

A STUDY OF THE CONDENSATION OF
THIOISOPHTHALALDEHYDE

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THIOISOPHTHALALDEHYDE

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CHAPTER I

INTRODUC TION

A STUDY OF THE CONDENSATION OF
THIOISOPHTHALALDEHYDE

CHAPTER I

INTRODUCTION

Thioaldehydes and thioketones have been used effectively as starting materials in the synthesis of substituted stilbenes¹ and similar ethylenic compounds. The method involves the condensation of two thiocarbonyl groups with the removal of the sulfur atoms. Copper powder has been used as the condensing agent, but in some instances when copper failed, Raney nickel was used successfully.

At the present time, only monothio compounds have been successfully condensed in this manner. The treatment of a dithio compound could give two different products: a linear polymer, or under suitable conditions, a cyclic hydrocarbon. The latter could prove to be a more direct method for the preparation of certain polynuclear hydrocarbons. An attempt has been made to synthesize coronene by this method.² The 2,7-dithioaldehyde of naphthalene was heated with copper powder but failed to give the desired product.

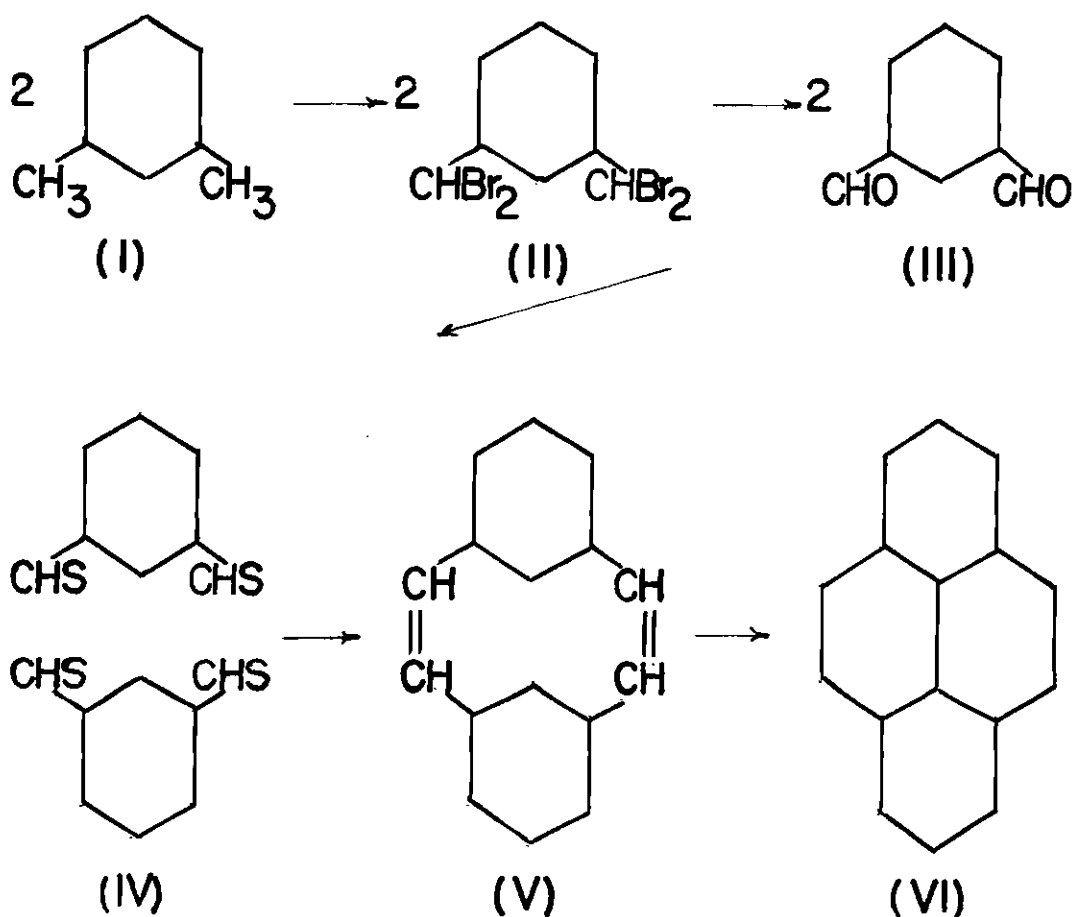
This present work was undertaken in order to study the condensation of thioisophthalaldehyde, a simpler dithio compound than the one previously

¹Wood, Bacon, and Meibohm, et. al., J. Am. Chem. Soc., 63, 1334 (1941).

²Wood and Stanfield, J. Am. Chem. Soc., 64, 2343 (1942).

studied. It was proposed to study the condensation in an effort to produce the cyclic hydrocarbon (V) which could then be dehydrogenated to yield the polynuclear hydrocarbon, pyrene (VI).

The reactions proposed are as follows:



Dithioisophthalaldehyde (IV) has not been previously reported in the literature. It was proposed to prepare it by conversion of the corresponding oxyaldehyde (III). This can be prepared from m-xylene (I) via the tetrabromo derivative (II). The conversion of a dialdehyde into

a dithioaldehyde has been reported by Wood and Stanfield.³ It was assumed, however, that both aldehyde groups had been converted and no analysis was made. In this present work it was planned to prepare both the monothioisophthalaldehyde and dithioisophthalaldehyde and to prove their structures by analysis.

The tetrabromo compound has been prepared by direct bromination of m-xylene.⁴ The literature reference, however, does not describe the procedure in any detail and, hence, it was desirable to study the preparation in order to arrive at the optimum conditions for carrying out the reaction. A similar reaction is described in Organic Syntheses⁵ for the preparation of the tetrabromo derivative of p-xylene. Hydrolysis of the *W,W,W',W'* tetrabromo m-xylene gives isophthalaldehyde.

This investigation, therefore, has the following purposes:

1. To study the preparation of *W,W,W',W'* tetrabromo m-xylene by direct bromination of m-xylene in order to arrive at the optimum conditions for carrying out this reaction.
2. To prepare monothioisophthalaldehyde and dithioisophthalaldehyde and to prove their structures by analysis.
3. To study the condensation of dithioisophthalaldehyde in order to produce a cyclic hydrocarbon which can be dehydrogenated to pyrene.

³Ibid.

⁴Thiele and Gunther, Ann., 347, 109 (1906).

⁵Allen, Organic Syntheses, Vol. 20, (New York: John Wiley and Sons, Inc., 1940), p. 92.

CHAPTER II

HISTORICAL

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HISTORICAL

A. *w,w,w,w'* tetrabromo m-Xylene

This compound has been prepared by Thiele and Gunther¹ by refluxing m-xylene with bromine over a period of three hours. A 75% yield of long colorless needles was reported.

A similar procedure is described in much greater detail in Organic Syntheses² for the preparation of *w,w,w,w'* tetrabromo p-xylene. p-Xylene is refluxed in an oil bath maintained between 140° C. and 160° C. The reaction mixture is continually stirred while bromine is added dropwise over a period of from 8 to 10 hours. A tungsten lamp is used as a source of ultraviolet light. Yields ranging from 51 to 55% have been reported.

B. Isophthalaldehyde

The hydrolysis of *w,w,w,w'* tetrabromo m-xylene yields isophthalaldehyde. This has been carried out by Thiele and Gunther.³ Mild hydrolysis by potassium oxalate in 50% ethanol for 30 to 36 hours gave a 95% yield of the aldehyde melting at 89.5° C. The hydrolysis was also carried out by concentrated sulfuric acid in a much shorter time but the yield was somewhat lower, being 70%.

¹Thiele and Gunther, Ann., 347, 109 (1906).

²Allen, Organic Syntheses, Vol. 20, (New York: John Wiley and Sons, Inc., 1940), p. 92.

³Thiele and Gunther, loc. cit.

Isophthalaldehyde has been prepared by several other methods, but these usually involve difficultly available starting materials or give low yields. The oxidation of m-xylene by chromic acid in acetic acid followed by hydrolysis of the resulting tetraacetate is reported by Thiele and Winter.⁴ Yields range from 40 to 50%. Rosenmund⁵ has carried out the reduction of isophthalyl chloride to the aldehyde with an 83% yield. A more recent preparation⁶ makes use of the Reimer-Tiemann reaction, benzaldehyde being treated with chloroform and potassium hydroxide and the resulting 3-oxobenzilidene chloride hydrolyzed. Isophthalaldehyde can also be prepared by hydrolysis of the tetrachloro xylene.^{7,8}

C. Thioisophthalaldehyde

This compound has not been previously prepared. There are several methods known for preparing thioaldehydes. The simplest, and hence the one most often used, consists of conversion of the corresponding oxyaldehyde. The aldehyde is dissolved in a suitable solvent and dry hydrogen chloride and hydrogen sulfide is passed in. The solution is kept at 0° C. Precipitation of the thioaldehyde usually results in from 10 to 30 minutes. This may be in the form of a linear polymer, in which case it is usually insoluble in the common solvents, or it may come down as a trimer with a definite melting point. Ethanol, methanol, ethyl acetate-

⁴Thiele and Winter, Ann., 311, 359 (1900).

⁵Rosenmund, Ber., 54B, 2888 (1921).

⁶Chaudhuri, J. Am. Chem. Soc., 64, 316 (1942).

⁷Colson and Gautier, Bull. Soc. Chim., 45, 509 (1886).

⁸Meyer, Ber., 20, 2005 (1887).

benzene, as well as pure benzene have been used as reaction solvents.

Thioaldehydes have been known for many years. Such compounds as trithiobenzaldehyde, trithiosalicylaldehyde, and trithiomethyl vanillin, to name but a few, have been made from the corresponding oxyaldehyde. Recently several new thioaldehydes have been prepared by Wood and Bost⁹ in a study of the properties of sulfur compounds.

D. Condensation of Thioaldehydes

When a thioaldehyde is heated to pyrolysis either alone or with some sulfur-liking metal, a type of condensation reaction occurs. This consists of a removal of the sulfur atoms from the thioaldehyde and the subsequent joining up of two molecules to form an ethylenic linkage. The reaction was first reported by H. Klinger¹⁰ who noticed a considerable amount of stilbene in the decomposition products resulting from the distillation of trithiobenzaldehyde. He then heated the thioaldehyde with finely divided copper powder and produced stilbene in large amounts. Since then, other thioaldehydes and also some thioketones have been successfully condensed in this manner. Wood and co-workers¹¹ have made use of this reaction in preparing several substituted stilbenes as well as their analogues in the naphthalene, anthracene, and phenanthrene series.

The condensations were carried out by grinding the thioaldehyde to a fine powder and then mixing it intimately with 3 to 4 times the theo-

⁹Wood and Bost, J. Am. Chem. Soc., 59, 1721 (1937).

¹⁰Klinger, Ber., 9, 1893 (1876).

¹¹Wood, Bacon, Meibohn, et al., J. Am. Chem. Soc., 63, 1334 (1941).

retical amount of freshly reduced copper powder. The mixture was then heated for 30 to 60 minutes in a small flask by means of an oil bath. The temperature used was that at which pyrolysis of the thioaldehyde began. The ethylene compound was then extracted from the reaction mixture by boiling benzene.

In some cases the condensations have been carried out successfully using Raney nickel instead of copper powder. Thiocetophenone¹² has been condensed by Raney nickel while copper powder fails. Bergman¹³ reports the condensation of 9-phenanthrene thioaldehyde by Raney nickel with a 20% yield. Because of the pyrophoric nature of Raney nickel the reactions were carried out in a solvent which boiled at or near the pyrolysis temperature of the thioaldehyde.

E. Diphenylene Diethene

When thioisophthalaldehyde is condensed so that the two aldehyde groups of one molecule react with the two aldehyde groups of another molecule a new cyclic hydrocarbon is formed. Pellegrin¹⁴ has reported a compound which he believed to be this hydrocarbon. He proposed the name diphenylene diethene.

While making a study of the Fittig reaction, Pellegrin treated a quantity of dibromo m-xylene and bromobenzene with sodium. Upon separation of the products by vacuum distillation he obtained a small quantity

¹²Cline, Campaigne, and Spies, J. Am. Chem. Soc., 66, 1136 (1944).

¹³Bergmann and Israelashwili, J. Am. Chem. Soc., 67, 1951 (1945).

¹⁴Pellegrin, Rec. Trav. Chim., 18, 452 (1889).

of a yellow viscous liquid boiling at 258° C. at 15 mm. This was recrystallized from an alcohol-ether mixture and gave colorless needles melting at 191° C. The compound analyzed for $C_{16}H_{12}$ and was found to add four bromine atoms.

F. Pyrene

This hydrocarbon has been known for several years. It occurs in nature in carbonaceous materials such as tar, coal, and heavy hydrocarbon oils. Pyrene is obtained commercially from such materials in sufficient quantities to meet any demand for its use. The process consists of the destructive hydrogenation of bituminous coal and coal tars followed by extraction of the pyrene from the mixture of hydrocarbons that are produced. Many syntheses of pyrene have been devised but in all cases either the yields have been too small or the starting materials have not been readily available. There is no suitable synthesis starting from a simpler ring system.

Pyrene, because of its reactivity, is being considered as a possible starting material in the synthesis of higher polycyclic hydrocarbons. It is difficult, however, to prove the location of substituents in pyrene derivatives. Degradation does not serve to establish the position of the substituent in that the 1,4,5,8,-tetra carboxylic acid of naphthalene is formed. On the other hand suitable synthesis methods are not, at present, available.

In this present work a synthesis of pyrene starting from a dithioaldehyde of benzene is proposed. In a like manner a substituted thioisophthalaldehyde may be used to prepare a substituted pyrene compound.

This would then serve as a proof of the structure of the pyrene derivative by synthesis.

CHAPTER III

EXPERIMENTAL

CHAPTER III

EXPERIMENTAL

A. Preparation of w,w,w',w' tetrabromo m-Xylene

The procedure given in Organic Syntheses¹ for the preparation of w,w,w',w' -tetrabromo p-xylene was followed but with some modifications. Bromine (220 ml.), previously dried by shaking with concentrated sulfuric acid, was added dropwise to 100 g. of m-xylene. The reaction vessel was a one liter three-necked flask fitted with a mechanical stirrer, a 500 ml. dropping funnel and a reflux condenser. Glass helices were packed into the condenser in order to minimize losses of bromine and xylene by entrainment in the hydrogen bromide given off in the reaction. A 300-watt unfrosted tungsten lamp was used as a source of ultra violet radiation. The flask was heated in an oil bath.

The reaction was started with the temperature between 125 and 130°

C. Bromine was added gradually at such a rate that there was never any large amount of unreacted bromine in the flask. After one hour about half the bromine had been added and during this period the temperature was slowly raised to 150° C. This temperature was maintained for another six hours until all the bromine had been added after which stirring and heating was continued for an additional hour.

Upon cooling the reaction mixture solidified into a brown mass which was recrystallized from 95% ethanol. A second recrystallization from the same solvent gave pale brown needles melting at 107° C. (uncorr.).

¹Allen, Organic Syntheses, Vol. 20, (New York: John Wiley and Sons, Inc., 1940), p. 92.

Total yield was 211 g. or 53%.

Several attempts were made to increase the yield. It was found that starting the bromination at the boiling point of xylene, as suggested by Organic Syntheses², caused appreciable losses of xylene by entrainment in the hydrogen bromide. Too large an excess of bromine also caused a lowering of the yield as well as making the recrystallization difficult. Continuation of the stirring and heating for another hour after the bromination had been completed gave a product of higher purity.

B. Preparation of Isophthalaldehyde

The procedure followed was that given for the preparation of terphthalaldehyde in Organic Syntheses.³ The *m,m',m''* tetrabromo m-xylene was hydrolyzed by concentrated sulfuric acid to yield isophthalaldehyde. A two liter distilling flask with a capillary ebullition tube and a receiver was arranged as for a vacuum distillation. Finely powdered *m,m',m''* tetrabromo m-xylene (84 g.) and 200 ml. of 95% sulfuric acid was introduced into the flask. A vacuum was applied by means of a water aspirator and a stream of air was allowed to pass through the capillary tube to facilitate the removal of the hydrogen bromide. The flask was heated on an oil bath to 70° C. and when the evolution of the gas became less vigorous the temperature was slowly raised to 110° C. The entire reaction time was about two and one-half hours.

When the reaction was complete, as shown by a clear solution and lack of hydrogen bromide being given off, the flask was allowed to cool

²Ibid., p. 92.

³Ibid., p. 93.

and the contents poured on 600 g. of crushed ice. A brown solid precipitated which after filtering off was recrystallized from 10% methanol. The color was removed by the addition of a small amount of Norite. The yield was 17 g. or 70% of white needles melting at 87° C. (uncorr.).

The hydrolysis of larger amounts of tetrabromo compound was less satisfactory, as indicated by inferior yields. It was possible to recover some of the unreacted tetrabromo compound.

C. Preparation and Properties of Monothioisophthalaldehyde and Dithioisophthalaldehyde

The thio compounds were prepared by treating a solution of isophthalaldehyde with dry hydrogen chloride and dry hydrogen sulfide. The hydrogen chloride generator consisted of the outer jacket of a Victor Meyer vapor density apparatus which was fitted with a three hole rubber stopper containing a side arm, a dropping funnel and a tube to equalize the pressure between the funnel and the inside of the generator. Concentrated hydrochloric acid was added through the dropping funnel into the generator which contained concentrated sulfuric acid. This gave dry hydrogen chloride at a rate easily controlled by the rate of addition of the hydrochloric acid. An ordinary Kipp Generator was used to produce the hydrogen sulfide which was then passed through a calcium chloride tube to remove any moisture.

The reaction tube consisted of a large test tube, 24 cm. x 4 cm., fitted with a mechanical stirrer and two small gas-inlet tubes. In order to allow the gases to pass through as large a portion of the reaction mixture as possible, the inlet tubes were extended to within 4 cm. of the

bottom of the test tube. Before entering the reaction vessel each gas was passed through a large trap and then through a bubble counter containing the liquid used as the reaction solvent.

Monothioisophthalaldehyde

Isophthalaldehyde (5 g.) was dissolved in 120 ml.'s of ethyl acetate and placed in the reaction vessel. Hydrogen chloride was passed through the solution for one hour. The Kipp Generator was then started and the hydrogen sulfide and hydrogen chloride was bubbled through the solution together. The temperature during the reaction was maintained at 0° C. The low temperature aided the reaction as larger amounts of the gases could be dissolved in the solvent.

As soon as the hydrogen began bubbling through, the solution took on a blue-grey color which became more intense as the reaction proceeded. After 10 to 15 minutes a white solid began to precipitate from the solution. The reaction was continued for another 45 minutes after which the precipitate was filtered off and washed with boiling ethanol to remove any occluded isophthalaldehyde and then with carbon disulfide to remove any precipitated sulfur. The product was dried for six hours in a drying pistol at 56° C. and under a vacuum from a water aspirator. The yield of crude material was three grams or 50%.

The product, a fine white powder, did not melt but decomposed gradually over a range from 220° C. to 250° C. It was insoluble in all of the common solvents and hence could not be purified by recrystallization. When heated with concentrated sulfuric acid a deep red color resulted. An analysis was made with the following results: Calculated

for C_6H_6OS : sulfur, 21.4%; hydrogen, 4.00%; carbon, 64.0%. Found: sulfur, 21.7%; hydrogen, 4.62%; carbon, 61.0%. A discussion of these analyses will be found in Chapter IV.

Dithioisophthalaldehyde

The procedure was exactly the same as for the monothioaldehyde except for the reaction time. Isophthalaldehyde (5 g.) was dissolved in 120 ml. of ethyl acetate and treated as before. The reaction was continued for a period of 15 hours in order to complete the conversion of both aldehyde groups. The precipitate was filtered off, washed with boiling ethanol and carbon disulfide, then dried in a drying pistol at $56^{\circ}C$. under vacuum. The yield of crude material was 5.1 g. or 82%.

The product was a fluffy white powder. It was much lighter than the monothioaldehyde in that an equal weight occupied about three times the space of the monothio compound. It decomposed gradually from $240^{\circ}C$. to $270^{\circ}C$. and did not dissolve in any of the common solvents. Upon heating with concentrated sulfuric acid it gave the same deep red color as did the monothioisophthalaldehyde. An analysis was made with the following results: Calculated for $C_6H_6S_2$: sulfur, 38.6%; hydrogen, 3.61%; carbon, 57.8%. Found: sulfur, 37.8%; hydrogen, 4.17%; carbon, 54.2%. A discussion of these analyses will be found in Chapter IV.

Attempts were made to improve the purity of the product as well as to increase the yields. Several runs were made at various reaction times and led to mixtures of monothio and dithioaldehydes. The effect of the reaction time on the per cent sulfur and on the yield of product is shown below:

1 hour	21.7%	2.98 g.
6 hours	32.3%	4.53 g.
12 hours	37.7%	5.06 g.
15 hours	37.8%	5.10 g.

Ethyl acetate was found to be a suitable solvent. A solution in benzene was treated for 15 hours and yielded a product containing only 31.5% sulfur. Ethanol solutions led to a less pure product due to the precipitate coagulating and forming hard lumps. As this did not occur in benzene or in ethyl acetate, it was thought to be due to the presence of water in the ethanol.

D. Attempted Condensation of Dithioisophthalaldehyde

The condensation of a thioaldehyde by heating with copper powder has been described in Chapter II. The copper powder was prepared by the displacement of the copper in a solution of copper sulfate with metallic zinc. Zinc dust was slowly added to a known solution of copper sulfate until the amount theoretically needed to replace all the copper had been added. During this addition the solution was stirred continuously. The precipitated copper was removed by suction filtration and washed with dilute hydrochloric acid to remove any unreacted zinc, then with distilled water to remove the acid and finally with several portions of methanol. It was then dried in a drying pistol at 56° C. The copper powder was always prepared immediately before using.

Trial 1

Dithioisophthalaldehyde (4 g.) and finely divided copper powder (20 g.) were mixed intimately in an agate mortar. The mixture was placed

in a 125 ml. pyrex flask fitted with a reflux condenser. A sand bath was used at an approximate temperature of 250° C. for a period of two hours. After the heating was completed the flask was removed from the sand bath and allowed to cool.

The black mass was extracted with several portions of boiling benzene. The benzene extract had a pale green color with a slight blue fluorescence. No precipitate resulted when the benzene was evaporated down to 25 ml. and cooled. The remaining benzene was then evaporated leaving a very small amount of a greenish-brown, oily residue. This was extracted with a little ethanol and formed an oily brown material, which upon filtration remained as an oily paste on the filter paper. Attempts to improve the material by recrystallizing from various solvents were not successful.

The trial was repeated several times with smaller quantities of the thioaldehyde. Temperatures tried were 210° C., 225° C., 270° C., and 300° C. Heating periods were varied from one to four hours. In all cases the same greenish-brown oil resulted on evaporating the benzene. The amounts of this residue did not change noticeably in the various runs.

The material was tested by sodium fusion and sulfur was shown to be present. The absence of any olefinic linkages was indicated when the material did not react with a solution of bromine in carbon tetrachloride.

Trial 2

It was then decided to dilute the reaction mixture with a large volume of fine sand. The basis for this will be discussed in Chapter IV. Dithioisophthalaldehyde (4 g.) and copper powder (20 g.) were mixed intimately as before, added to three times its volume of fine sand, and

again mixed. The mixture was heated for two hours at 270° C. in the same manner as described in trial 1. Upon extraction with benzene and subsequent evaporation the usual small amount of a greenish-brown oil resulted.

Trial 3

As satisfactory results were not obtained on heating with copper powder it was decided to try Raney nickel as the condensing agent. The Raney nickel was prepared from nickel aluminum alloy by the method suggested by Adkins.⁴ The time of washing was considerably diminished by simply shaking the nickel with portions of water until the washings no longer tested basic to litmus.

Because of the pyrophoric nature of the Raney nickel, the reaction could not be carried out in the dry state as was the case in the copper trials. A liquid reaction medium was decided upon. It was necessary, of course, for the reaction medium to be inert towards Raney nickel and the thioaldehyde as well as to have a boiling point above the temperature at which the trial was to be run.

Dithioisophthalaldehyde (2 g.) and Raney nickel (20 g.) were added to 50 ml. of chloronaphthalene in a 200 ml. three-necked flask fitted with a reflux condenser and a mechanical stirrer. The flask was heated by means of an oil bath to 250° C. and held at this temperature for a period of 45 minutes. The reaction mixture was cooled and filtered. The residue was extracted with 50 ml. of boiling chloronaphthalene. This was added to the filtrate which was a dark red. The chloronaphthalene

⁴Adkins and Palvic, J. Am. Chem. Soc., 68, 1471 (1946).

was removed by vacuum distillation leaving a viscous red oil. Attempts to cause this oil to become a solid were unsuccessful.

In order to ascertain if the chloronaphthalene entered into a reaction with the Raney nickel, the trial was repeated without the thioaldehyde. When the chloronaphthalene was vacuum distilled a viscous red oil remained in the distilling flask. This apparently resulted from interaction between the chloronaphthalene and the nickel.

Trial 4

In view of the results of the previous trial it was found necessary to pick a different medium for the reaction. Benzyl ether was found to be suitable. The thioaldehyde (2 g.), Raney nickel (20 g.), and 50 ml. of benzyl ether were heated as in trial 3. The temperature was held at 250° C. for one hour. A small quantity of water apparently remained in the nickel and this caused much splattering and bumping during the trial. After the heating period was over the contents were cooled and filtered and the residue extracted with several portions of boiling benzene. The benzene extract was added to the filtrate which was a dark red. Upon vacuum distillation of the benzene and benzyl ether a viscous red oil remained. Attempts to cause this oil to crystallize were unsuccessful.

It was decided to try to purify this oil by chromatographic adsorption. A glass column, 30 cm. X 3 cm., was packed to a depth of 25 cm. with activated alumina. The oil was dissolved in 50 ml. of petroleum ether and this solution was poured into the column and allowed to pass through by gravity flow. The color was adsorbed at the top of the column and the liquid leaving the bottom was clear. About two liters of a ten per cent solution of benzene in petroleum ether were then poured

through the column. A number of colored bands appeared. They were mainly green and brown. The green bands were slowly eluted down the column while the brown bands remained in the upper portion. The aluminum oxide was then carefully removed from the glass column and each colored band was separately extracted with boiling benzene. The benzene was evaporated from each extract but the residues consisted only of oils and no solid material resulted.

Only the first three bands yielded sufficient material to warrant further study. They were numbered one, two, and three, counting down from the top of the column. The majority of the material was in band one. This was dissolved in a little hot ethanol and cooled. A small amount (0.01 g.) of a reddish brown solid resulted. This decomposed over a range from 115° C. to 130° C. A sodium fusion test showed the presence of sulfur and the absence of any olefinic linkages was indicated by no reaction with bromine in carbon tetrachloride.

Bands two and three were taken up in hot ethanol, but attempts to cause the oily residues to solidify did not succeed. The residues were analyzed as before. No sulfur was found in either and no olefinic linkages were indicated.

Trial 5

This was a repeat of the previous trial with the exception that 4 g. of the thiocompound was used. Care was taken to omit any possibility of water entering the reaction vessel. The benzyl ether was carefully redistilled. Any liquid remaining on the Raney nickel was removed by washing with benzyl ether. The flask was heated as in the previous trial to around 260° C. and the temperature was maintained for two hours. The

contents were cooled and extracted as before. This time, however, the filtrate had a pale green color as in trials 1 and 2 with copper powder. Both benzene and benzyl ether were removed by vacuum distillation leaving a small quantity of a brown oil. Upon the addition of a little ethanol an oily brown material resulted which resembled the product obtained in the previous trials with copper powder.

The nature of the material was not improved by treatment with ethanol and when it was removed from the solvent it was plastic and sticky and seemed to sink into the filter paper. The material was found to contain sulfur when tested by sodium fusion. It did not react with a solution of bromine in carbon tetrachloride indicating the absence of any olefinic linkages.

The trial was repeated twice with the same results. Lowering the temperature to 220° C. had no noticeable effect and neither did adding the thioaldehyde gradually during the first hour of the reaction.

Trial 6

It was of interest to investigate the behavior of the thioaldehyde when heated under the same conditions as in the previous trial but without any Raney nickel. A mixture of 2 g. of the thioaldehyde and 75 ml. of benzyl ether were heated in a 200 ml. flask fitted with a reflux condenser. The temperature was held at approximately 260° C. for two hours. After five minutes of heating the mixture began turning pink, then red and finally a dark red. Most of the thioaldehyde seemed to have gone into the benzyl ether. A small amount of a red solid remained. This was filtered off and dried. It was insoluble in benzene and ethanol and decomposed over a range from 250° C. to 270° C.

The benzyl ether was vacuum distilled and about 2 ml. of a viscous dark red oil remained in the distilling flask. This oil still had the characteristic odor of the thioaldehyde. It was found to be very soluble in benzene and gave a definite test for sulfur.

CHAPTER IV

DISCUSSION OF RESULTS

CHAPTER IV

DISCUSSION OF RESULTS

The preparation of *N,N,N',N'* tetrabromo *m*-xylene by direct bromination of *m*-xylene was carried out with a yield of 53% of the desired product. Thiele and Gunther¹ have carried out this bromination and report a yield of 70% of the tetrabromo compound. In a similar preparation given in Organic Syntheses² a yield of 55% was obtained. This is in agreement with the present yield of 53%.

The low yield may be attributed mainly to pyrolysis and polymerization reactions that occur to some extent in any vigorous reaction such as bromination, especially at high temperatures. This is represented by the viscous black material which remains when the tetrabromo compound is separated from the products of bromination.

The formation of penta- and hexabromo compounds should also be considered. The bromination of methyl groups on an aromatic nucleus proceeds in a stepwise manner. With one bromine atom the methyl group becomes more reactive towards further bromination and with two bromine atoms the reactivity is still greater. Thus the tetrabromo compound is more easily brominated than is the *m*-xylene. Any local concentration of bromine that might form during the bromination may lead to the formation of some penta or hexabromo compounds. By adding the bromine slowly and never allowing any large excess of bromine in the reaction vessel, losses

¹Thiele and Gunther, Ann., 347, 109 (1906).

²Allen, Organic Syntheses, Vol. 20, (New York: John Wiley and Sons, Inc., 1940), p. 92.

of this kind may be kept at a minimum. This explains the low yield of a product which was difficult to crystallize when too large an excess of bromine was used.

The bromination of *m*-xylene is a photochemical reaction in that it is initiated by ultraviolet light. In this present work a 300-watt, unfrosted, tungsten lamp was used as a source of ultraviolet light. The intensity of these rays, however, was diminished almost 90% in passing through the pyrex-glass walls of the reaction vessel. Further study on the effect of using a quartz-windowed reaction vessel as well as a more powerful source of ultraviolet light is suggested.

The hydrolysis of the tetrabromo compound was carried out rapidly and smoothly using concentrated sulfuric acid. A yield of 70% was obtained. A similar hydrolysis given in Organic Syntheses³ reports a yield of 80%.

The treatment of the isophthalaldehyde with hydrogen sulfide and hydrogen chloride yielded two new thioaldehydes, monothioisophthalaldehyde and dithioisophthalaldehyde. These compounds are fine white powders which have no melting points but decompose gradually over a range of about thirty degrees. They were found to be insoluble in all of the common solvents. Thiocompounds do not normally exist as single molecules but form either trimers or polymers. The trimers are usually crystalline solids with definite melting points while the polymers are amorphous materials with no definite melting points and are often found to be insoluble. The properties of these new thioaldehydes strongly suggest

³Ibid., p. 93.

that they are polymeric.

The two thiocompounds were obtained in an impure state. Usual methods of purification were not possible due to their insolubility. The extent of the impurities can easily be seen from the analyses that were made. In the case of the monothioisophthalaldehyde the per cent sulfur was 21.7% or three tenths of a per cent higher than the calculated value. This would infer that some dithioaldehyde was present as an impurity. The per cent sulfur in the dithioisophthalaldehyde was 37.8% or eight tenths of a per cent lower than the calculated value. This, in turn, may be explained by the presence of some monothioaldehyde as an impurity. In both compounds the per cent carbon is approximately 2.8% lower than the calculated value, indicating some non-carbon containing impurities which were probably occluded as the polymers were being formed. These impurities were not removed by washing with 95% ethanol and carbon disulfide.

During the course of the investigation it was found that a reaction period of one hour gave a product which analyzed for monothioisophthalaldehyde. A much longer time was needed to produce the dithioaldehyde. The conversion of the isophthalaldehyde proceeded in two definite steps as may have been expected. The second step, that of converting the monothioaldehyde to the dithioaldehyde, takes place more slowly and the monothioaldehyde may be isolated by stopping the reaction at the proper time. The yield, however, is only 60%. By increasing the reaction time a higher yield may be obtained but some dithioaldehyde is also formed and this contaminates the product.

The monothioisophthalaldehyde is only very slightly soluble in the

reaction medium. As the reaction occurs in solution, the amount of monothio available for conversion to dithio at any one time is very small. This would explain the long reaction time needed to produce the dithioaldehyde.

The condensation of thioaldehydes have been brought about by heating the materials at their pyrolysis temperatures in the presence of finely divided copper powder or in some cases Raney nickel. It was assumed that the pyrolysis temperature was in the vicinity of 250° C., since the thioaldehyde decomposed near this value.

Because of the presence of two reactive groups on a single molecule, the condensation of dithioisophthalaldehyde could possibly lead to the formation of a linear polymer. On the other hand, if the two groups of one molecule were condensed with two groups on another molecule a simple cyclic hydrocarbon would be formed. This latter condensation product is the desirable one as it could then be dehydrogenated to yield pyrene. In order to decrease the rate of formation of the linear polymer and to enhance the possibility of condensation taking place between two molecules, the reaction was carried out using low concentrations of the thio compound. This was in accordance with the dilution principle which has been used successfully in various organic syntheses to permit the formation of large cyclic compounds when a linear polymer may also be formed.

Heating the dithioisophthalaldehyde with a large excess of copper powder yielded a small amount of a brown oil. This material still contained sulfur and was not unsaturated indicating that it had not resulted from any condensation of the thiocompound. The addition of a large amount of fine sand to further increase the dilution gave the same result

as before.

On heating the dithioaldehyde with Raney nickel in a medium of chloronaphthalene a small amount of a dark red oil was produced. It was discovered later, however, that apparently a reaction was taking place between the Raney nickel and the chloronaphthalene and a small amount of solid was obtained. A possible explanation of this phenomena could be the removal of the chlorine atoms by the active nickel and the subsequent formation of binaphthyl. This reaction would be comparable to the Ullman biaryl synthesis with copper powder. Further investigations of this reaction are planned.

The first attempted condensation using Raney nickel and benzyl ether as the reaction medium yielded a small quantity of a red oil. This was purified by chromatographic adsorption and gave several colored bands indicating the presence of several different materials. The top band, which contained the major portion of the material, contained sulfur and was not unsaturated. This would indicate that it was not produced by a condensation reaction. The next two bands were found to contain no sulfur and again showed no unsaturation. These materials may have been formed by a partial decomposition of the thiocompound.

When the trial was repeated with the reaction time doubled a brown oil was produced similar to the material obtained in the copper trials. This run was repeated three times with the same result. Again only a very small quantity (on the order of 0.04 g.) was produced. As it still contained sulfur and was not unsaturated, it did not result from a condensation of the thiocompound.

Heating dithioisophthalaldehyde (2 g.) under the same conditions

as in the previous trials but without the Raney nickel gave three milliliters of a heavy red oil. This material still retained the characteristic odor of the thiocompound and was found to contain sulfur. It did not show any unsaturation and was soluble in benzene. The possibility that the material resulted from the partial depolymerization of dithioisophthalaldehyde is suggested. In view of these results it would seem that the red oil obtained in the first nickel trial was a result of an insufficient reaction period.

The possibility that condensation has taken place to form a three-dimensional polymer must not be overlooked. Such a polymer would likely have been insoluble in the solvents used, and thus was not extracted from the reaction mixture. The low yields of materials that were extracted indicate that most of the reaction products had remained in the residues. The thioaldehyde could not remain as such under the conditions of the reaction. If it formed the heavy red oil, as it did in the blank run, this material would have been extracted in the benzene. When the copper powder or the Raney nickel was present only a small amount of material could be extracted and this was not a red oil. The condensing agent did play a part as the results were different when it was present. An insoluble three-dimensional polymer would explain these results.

Further investigations are definitely indicated. The residues from the copper and nickel trials should be analyzed to determine whether a three-dimensional hydrocarbon polymer is present. In order to utilize the dilution principle more effectively the condensations should be attempted in a solution. Methods of depolymerizing the dithioisophthalaldehyde in order to make it soluble must be investigated. The attempted

condensation of the soluble heavy red oil produced by heating the thio-
compound in benzyl ether might prove interesting.

CHAPTER V

SUMMARY

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The preparation of *w,w,w',w'* tetrabromo m-xylene by direct bromination of m-xylene has been studied. The reaction conditions finally arrived at gave a yield of 53% of the desired product.

Two new thioaldehydes, monothioisophthalaldehyde and dithioisophthalaldehyde, have been prepared. Their properties were determined and each compound was analyzed for carbon, sulfur and hydrogen.

Several attempts were made to condense dithioisophthalaldehyde by heating with copper powder or Raney nickel in a manner that would lead to the cyclic dimer, diphenylene diethene. These attempts were not successful.

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