 hr. in the dry state. Working up in the usual way gave only impure di-1-naphthyl sulphide (0.142 g., 95%). No other products were found.

The results of these desulphurisations have been summarised in Table 4.2.

Comparison of Raney metals using dihexyl sulphide.

The Raney metals were prepared under hydrogen from their aluminium alloys, essentially by the method of Johnston et al.⁶⁶ The metals were washed free from water with ethanol and then dried from ethanol and the last traces of water by azeotropic distillation with toluene. The reduced nickel used here was prepared by reduction of the oxide with hydrogen at 500° , and was moistened with a little toluene prior to use.

Dihexyl sulphide (2 g.) was added to the toluene-moist metal (5 g. of nickel, iron, cobalt or tungsten, and 5.4 g. of copper) and the mixture heated in a slow stream of

hydrogen at 220° for 15 hr. The low-boiling material was separated in a small fractionating column during the course of the experiment and collected in a trap surrounded with solid carbon dioxide. The collected material was weighed and analysed by gas-liquid chromatography at 85° on a Celite-Apiezon L column using a Griffin and George apparatus modified for the collection of samples.¹²⁹ The cooled reaction mixture was extracted with toluene in a small Soxhlet extractor (5-10 hr.) and analysed by gas-liquid chromatography at 200°. Yields of unchanged dihexyl sulphide and of hexane were calculated from the weight of the crude material and the areas under the peaks (to eliminate toluene), taking the average of 2-4 separate determinations. No dodecane could be detected in any experiment.

The results are summarised in Table 4.3.

TABLE 4.3

Comparison of Raney metals using dihexyl sulphide at
220° under hydrogen

Metal	Time (hr.)	metal sulphide, $\frac{w}{w}$	% recovd.	% <u>n</u> -hexane
R/Cu	11	15:5	82	15.3
R/Cu	15	5.4 : 2	70	22.4
R/Fe	15	5 : 2	-	84.2
R/Co	15	5 : 2	-	82.0
R/Ni	15	5 : 2	-	82.5
R/W	13	5 : 2	72.3*	13.6
Red.Ni	13	5 : 2	89 *	0.82

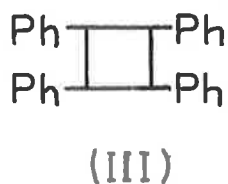
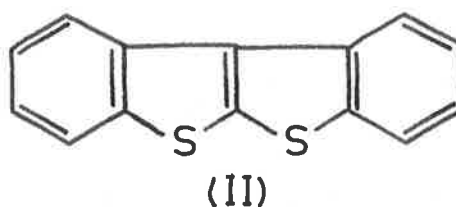
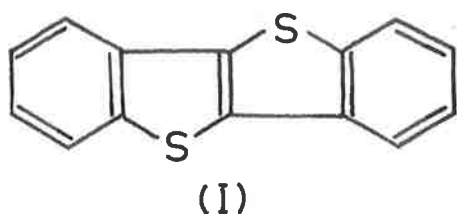
* Yield obtained by distillation and isolation.

CHAPTER V

THE DESULPHURISATION OF
THIONAPHTHENO(3,2-b)THIONAPHTHEN

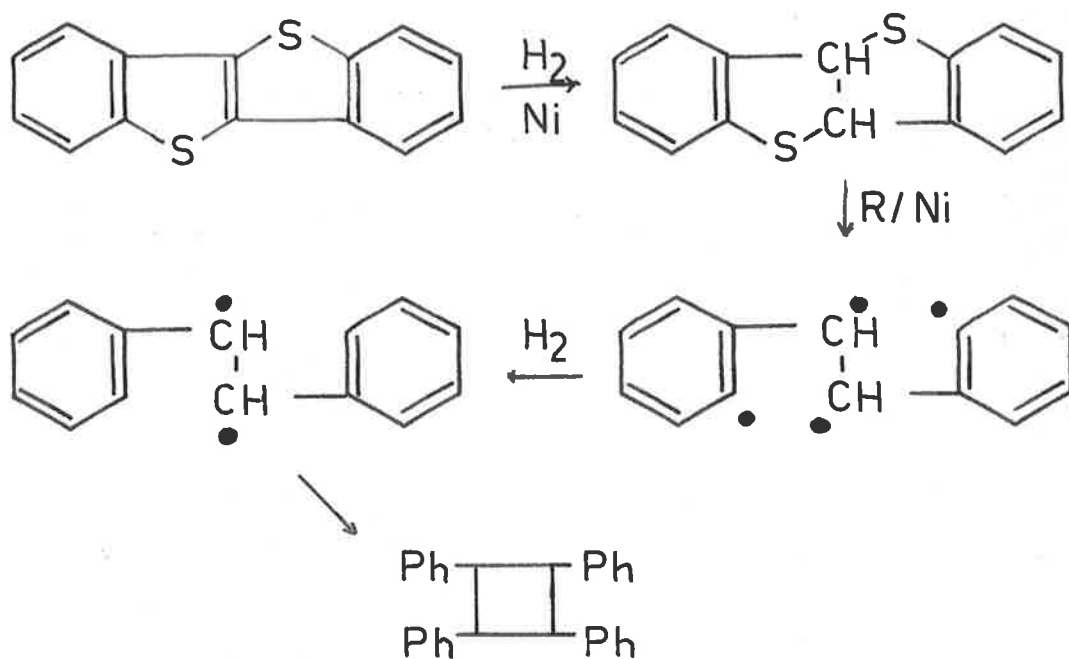
Introduction

Thionaphtheno(3,2-b)thionaphthen (I) was first obtained by Anschütz and Rhodius¹³⁰ as a by-product following the distillation of acetylthiosalicylic acid. These workers were able to limit the structure of their product to (I) or (II), but could not distinguish between them. Structure (I) was also suggested by Horton¹³⁷ for the compound $C_{14}H_8S_2$ isolated by Renard¹³² after heating toluene with sulphur. In 1952 Baker, Ollis and El-Nawawy¹³³ obtained the same compound by pyrolysis of thiosalicylic acid in tetralin in the presence of phosphorus pentoxide. Its structure was proved by Raney nickel desulphurisation, which was reported¹³³ to yield bibenzyl and 1,2,3,4-tetraphenylcyclobutane (III). These workers argued that as in both of these products the phenyl groups were separated by a C_2 unit, they must have arisen from structure (I) rather than (II). More recently Tilak *et al.* have confirmed the structures of the thionaphthenothionaphthens by unambiguous syntheses of both (I) and (II).¹³⁴



The desulphurisation of thionaphtho(3,2-b)thionaphthen is of considerable interest in its own right, but it will be seen that it can also be used to investigate some aspects of the general mechanism of the desulphurisation of thiophen derivatives.

Let us consider the implications of the reported isolation of 1,2,3,4-tetraphenylcyclobutane following the desulphurisation of thionaphtho(3,2-b)thionaphthen. Baker et al.¹³³ have suggested that this cyclobutane is probably formed by dimerisation of an intermediate diradical $\text{Ph}-\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}-\text{Ph}$, and it is thought that the most reasonable pathway for the whole reaction would be as follows:



For this reaction to occur, several significant conditions must be met. Firstly, the molecule must presumably be adsorbed flat on the catalyst surface, using the π -electrons, if hydrogenation of the double bond is to occur.^{9,52,135-137} Secondly, both sulphur atoms must be removed simultaneously to give, after partial saturation, the required diradical, dimerisation of which would lead to the cyclobutane.

It will be shown in the remainder of this chapter that the formation of the cyclobutane is unlikely in view of the existing experimental evidence, and that its isolation could

not be repeated in practice. Moreover, it will be shown that chemisorption of the thionaphthenothionaphthen molecule probably occurs in a more or less perpendicular fashion, via the sulphur atom, leading to stepwise desulphurisation involving unsaturated intermediates.

Results and Discussion.

Several desulphurisations were carried out as described by Baker et al.,¹³³ but using the more common W7 Raney nickel.³⁹ Under these conditions thionaphthenothionaphthen gave bibenzyl as only product in 63 and 64% yield when ethanol or methanol solvents were used. A W7 catalyst which had been kept for three months gave bibenzyl in 66% yield, and a similar catalyst aged for 18 months gave 94.5% of the same substance. Desulphurisation of thionaphthenothionaphthen by the method of Baker,¹³³ and using a catalyst prepared according to Brown¹⁶ (which was reported to yield tetraphenylcyclobutane only) led in our hands to bibenzyl as sole product, in 91% yield. The comparatively low yields obtained with the very active W7 catalysts may be due to some C-C hydrogenolysis of bibenzyl to toluene. However, no toluene could be detected under the conditions used. Hydrogenolysis of this type has been observed in the desulphurisation of 2,3,4,5-tetraphenylthiophen, which gave

inter alia bibenzyl.¹³⁸

When Raney cobalt was used in the desulphurisation, most of the thionaphthenothionaphthen was recovered unchanged, but small amounts of bibenzyl, and a material m.p. ca. 160-165° were obtained. The latter was depressed by admixture to authentic tetraphenylcyclobutane, m.p. 163°, and was found to be a mixture of trans-stilbene and unchanged thionaphthenothionaphthen. This finding led to a study of the temperature-composition curve of the system stilbene - thionaphthenothionaphthen.

The T-C diagram (Fig. 5.2 Experimental section) shows that a eutectic (U_1), containing 90% stilbene by weight, and melting at 120° is formed at A. This is confirmed by the fact that mixtures containing 90-60% of stilbene exhibit a thaw point at that temperature. It is difficult to decide whether C represents a second eutectic (U_2) (therefore there is true compound formation at B), or whether it is a peritectic (i.e. the compound formed decomposes below its melting point). As samples containing 60-10% of stilbene exhibit a thaw point at ca. 159° it seems probably that C is another eutectic, and that there is true compound formation at B. It should be noted that recrystallisation of mixtures of composition A, B or C from ethanol and from

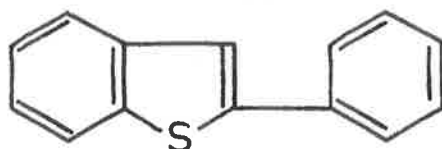
aqueous methanol led to a considerable change in composition and was accompanied by an observable change in the m.p.

A reference sample of 1,2,3,4-tetraphenylcyclobutane was prepared by the photodimerisation of stilbene in benzene solution.^{13,14} Surprisingly, the best results were obtained in dilute solution, and using a mercury lamp without its Woods glass filter. The properties of this cyclobutane differed considerably from those of the mixture obtained with Raney cobalt.

W7 Raney nickel³⁹ is known to be a much more powerful hydrogenation catalyst than Raney cobalt.³⁰ It was therefore suspected that stilbene was also formed in the desulphurisations with Raney nickel, but that the olefin was hydrogenated to bibenzyl during the course of the reaction. Several experiments were therefore carried out using degassed and poisoned nickel catalysts (which would be expected^{47,100,139} to have lesser hydrogenating ability), in order to test this hypothesis.

Accordingly, degassed (W7-J) Raney nickel³⁷ was found to convert thionaphthenothionaphthen to a mixture of stilbene (17.5%), bibenzyl (34%), and 2-phenylthionaphthen (32%) (IV), which was readily separated. In addition to confirming the hypothesis, this reaction may be recommended as an easy

alternative two-step synthesis of 2-phenylthionaphthen, starting with thiosalicylic acid. Other syntheses have been described by Horton¹³¹ and by Banfield, Davies, Gamble and Middleton.¹⁴⁰



(IV)

Although pyridine bases are well known catalyst poisons,^{47,100,139} as much as 40% (w/w) of 2,4,6-collidine had no effect on the desulphurisation of thionaphtheno-thionaphthen (except that C-C hydrogenolysis was avoided), and bibenzyl was formed as the only product, in 98% yield. Reaction with W7 nickel³⁹ poisoned with 10% copper¹⁰⁰ resulted in incomplete desulphurisation, giving a mixture of bibenzyl (73.5%) and 2-phenylthionaphthen (14.3%); but no stilbene was found. However, a small amount of the olefin, in addition to 2-phenylthionaphthen and bibenzyl, was obtained when a much less active nickel catalyst, poisoned with 20% of copper was used. No stilbene was obtained when a similar lead-poisoned catalyst was used,

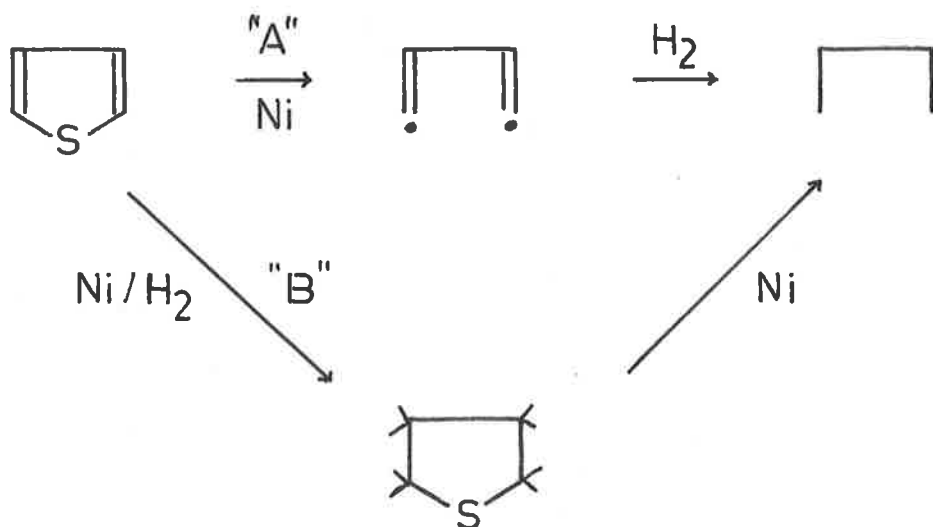
the product being a mixture of unchanged thionaphthenthionaphthen, 2-phenylthionaphthen, and bibenzyl. It may be mentioned that a mixture of thionaphthenothionaphthen and 2-phenylthionaphthen (1:2.5) showed a m.p. of 165-166°, unaltered by repeated recrystallisation from ethanol, although separation could be achieved by other means.

It is generally accepted that the first step in the desulphurisation of a thiophen derivative must be the chemisorption of the sulphur compound on the catalyst surface.⁹ Such chemisorption could occur in two ways, namely (a) more or less perpendicularly to the catalyst surface, via the lone pair electrons of the sulphur atom, or (b) more or less flat, involving the π -electrons of the aromatic system.⁹ The results of the desulphurisation of thionaphthenothionaphthen seem to provide useful data on this point. Thus, if the formation of 1,2,3,4-tetraphenylcyclobutane could have been confirmed, it would follow that desulphurisation must, in all probability, occur with the molecule flat on the catalyst surface, as was pointed out in the introduction. However, no tetraphenylcyclobutane was obtained in the above work; but in several experiments 2-phenylthionaphthen and trans-stilbene were isolated. This

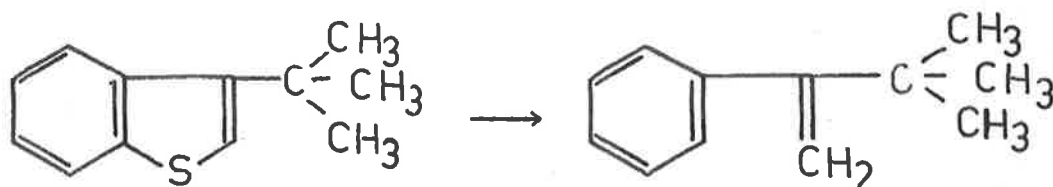
result lends support to the opposite view, namely, that the desulphurisation of thionaphthenothionaphthen takes place in two distinct stages, and that the sulphur compound is chemisorbed more or less perpendicularly to the catalyst.

Badger⁹ has pointed out that two possible pathways can operate in the actual desulphurisation of a thiophen derivative, namely:

- A. desulphurisation and subsequent hydrogenation of the unsaturated diradical intermediate, or
- B. hydrogenation to a tetrahydrothiophen, and subsequent easy desulphurisation to give the saturated product.



That path "B" is the less likely is borne out by the fact that for hydrogenation to occur, chemisorption must necessarily involve the π -electrons, with the molecule lying flat.^{9,52,135-7} This seems to be precluded in the light of the foregoing argument. Furthermore, hydrogenation of olefinic compounds is known⁴⁷ to be inhibited by sulphur compounds. Also, available evidence indicates that the chemisorption of dimethylbenzylamine and of chlorobenzene involves the lone pair electrons of the functional group, rather than the π -system of the benzene ring.¹⁴¹ Desulphurisation of dibenzothiophens^{68a,142} certainly proceeds without hydrogenation, except for saturation of the free valences, which would indicate that path "A" is followed in this case at least. Path "A" finds further support in a report from Corson et al.¹⁴³ These workers detected 10% of olefin, in addition to the expected hydrocarbon, in the desulphurisation of 3-t-butylthionaphthen (V). Although the olefin was not isolated, its presence was inferred from infra-red spectra and from quantitative hydrogenation.



(V)

In the present work it was found that the desulphurisation of thionaphthenothionaphthen yielded as much as 17.5% of trans-stilbene (isolated and positively identified) when a deactivated catalyst was used. This result, together with the foregoing evidence is taken as strong support of the view that desulphurisation of thiophene gives unsaturated intermediates which are subsequently hydrogenated. The alternative pathway, namely, hydrogenation of the thiophene to a tetrahydrothiophene, and subsequent removal of sulphur, seems to be excluded.

EXPERIMENTAL

Thionaphtheno(3,2-b)thionaphthen.

The material used in the first three experiments was prepared by Mr. A.F. Isaac according to the method of Baker, Ollis and El-Nawawy.¹³³ No depression of m.p. was observed when a sample of this material was mixed with subsequent preparations using a modified technique.

The following synthesis was found to be simpler than that described by Baker et al.¹³³ A mixture of thiosalicylic acid (25 g., B.D.H.), phosphorus pentoxide (40 g.), and tetralin (150 ml.) was refluxed over a free flame for 3 hr., the liquid decanted, and the remaining cake extracted with boiling tetralin. The combined tetralin extracts were evaporated to dryness in vacuo and the residue refluxed with a solution of potassium hydroxide (20 g.) in water (50 ml.) and ethanol (100 ml.) for 1 hr. After removal of ethanol, water was added and the mixture extracted with benzene. The benzene extracts were concentrated, treated with animal charcoal, and the solid allowed to crystallise. Further recrystallisation from light petroleum (b.p. 80-100°) (charcoal) gave thionaphtheno(3,2-b)thionaphthen (1.6 g.), m.p. 214-216° (lit. m.p. 209-210°, 216°). A further 0.45 g. of the pure thionaphtheno(3,2-b)thionaphthen was obtained by

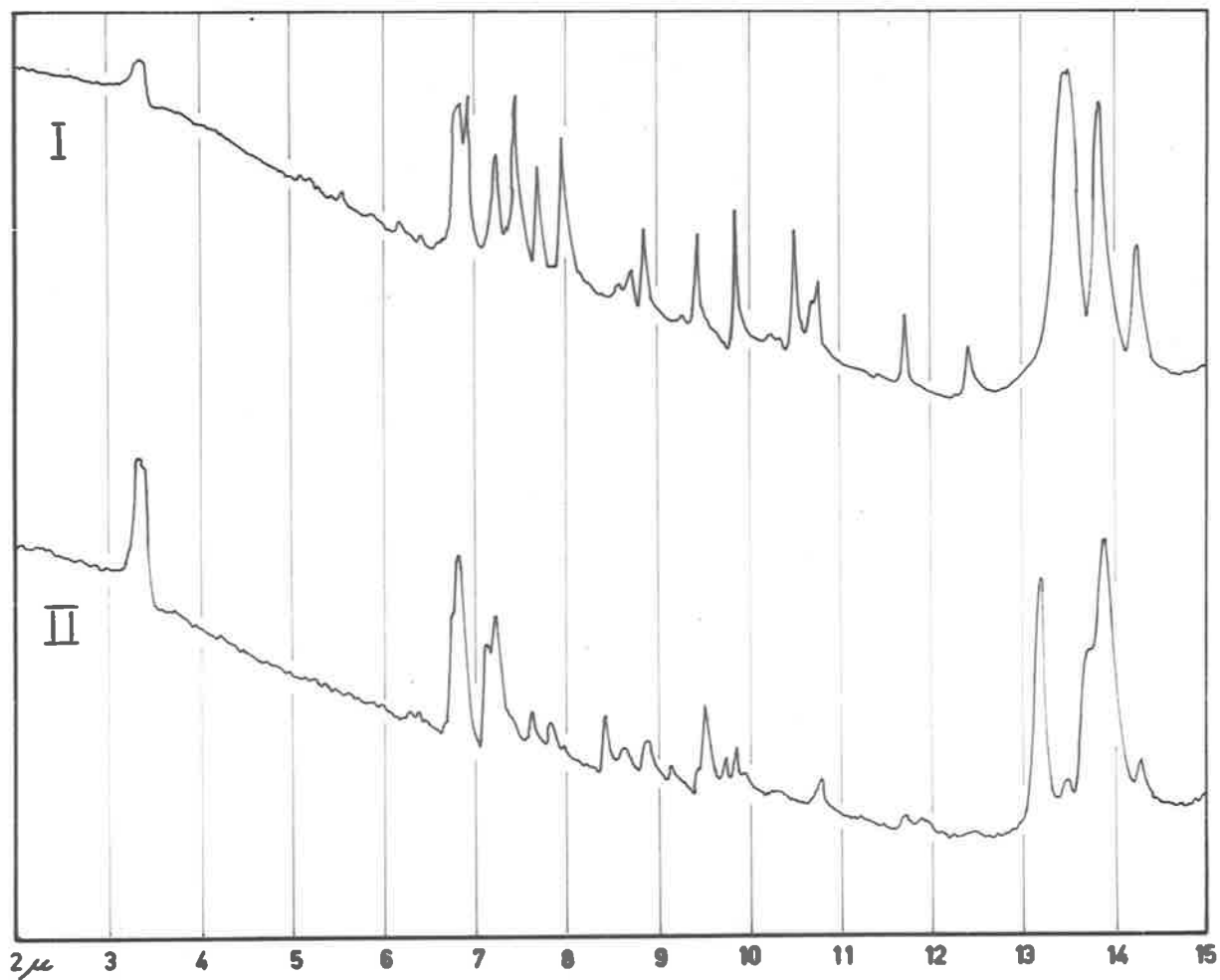


Figure 5.1, Infrared Spectra, nujol,
NaCl prism, 25°C.

- I Thionaphtheno [3,2-b] thionaphthen.
- II Thionaphtheno [2,3-b] thionaphthen.

filtration of the mother liquors through alumina, and further recrystallisation of the product. The m.p. was not depressed by admixture to an authentic specimen kindly supplied by Professor B.D. Tilak,¹³⁴ and both samples showed identical infrared spectra. None of the isomeric thionaphthene(2,3-b)thionaphthen (which was also kindly made available by Professor Tilak) could be found in our material. (See Fig. 5.1)

Found: C, 70.5; H, 3.5; S, 26.3.

Calc. for $C_{14}H_8S_2$: C, 69.9; H, 3.3; S, 26.7%.

Desulphurisations with Raney nickel.-

(1) With W7 Raney nickel in ethanol. A mixture of thionaphthenothionaphthen (0.5 g.), W7 Raney nickel³⁹ (10 g., from 20 g. of alloy), and ethanol (85 ml.) was refluxed for 3.5 hr., filtered, and the catalyst extracted three times with boiling ethanol. Evaporation of the solvent and distillation of the residue gave an oil (0.236 g., 62.2%), b.p. ca. 70°/0.05 mm., which gave an infrared spectrum identical with that of bibenzyl. No high-boiling residue was found. Examination of the oil by gas-liquid chromatography on Celite - Apieson L showed the presence of a small impurity as a shoulder before the major peak. Using a Griffin and George apparatus modified for the collection of samples¹²⁹ it was

possible to collect solid bibenzyl (m.p. and mixed m.p. 52°) from the gas-liquid chromatogram, but attempts to collect the impurity were not successful. The oil did not crystallise on cooling in dry ice, or after repeated vacuum distillation.

When the experiment was repeated the yield of oil, b.p. ca. $70^{\circ}/0.05$ mm. was again 0.236 g. (after two distillations).

(ii) With W7 Raney nickel in methanol. In a similar experiment a mixture of thionaphthenothionaphthen (0.5 g.) and Raney nickel³⁹ (10 g.) was refluxed in methanol (250 ml.) for 3.5 hr. The product was distilled twice to give bibenzyl (0.239 g., 63%), b.p. ca. $70^{\circ}/0.05$ mm., which crystallised on stirring. After recrystallisation from light petroleum (b.p. below 40°) it had m.p. $51-51.5^{\circ}$, not depressed by admixture with an authentic specimen. No higher boiling products were found.

(iii) With W7 Raney nickel aged for 3 months. Thionaphtheno(3,2-b)thionaphthen (0.5 g.) was also desulphurised, in ethanol, as described in (i) above, except that the catalyst had been kept at room temperature under ethanol for 3 months. Bibenzyl was again obtained as an oil, b.p. ca. $70^{\circ}/0.05$ mm., (0.247 g., 65%), and was identified by its infrared spectrum. A small amount of residue after distillation was found to be

pure bibenzyl, m.p. and mixed m.p. 50-51° (from aqueous methanol). No toluene could be found in this experiment.

(iv) With W7 Raney nickel aged for 18 months. In another experiment the catalyst used (10 g.) had been kept under aqueous methanol at 4-10° for 18 months. It was washed twice by decantation with ethanol prior to use. Desulphurisation of the sulphur compound (0.5 g.), in ethanol (85 ml.), as described in (i) above gave bibenzyl as an oil, b.p. ca. 60°/0.01 mm., (0.368 g., 94.5%), identified by its infrared spectrum. No residue was obtained after distillation. Gas-liquid chromatography on a Celite - silicone column showed only one peak with retention time corresponding to bibenzyl. Under identical conditions small amounts of trans-stilbene and of phenanthrene could be easily detected in a reference sample of impure bibenzyl.

(v) By the method of Baker et al.¹³³ A mixture of thionaphthene(3,2-b)thionaphthen (0.44 g.), in ethanol (75 ml.) and Raney nickel (8 g., prepared by the method of Brown,¹⁶ using 16 g. of 50-50 alloy) was refluxed for 3.5 hr. The reaction mixture was filtered hot and the catalyst washed twice with boiling ethanol. Concentration of the liquors, followed by distillation in vacuo gave bibenzyl (0.304 g., 91%), b.p. ca. 70°/0.01 mm., identified by its infrared

spectrum. No other products could be found.

Desulphurisations with Raney cobalt.-

(1) A mixture of thionaphtheno(3,2-b)thionaphthen (0.5 g.), W7 Raney cobalt (ca. 7 g., prepared from 20 g. of 30-70 alloy by the method for W7 nickel³⁹), and ethanol (50 ml.) was refluxed for 5 hr., filtered, and the catalyst extracted repeatedly with boiling solvent. After concentration to 50 ml. and cooling, the combined filtrate and extracts deposited unchanged starting material (0.290 g.), m.p. and mixed m.p. 214°. Further concentration of the liquors gave a material "A" (0.020 g.), thaw point ca. 160°, m.p. 200°. Concentration of the filtrate from this recrystallisation to small volume and cooling gave material "B" (0.040 g.), thaw point ca. 155°, m.p. 160°. Repeated recrystallisation of "B" from light petroleum (b.p. below 40°) raised its m.p. to 165° (thaw point 155°), depressed by a synthetic sample of 1,2,3,4-tetraphenylcyclobutane (m.p. 163°), and by 1,2,3,4-tetraphenyl-n-butane (m.p. 178°). Evaporation of the mother liquors from the recrystallisation of "B", and repeated recrystallisation of the residue from ethanol in a capillary tube gave impure trans-stilbene, m.p. 118°. The m.p. rose to 121-123° when the material was mixed with authentic stilbene (m.p. 124-125°). A temperature -

composition curve was drawn up for the system thionaphthenthionaphthen / stilbene. (See Fig. 5.2.) From this "A" is a mixture of starting material (16 mg.) and stilbene (4 mg.), and "B" of stilbene (27 mg.) and starting material (13 mg.). Estimated yields: unchanged thionaphthenthionaphthen (0.306 g., 61.2%) and stilbene (0.031 g., 8%).

(ii) A mixture of W7 Raney cobalt (11 g.), thionaphthenthionaphthen (1.0 g.) and ethanol (50 ml.) was refluxed for 5.5 hr. The cooled mixture was filtered and the residue continuously extracted with ether for 10 hr. and then with benzene for 12 hr. Evaporation of the benzene and recrystallisation of the residue from benzene - light petroleum gave unchanged thionaphthenthionaphthen (0.268 g.), m.p. 214-216°. The combined ethanol solutions were concentrated to small volume and cooled to give a further quantity of unchanged sulphur compound, m.p. 216° (0.535 g.). The mother liquors were diluted with water and extracted with benzene. (Examination by gas-liquid chromatography showed two peaks with retention times corresponding to bibenzyl and stilbene). Evaporation of the benzene and distillation of the residue gave the following fractions:

- (a) bibenzyl (0.075 g.), m.p. and mixed m.p. 52°;
- (b) b.p. 150°/0.01 mm. (0.038 g.), m.p. 140-150°;

(c) a residue consisting of thionaphthenthionaphthen (0.012 g.).

After recrystallisation from ethanol, fraction (b) gave needles m.p. 160° ; but this m.p. was depressed by admixture to authentic 1,2,3,4-tetraphenylcyclobutane. Treatment of fraction (b) with bromine in carbon bisulphide gave stilbene dibromide, m.p. and mixed m.p. 237° . Under these conditions tetraphenylcyclobutane gave no reaction. The mother liquors yielded a small amount of unchanged thionaphthenthionaphthen. The T-C curve (Fig. 5.2) showed that m.p. 160° corresponds to a mixture of 60% stilbene and 40% thionaphthenthionaphthen.

1,2,3,4-Tetraphenylcyclobutane.-

The cyclobutane derivative was prepared by photodimerisation of stilbene in benzene solution essentially by the methods of Fulton¹⁴⁴ and of Pailer and Müller,¹⁴⁵ but differing in the methods of working up.

(1) A saturated solution of trans-stilbene in pure benzene (100 ml.) was placed in a quartz flask and irradiated for 10 days. The light source was a mercury vapour lamp fitted with a Woods glass filter, emitting essentially the 3650-3663 Å radiation (Philips, 125 W,

type MBW/U). After evaporation of benzene the residual material was distilled in vacuo to remove benzaldehyde and most of the unreacted stilbene, and the residue chromatographed on alumina. Elution with light petroleum (b.p. 55-65°) gave a forerun of stilbene, followed by a mixture (0.12 g.), m.p. 105°, which could be resolved into stilbene and the desired 1,2,3,4-tetraphenylcyclobutane (m.p. 163°) by fractional crystallisation from light petroleum. The yield of the pure cyclobutane was very small (ca. 10 mg.). Further elution with benzene gave a material (ca. 100 mg.), m.p. 143-146°, which after repeated recrystallisation melted at 147°. It is thought that this material is an isomeric 1,2,3,4-tetraphenylcyclobutane (lit. m.p. 149°), which was also found by Fulton¹⁴⁴ in a similar reaction.

(ii) A dilute solution of stilbene (5.0 g.) in benzene (250 ml.), contained in a quartz flask, was placed 12" from a mercury vapour lamp similar to the one used in the previous experiment, but from which the Woods glass filter had been removed, and irradiation continued for 10 days. After removal of benzene the residue was distilled in vacuo, and the material boiling below 120°/0.03 mm. (consisting of benzaldehyde, stilbene, and benzoic acid) discarded. A

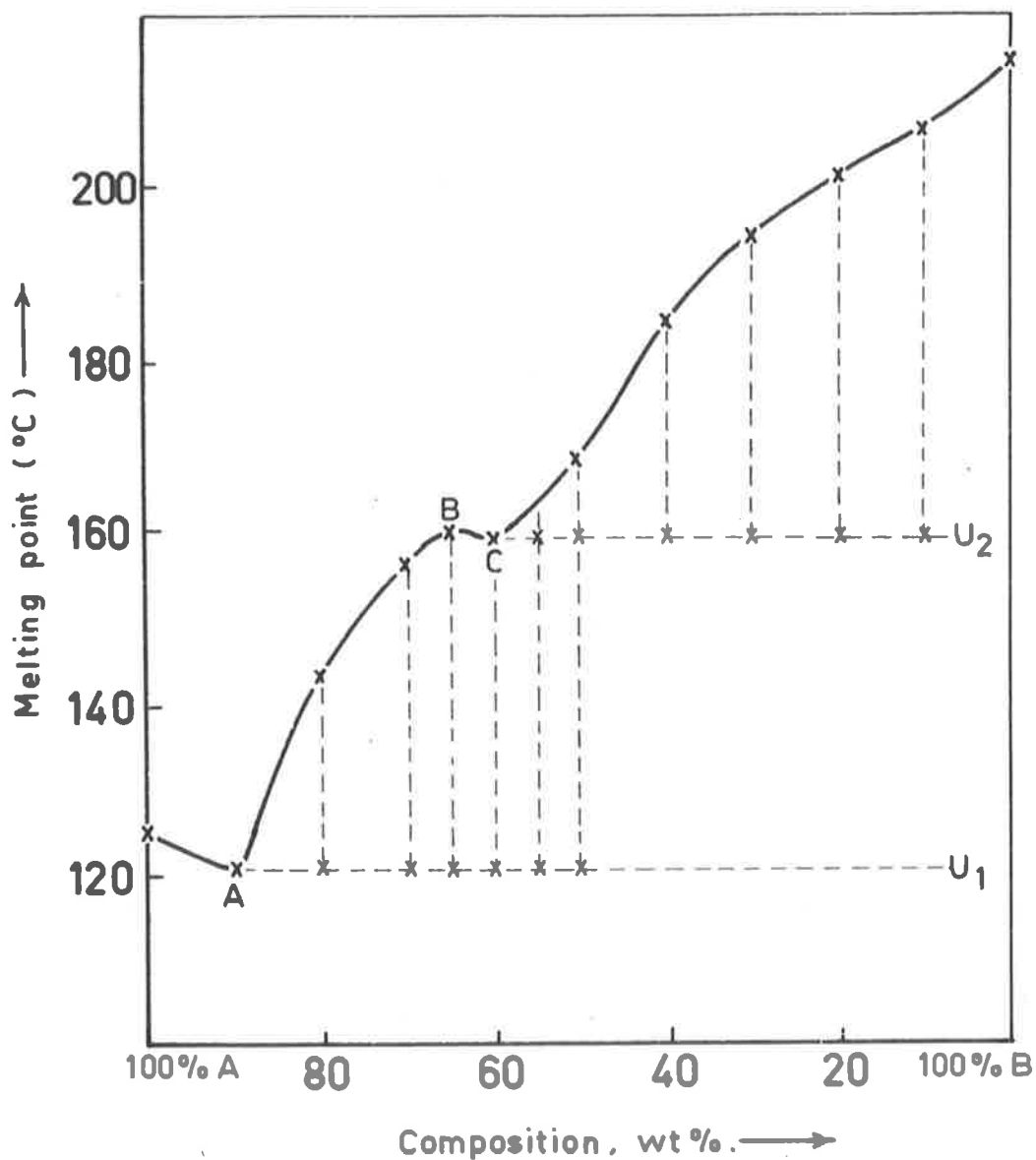


Figure. 5.2. A = trans-stilbene.
B = thionaphtheno(3,2-b)thionaphthen.

viscous liquid (0.692 g.), b.p. 180-200°/0.03 mm. (bath temperature 240-250°) was collected. This solidified on trituration with light petroleum. Recrystallisation from benzene - light petroleum (charcoal) gave 1,2,3,4-tetraphenylcyclobutane (0.201 g.), m.p. 163°, not depressed by admixture with the material obtained in (i) above. A further 50 mg. of the pure cyclobutane were obtained from the liquors by repeated crystallisation from ether.

Found: C, 93.6; H, 6.9.

Calc. for $C_{28}H_{24}$: C, 93.3; H, 6.7%.

Construction of a temperature - composition curve for a mixture of stilbene and thionaphtheno(3,2-b)thionaphthen.-

Mixtures of the two components were made up by weight, fused together in a sealed tube, the cooled melt ground and the m.p. determined. The average of three determinations was recorded, using the thaw - melt method. Results are summarised in Table 5.1 and in Fig. 5.2. It must be noted that the m.p. of a mixture of 2 mols. stilbene to 1 mol. thionaphtheno(3,2-b)thionaphthen (60% stilbene w/w) showed a very indefinite m.p. (158-161°, recorded as 159.5°) (ten separate determinations).

TABLE 5.1

Weight % of stilbene ($\pm 1\%$)	Thaw point ($\pm 1^\circ$)	Melting point ($\pm 1^\circ$)
100	-	124.5
90	-	120
80	120	144
70	120	156
65	120	160
60	120	159.5
55	(120) 159	163
50	(120)? 159	168
40	159	185
30	159	194.5
20	159	201
10	159 (?)	206
0	-	214.5

Desulphurisation with degassed Raney nickel.-

Diethylphthalate (6 ml.) was introduced to wet W7-J Raney nickel³⁷ (10 g.), the pressure released, and the thionaphthenoethionaphthen (1.0 g.) added. The resulting mixture was heated at 200° for 2 hr., cooled, and continuously extracted with ether (6 hr.), the extract dried and evaporated. The residue was saponified by refluxing with alcoholic

potassium hydroxide for 8 hr. Water was added, most of the ethanol was removed by distillation, and the residue was again extracted with ether. Evaporation and distillation gave 5 fractions:

- (a) bibenzyl (0.240 g.), b.p. $70^{\circ}/0.01$ mm.; m.p. and mixed m.p. 52° ;
- (b) a solid (0.109 g.), b.p. $100^{\circ}/0.01$ mm.; m.p. $95-100^{\circ}$;
- (c) a solid (0.069 g.), b.p. $120^{\circ}/0.01$ mm.; m.p. $135-140^{\circ}$;
- (d) a solid (0.216 g.), sublimed at $125-135^{\circ}/0.01$ mm.; m.p. 172° ; and
- (e) a residue (0.037 g.), m.p. $172-173^{\circ}$.

Fraction (b) was examined by gas-liquid chromatography and found to consist of bibenzyl (0.018 g.) and trans-stilbene (0.091 g.) (yields calculated from areas under the peaks). The stilbene was identified by treating the fraction with bromine in carbon bisulphide; the resulting dibromide had m.p. and mixed m.p. $237-240^{\circ}$. Fraction (c) was recrystallised from ethanol to give 2-phenylthionaphthen (0.27 g.), m.p. 176° , not depressed by admixture with an authentic specimen kindly supplied by Mr. S. Middleton,¹⁴⁰ and both samples gave identical ultraviolet absorption spectra. The mother liquors after evaporation were treated with bromine in carbon bisulphide to give stilbene dibromide (0.075 g.; corresponding to 0.040 g. of stilbene), m.p. and mixed m.p.

237°. Recrystallisation of fractions (d) and (e) from ethanol gave 2-phenylthionaphthen, m.p. and mixed m.p. 175-176°. Total yields: bibenzyl, 34.2%; stilbene, 17.5%; 2-phenylthionaphthen, 32.0%.

Desulphurisation with poisoned Raney nickel.-

(i) Using Raney nickel poisoned with 2,4,6-collidine.

2,4,6-Collidine (4 g.) was added to a stirred suspension of W7 Raney nickel (10 g.) in methanol (100 ml.) and the mixture warmed gently. The smell of collidine disappeared almost completely after 2 min., suggesting complete chemisorption of the base on the catalyst. Thionaphtheno-thionaphthen (1 g.) was added and the mixture refluxed for 4 hr., transferred to a hot Soxhlet extractor and extracted for 12 hr. with methanol. After removal of the solvent, using a fractionating column, the residue was taken up in ether, freed from base by extraction with dilute hydrochloric acid, and the ether dried and evaporated. Distillation of the product gave bibenzyl (0.745 g., 98%). No other products could be found.

(ii) Using W7 Raney nickel poisoned with copper.¹⁰⁰ W7

Raney nickel (20 g., from 40 g. of alloy) was washed with ethanol and added to a solution of neutral copper acetate (2 g.) in ethanol (120 ml.). The mixture was stirred on the

water bath for 20 min. and washed three times by decantation with ethanol. Thionaphthenothionaphthen (1.0 g.) and ethanol (100 ml.) were added to the catalyst sludge and the mixture refluxed for 6 hr. (and stood for three days). Continuous extraction of the mixture for 10 hr. with ethanol, followed by removal of the solvent using a fractionating column, gave a residue which was distilled to give bibenzyl (0.557 g., 73.5%), m.p. and mixed m.p. 52°; and 2-phenylthionaphthen (0.129 g.), m.p. and mixed m.p. 172-173°.

(iii) Using less active Raney nickel poisoned with copper.

The Raney nickel was prepared from nickel-aluminium alloy (20 g.) by the method used for W7 catalyst except that the alloy was added as quickly as possible to the alkali at 100°, and the catalyst was digested at that temperature for 20 min. After four decantations with water and one with ethanol the catalyst was added to a solution of neutral copper acetate (2 g.) in ethanol (120 ml.), and the mixture stirred for 20 min. on the water bath, decanted twice with ethanol and used at once. Desulphurisation was effected by refluxing a mixture of thionaphthenothionaphthen (1.0 g.) and ethanol (100 ml.) with the poisoned catalyst for 1 hr. Soxhlet extraction and concentration of the extract gave unchanged starting material (0.384 g.), m.p. and mixed m.p. 215-216° (after recrystallisation from light petroleum (b.p. 70-90°)).

Concentration of the filtrate gave a material "M" (0.282 g.), m.p. 165-166°, and mother liquors which were distilled to give two fractions:

- (a) bibenzyl (0.175 g., 23.1%), b.p. ca. 70°/0.01 mm.; m.p. and mixed m.p. 52°; homogeneous in a gas-liquid chromatogram;
- (b) trans-stilbene (0.009 g., 1.2%), b.p. ca. 110°/0.01 mm.; m.p. 124°; dibromide m.p. and mixed m.p. 237-240°.

Material "M" was unaltered by recrystallisation from ethanol, but one crystallisation from light petroleum (b.p. 70-90°) raised the m.p. to 172-178° (depressed by 2-phenylthionaphthen). Fractional sublimation at 120°/0.01 mm., and recrystallisation of the fractions gave 2-phenylthionaphthen, m.p. and mixed m.p. 172-173°, and thionaphtheno(3,2-b)thionaphthen, m.p. and mixed m.p. 214-215°. The composition of mixture "M" (which was shown to contain no other products) was determined by comparison of its ultraviolet absorption spectrum with those of mixtures of known composition (see Figs. 5.3-5.6). Total yields: unchanged thionaphtheno-thionaphthen (0.437 g., 43.7%); 2-phenylthionaphthen (0.193 g., 22.1%); stilbene (0.009 g., 1.2%); and bibenzyl (0.175 g., 23.1%).

(iv) Using Raney nickel poisoned with lead. Raney nickel (10 g.) was prepared as in (iii), and added to a

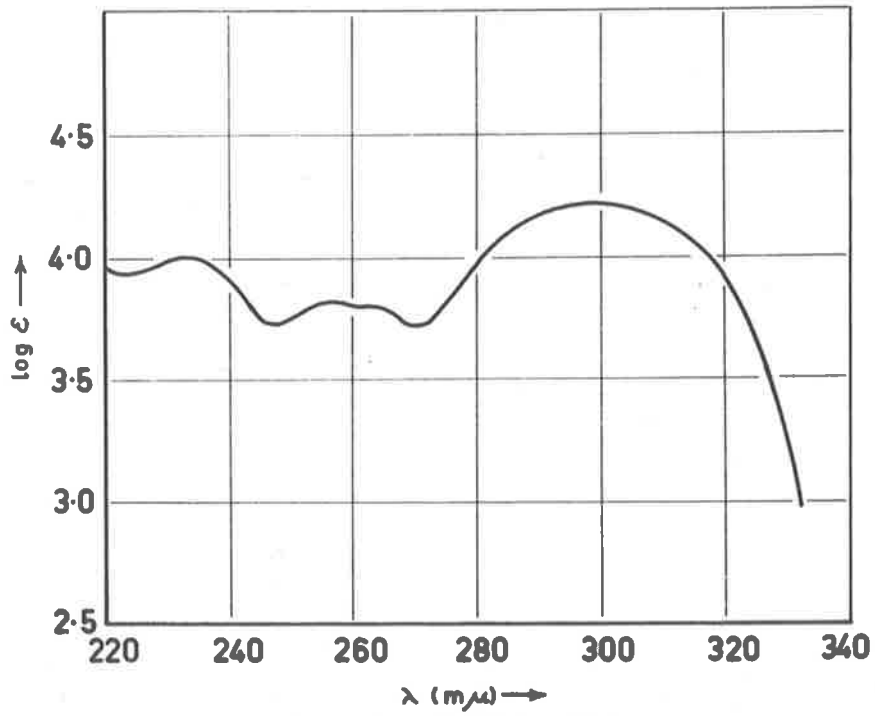


Figure. 5.4. Phenylthienophthen.

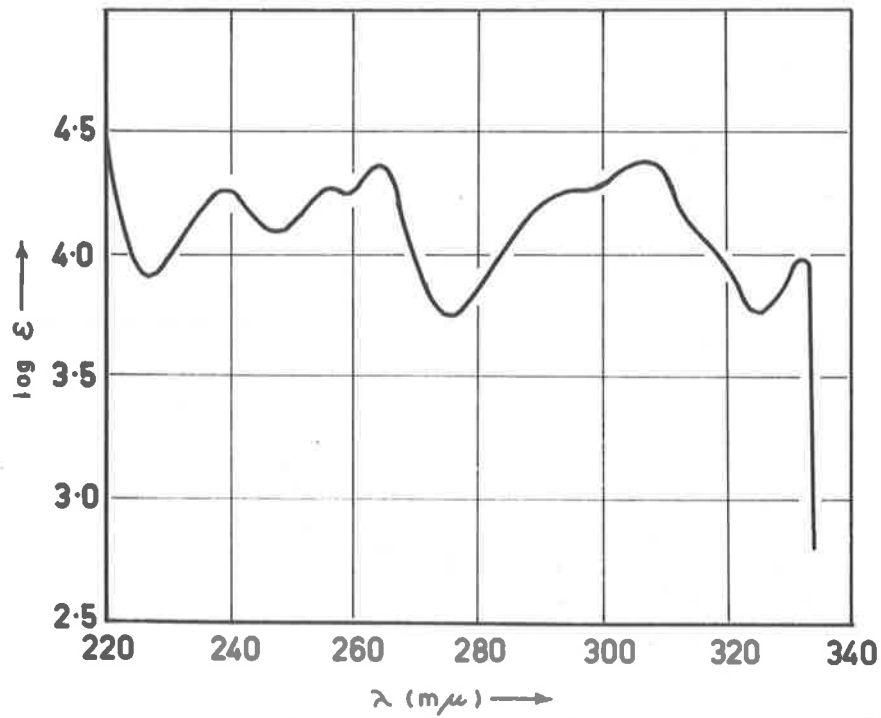


Figure. 5.3. Thienophthen(3,3-β)thienophthen.

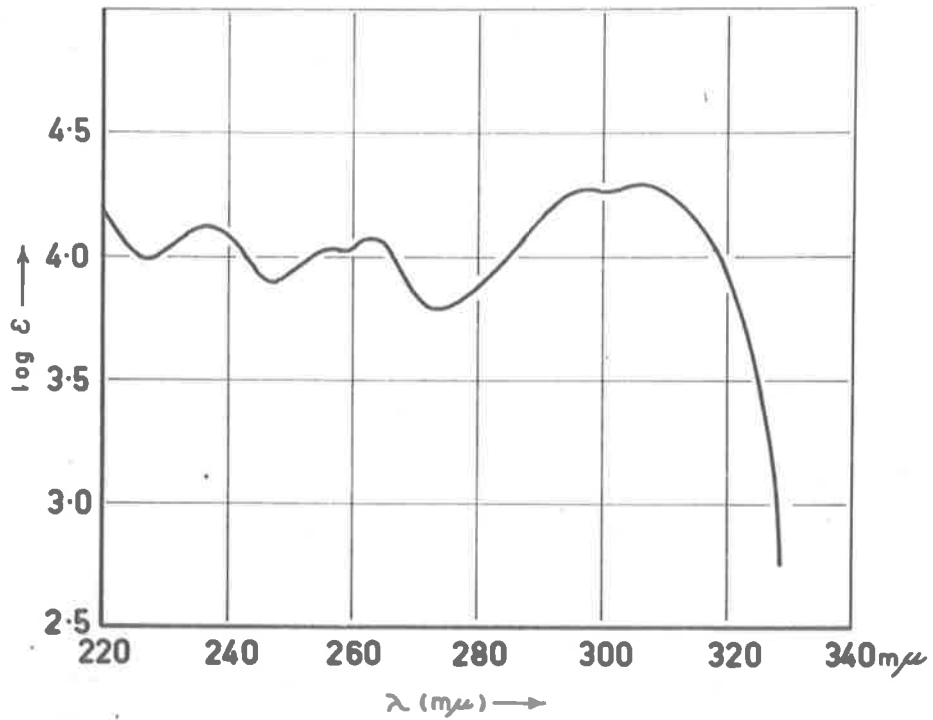


Figure. 5.5. Authentic mixture of thionaphthenothionaphthen and 2-phenylthionaphthen(1:2.5).

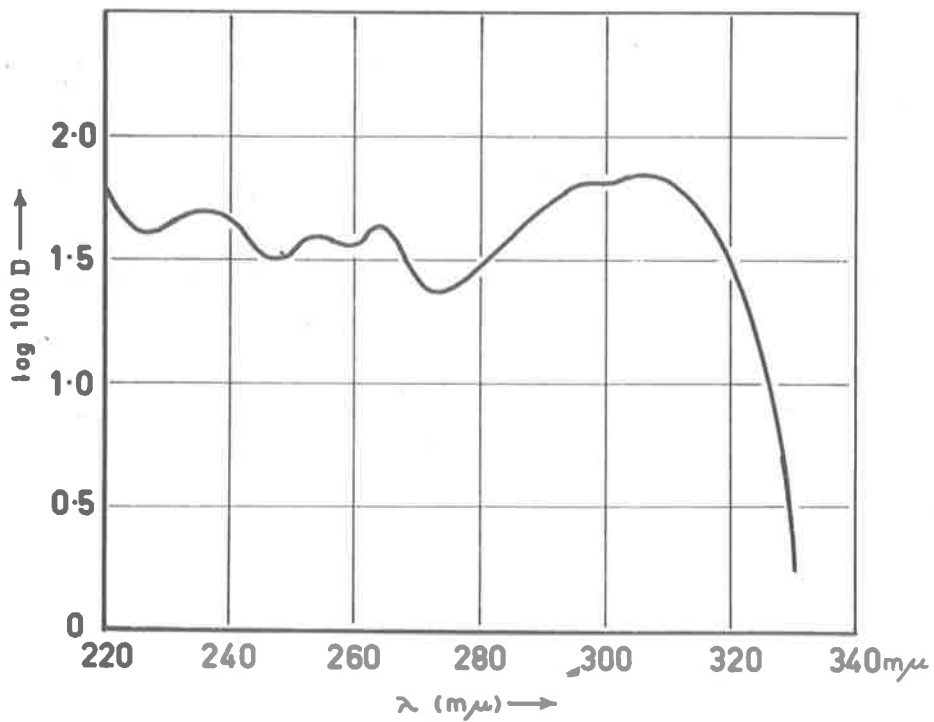


Figure. 5.6. Experimental mixture of thionaphthenothionaphthen and 2-phenylthionaphthen.

TABLE 5.2.

Desulphurisation of Thionaphthene(3,2-b)thionaphthen ("S.M.").

	Cat. Wt. (g.)	Solvent at b.p.	Sol. volume (ml.)	Time (hr.)	Wt. of S.M. (g.)	Recovered S.M.		dibenzyl		stilbene		2-Ph-thionaphthen		Total % accounted for
						Wt. (g.)	%	Wt. (g.)	%	Wt. (g.)	%	Wt. (g.)	%	
W7 Ni	10	EtOH	85	3.5	0.5	-	-	0.236	62.2	-	-	-	-	62.2
W7 Ni	10	MeOH	250	3.5	0.5	-	-	0.239	63	-	-	-	-	63
W7 Ni (3 months)	10	EtOH	85	3.5	0.5	-	-	0.247	65	-	-	-	-	65
W7 Ni (18-19 months)	10	EtOH	85	3.5	0.5	-	-	0.368	94.5	-	-	-	-	94.5
W7-J Ni	10	D.E.P. at 200°	6	2	1.0	-	-	0.258	34	0.131	17.5	0.280	32	83.5
W7 Co	7	EtOH	50	5	0.5	0.306	61.2	-	-	0.031	8	-	-	69.2
W7 Co	11	EtOH	50	5.5	1.0	0.815	8.15	0.075	10	0.03	4	-	-	95.5
W7 Ni/sym. collidine	10	MeOH	100	4.0	1.0	-	-	0.745	98	-	-	-	-	98
W7 Ni/Cu(OAc) ₂	20	EtOH	100	6	1.0	-	-	0.557	73.5	-	-	0.125	14.3	87.8
Ni/Cu(OAc) ₂	10	EtOH	100	1	1.0	0.473	47.3	0.175	23.1	0.009	1.2	0.193	22.1	93.7
Ni/Pb(OAc) ₂	10	EtOH	100	3	1.0	0.482	48.2	0.204	26.9	-	-	0.146	16.7	91.8
"Brown Ni" (repeat of Baker's)	8	EtOH	75	3.5	0.44	-	-	0.304	91	-	-	-	-	91

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solution of hydrated lead acetate (3.8 g.) in water (100 ml.), and the mixture stirred on the steam bath for 20 min., decanted twice with water, twice with ethanol, and used at once. Desulphurisation was effected by refluxing a mixture of thionaphthenthionaphthen (1.0 g.) in ethanol (100 ml.) with the poisoned catalyst for 3 hr. Working up as in (iii) gave unchanged thionaphtheno-(3,2-p)thionaphthen (0.482 g., 48.2%); 2-phenylthionaphthen (0.146 g., 16.7%); and bibenzyl (0.204 g., 26.9%).

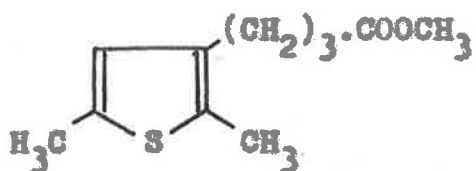
The results of these desulphurisations are summarised in Table 5.2.

APPENDIX TO CHAPTER V

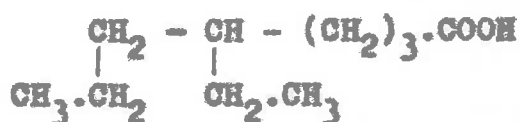
The evidence presented in Chapter V suggests that the desulphurisation of thiophen derivatives probably leads to olefins as primary products, but that these usually undergo subsequent hydrogenation.

It may be argued that the thionaphthenothionaphthen used to illustrate the formation of olefins in desulphurisation represents an exception by virtue of its favourable structure. The same criticism may be applied to the formation of an olefin following the desulphurisation of 3-t-butylthionaphthen.¹⁴³ It therefore became necessary to test the hypothesis on a simple thiophen derivative.

γ -2(,5-dimethyl-3-thienyl)butyric acid methyl ester (I) was desulphurised with a neutral, degassed Raney nickel at 210°. The product, after saponification, was examined by paper chromatography and found to consist of the unchanged thiophen acid and possibly 5-ethyloctanoic acid (II) (or other acids of a similar carbon skeleton). Although 5-ethyloctanoic acid did not react with acid permanganate, both spots gave positive tests for unsaturation, suggesting the presence of unsaturated acid(s) possessing the same carbon skeleton as 5-ethyloctanoic acid.



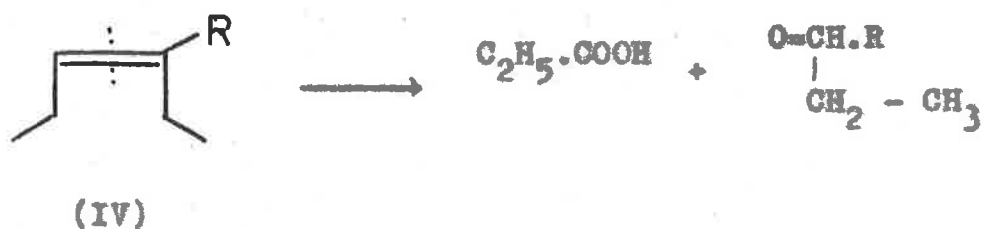
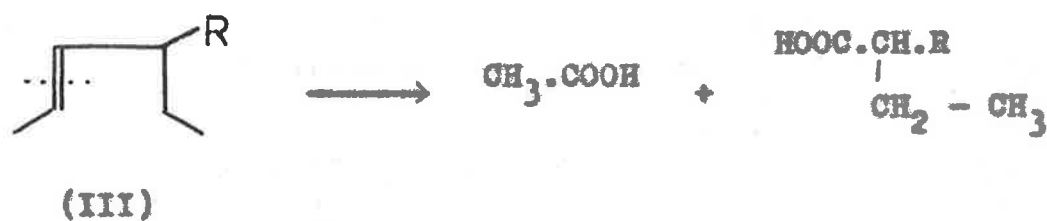
(I)



(II)

The products of desulphurisation were separated from unchanged sulphur compound and hydrogenated. 38 Mole % of hydrogen were taken up, suggesting that the desulphurisation produced 38% of olefinic materials. The hydrogenated product was again chromatographed on paper. Only one spot was found, corresponding to 5-ethyloctanoic acid, and no unsaturated material could be detected.

Oxidation of the products of desulphurisation with periodate - permanganate¹⁴⁶ confirmed the presence of olefins. The material obtained after oxidation was examined by paper chromatography and found to contain the expected 5-ethyloctanoic acid, as well as two keto acids, propionic acid, acetic acid (and possibly a dibasic acid). This result suggests that the three possible mono-olefins (III-V) were probably present in the mixture. It is possible that a small amount of diene was also present.



(Where R is $(\text{CH}_2)_3\text{-COOH}$)

This result is consistent with the view that the desulphurisation of γ -(2,5-dimethyl-3-thienyl)butyric acid methyl ester gives a diene as first step, partial hydrogenation of which produces three different mono-enes, while complete saturation gives 5-ethyloctanoic acid. The results of this desulphurisation also support the general hypothesis that the desulphurisation of thiophen derivatives proceeds via unsaturated intermediates.

In the course of this work it was found that Raney cobalt may be used as a selective adsorbent for sulphur compounds. The cobalt was mixed with clean sand and packed in a column as for chromatography. A mixture containing sulphur compounds was then applied to the column and eluted with methanol. Under these conditions iso-eugenol, geraniol, geranyl acetate and butyl acetate were readily eluted. 2,5-Dimethylthiophen and thiophen-2-ethylcarboxylate were completely retained, but could be recovered by prolonged Soxhlet extraction of the adsorbent. No desulphurisation or hydrogenation took place on the columns. These results may be compared with those of an attempted desulphurisation of di-1-naphthyl sulphide with W7-Raney cobalt in methanol described in Chapter IV.

EXPERIMENTAL

γ -(2,5-Dimethyl-3-thienyl)butyric acid was obtained in four steps according to Badger, Rodda and Sasse.¹⁷ Esterification of this acid with methanol by the Fischer - Speir method gave the methyl ester, b.p. 158-159°/19 mm.

Desulphurisation of γ -(2,5-dimethyl-3-thienyl)butyric acid - methyl ester.-

(i) Preparation of Raney nickel. Nickel-aluminium alloy (32 g.) was added with vigorous stirring to a cooled solution of sodium hydroxide (40 g.) in water (150 ml.) as quickly as frothing permitted, as in the case of W7-J nickel.³⁷ The mixture was then digested on the boiling water bath for 1 hr., washed ten times by decantation with water, and then washed until neutral in a tube, as in the case of W5 Raney nickel.³⁹ The resulting nickel was heated on the water bath for 6 hr., stood overnight, and degassed at 100°/20 mm. as for W7-J Raney nickel.

(ii) Reaction. The thiophen derivative (10 g.) was introduced to wet the freshly degassed catalyst, the pressure released, and the mixture heated in a metal bath at 210° for 1.5 hr. The cooled reaction mixture was extracted continuously with ether for 20 hr., the dried ether evaporated,

and the residue distilled to give three fractions:

(a) oil, b.p. 128-140°/20 mm. (0.822 g.);

(b) oil, b.p. 140-156°/20 mm. (0.764 g.);

(c) oil, b.p. 158°/20 mm. (5.049 g.), identified as starting material.

A drop of fraction (a) was saponified and chromatographed on paper in butanol/ammonia. Spraying with indicator showed two spots at R_f 0.76 and 0.83. The spot at R_f 0.76 corresponded to unchanged thiophen acid (run on the same chromatogram). Both spots decolourised dilute acidic potassium permanganate solution, but the thiophen more rapidly. As saturated aliphatic acids (such as 5-ethyloctanoic acid) did not react under these conditions, some unsaturated C_{10} acid was probably present at R_f 0.83. Both fractions (a) and the starting material decolourised acid permanganate and bromine in carbon bisulphide solution. Fractions (a) and (b) were combined and fractionally distilled in vacuo, collecting only the first fraction. After three distillations no more sulphur could be detected by sodium fusion. This material (ca. 0.3 g.) also gave a positive unsaturation test with acid permanganate and with tetranitromethane. Microhydrogenation of the ester(s) (14.8 mg., assume 0.0805 m.M.) over W7 Raney nickel took up 0.83 ml. of hydrogen at 22.5° and 765.5 mm. (0.0304 m.M.). Hence the mixture contained about 38% of

olefin. The hydrogenated material was recovered, saponified and chromatographed on paper in n-butanol/0.880 ammonia/toluene/water (50/10/50/100; using the upper layer as the mobile phase and the lower layer in the bottom of the tank), and the spots developed with indicator and with potassium permanganate (in separate portions of the same chromatogram). A very small amount of unchanged thiophen acid was found to be present before and after the hydrogenation. This explained the slow rate of hydrogenation (4 hr.) and the positive unsaturation test with tetranitromethane after hydrogenation. The main spots no longer reacted with potassium permanganate, but only with indicator, showing that the olefinic material was removed by hydrogenation.

Periodate - permanganate oxidation.-146

A portion of the partly olefinic product from above was saponified, and about 0.5 m.M. (0.086 g.) of the acids dissolved in water (100 ml.) containing potassium carbonate (0.207 g., 1.5 m.M.). The solution was added at room temperature to a solution (100 ml.) of potassium meta periodate (0.897 g., 3.9 m.M.), 1.0 ml. of a solution of potassium permanganate (0.1 molar.), and the mixture stood at room temperature for 20 hr. Sulphuric acid (10 ml., 10%) was added to stop the reaction, and enough sodium bisulphite solution was added to remove all the iodine. The resulting

clear solution was extracted continuously with ether for 24 hr., the extracts basified with a few drops of concentrated ammonia solution, and distilled to small volume. Some of this solution was spotted on paper and chromatographed in butanol/ammonia. Comparison with reference compounds showed the presence of 5-ethyloctanoic acid, two keto acids (brown spots with methanolic 2,4-dinitrophenylhydrazine hydrochloride, followed by potassium hydroxide solution), propionic and acetic acids, and possibly a dibasic acid. No unsaturation survived the oxidation, as none of the spots reacted with acid permanganate solution. These products indicate that the three possible mono-olefins were probably present in the mixture.

Raney cobalt columns.-

(1) Preparation of Raney cobalt. A solution of sodium hydroxide (80 g.) in water (300 ml.) was surrounded with ice and cobalt - aluminium alloy (65 g.) (Lights, 30% Co) was added with vigorous stirring as quickly as frothing allowed. After digesting the mixture on the water bath at 100° for 1 hr. the supernatant liquid was decanted and the cobalt washed by decantation with water (6 x 100 ml.) and twice with methanol.

(11) Selective adsorption. The cobalt (ca. 7.5 g.) was

mixed with clean sand and packed in a column with methanol as for chromatography (ca. 1.2 cm. x 10 cm.). A mixture of iso-eugenol (0.5 g.) and 2,5-dimethylthiophen (0.5 g.) was applied to the column and eluted with methanol.

(A three-foot head of liquid was required.) Evaporation of the first fraction (30 ml.) gave iso-eugenol (0.477 g.), sulphur-free. Subsequent fractions contained only trace amounts of iso-eugenol, but did not contain sulphur. The sulphur compound could be recovered by Soxhlet extraction of the cobalt with methanol.

(iii) A similar column of Raney cobalt retained thiophen-2-ethylcarboxylate, but allowed butyl acetate, geraniol and geranyl acetate to pass through. Saponification occurred to a very small extent only.

(iv) When similar experiments were conducted with cobalt which had been stored at room temperature under methanol for four days or more the sulphur compounds were eluted together with the other components of the mixture.

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SUMMARY

The desulphurisation of benzothiazoles gave secondary amines when W6 or W7 Raney nickel was used, but the weaker W5 nickel caused little reaction. In the presence of alkali, however, desulphurisation competed with alkaline ring fission, and a mixture of primary and secondary bases was obtained. The desulphurisation, with W6 and W7 nickel, of simple thiazoles was more complex. C₂ - N fission occurred and no secondary amines were obtained. Several competing reactions are thought to operate.

Raney cobalt has been used to desulphurise a number of thiophen carboxylic acids, acyl thiophens, thiazoles and thioamides. It was found that Raney cobalt generally gave the same products as nickel, but that it had a lesser activity; however, some differences between the two metals have been noted.

A direct comparison has been obtained between the desulphurising abilities of certain transition metals towards di-1-naphthyl sulphide and dihexyl sulphide. Although the untreated metals were inactive towards di-1-naphthyl sulphide at 200°, the Raney metals showed considerable activity in the order Ni > Co > Fe > Cu > W. Increase in the temperature and the presence of hydrogen were found to facilitate desulphurisation.

The desulphurisation of thionaphthene(3,2-b)thionaphthen under various conditions gave bibenzyl, trans-stilbene, and 2-phenylthionaphthen. The reported formation of 1,2,3,4-tetraphenylcyclobutane could not be confirmed. These results have been used to discuss the general mechanism of desulphurisation of thiophen derivatives. It is suggested that chemisorption of thiophens occurs via the sulphur atom and that desulphurisation proceeds via unsaturated intermediates. Accordingly, desulphurisation of methyl γ -(2,5-dimethyl-3-thienyl)butyrate with degassed nickel gave olefins.

The use of Raney cobalt as a selective adsorbent for sulphur compounds has been described.

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