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Preparation of thianthrene

Eugene Alton Talley

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PREPARATION OF THIANTHRENE

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THESIS

Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Science in the Graduate
Department of the University of Richmond

by

Eugene Alton Talley, B. Chem.

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The University of Richmond

1938

Approved by

J. Stanton Pierce

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INTRODUCTION

This work was begun in an attempt to study further the preparation of thianthrene from o-dichlorobenzene and alkali sulfides. o-Dichlorobenzene is a liquid by-product in the preparation of its solid isomer, p-dichlorobenzene, which is used extensively for controlling moths and peach tree borers. The study of the preparation of thianthrene from the liquid isomer was undertaken because the preparation might develop into a possible use for the large quantities available.

Thianthrene might be made from o-dibromo- and o-diiodo-benzene but these are not as cheap or as easily obtained as the dichloro derivative and were not used in this study. Various sulfides and hydrosulfides can be used for the preparation but again sodium sulfide and hydrosulfide were choices made because they are cheap and readily obtainable. Various runs were made with these materials in combination with other reagents in an attempt to prepare thianthrene in fair yield. The best results were obtained using equimolar quantities of o-dichlorobenzene and sodium hydrosulfide in water solution with a half molar quantity of calcium hydroxide. The calcium hydroxide may be added to the solution containing sodium sulfide or sodium hydroxide before saturating it with hydrogen sulfide to prepare the

sodium hydrosulfide, or after it is saturated. If the calcium hydroxide is added ahead of the hydrogen sulfide, the solution should not be agitated very much since if the hydrogen sulfide comes into intimate contact with the calcium hydroxide precipitate it may be converted partially to the sulfide and excess sulfide has been found to cut the yield of thianthrene.

HISTORICAL

In his work on the dry distillation of sodium benzene sulphonate, J. Stenhouse (1) reported a

(1) Proc. Lon. Royal Soc., XIV, 351 (1865)
 Ann. 140, 286 (1866)
 Hale, W. J.; Thianthrene (unpublished work), p. 1

product distilling above 300° from which needle-like crystals separated on long standing. Later, (2) he

(2) Proc. Lond. Royal Soc., XVII, 62
 Ann. 149, 247 (1869)
 Hale, W. J.; Ibid.; p. 2

found in this same fraction a compound which he termed "Phenylene Sulphide". This fraction, when redistilled, gave an orange colored distillate solidifying to a crystalline mass of formula C_6H_4S which could be crystallized from alcohol, benzene or carbon tetrachloride. This compound had a melting point of 159°. The long glancing prisms obtained dissolved in ethyl alcohol but not in water. A solution in concentrated sulfuric acid had a beautiful purple color. A. Kekulé and Szuch (3) repeated this work and obtained similar

(3) Zeit., f. Chemie 1867, 194
 Hale, W. J.; Ibid.; p. 3

results. In addition, they tried the action of phosphorus pentasulfide on phenol and obtained various sulfur derivatives including one product, boiling at a temperature above 300°, which crystallized out on

standing and might have been "Benzol Bisulfide"

((C₆H₅)₂ S₂). Fr. Schulze (4) obtained a small

(4) Ber., 4, 33 (1871)
Hale, W. J.; Ibid.; p. 4

quantity of long needles which may have been thianthrene,

when he heated benzene and sulfur together at 400-500°

for several hours. C. Graebe (5) repeated the work of

(5) Ber., 7, 50 (1874)
Hale, W. J.; Ibid.; p. 4
Deuss, J. J. B.; Ber., 41, 2329 (1908)

Kekule¹ and Szuch on heating phenol and phosphorus penta-

sulfide together and obtained similar products, one of

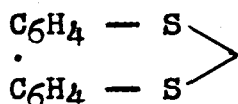
which was identical with the "Phenylene Sulphide" of

Stenhouse, mentioned above. Graebe (6) first proposed

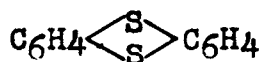
(6) Deuss, J.J.B.; Ber., 41, 2329 (1908)

the form I for this compound but later he proposed the

form II as the correct one:



I



II

E. B. Schmidt (7) obtained thianthrene and

(7) Ber., 11, 1173 (1878)
Hale, W. J.; loc. cit.; p. 5

other organic sulfur compounds by the action of zinc and

sulfur monochloride on benzene. C. Friedel and J. M.

Crafts (8) made thianthrene, along with diphenyl sulfide

(8) Ann. Ch. (6) 1, 530 (1884)
Hale, W. J.; Ibid.; p. 5

and thiophenol by the action of sulfur dichloride and aluminum chloride on benzene. Later (9), they obtained

 (9) Ann. Ch. (6) 14, 438 (1888)
 Hale, W. J.; Ibid.; p. 6

the same products by the action of sulfur and aluminum chloride on benzene at higher temperatures. P. Jacobson and E. Ney (10), in their work on o-phenyldiazosulfide,

 (10) Ber., 22, 910 (1889)
 Deuss, J. J. B.; Ber., 41, 2329 (1908)

made the observation that it changes directly to diphenylene disulfide at 200-250° with the loss of nitrogen.

They also advance form II above for the structure of thianthrene. P. Genvresse (11) obtained thianthrene

 (11) Bull. Soc. Chim., (3), 15, 409 (1896)
 Hale, W. J.; loc. cit.; p. 6

by the action of aluminum chloride and sulfur dichloride on benzene, following the first method of Friedel and Crafts mentioned above. Toluene and nitrobenzene reacted similarly to form dimethylthianthrene and dinitrothianthrene, respectively. F. Krafft and R. E.

Lyons (12) prepared diphenylenedisulfide from sulfur

 (12) Ber., 29, 436 (1896)
 Deuss, J. J. B.; Ber., 41, 2329 (1908)

and phenyl sulfide. Because of its stability and behavior, which are similar to that of anthracene, they named the compound "Thianthrene" for the first time.

J. B. Cohen and F. W. Skirrow (13) condensed

(13) J. Chem. Soc., 75, 887 (1899)

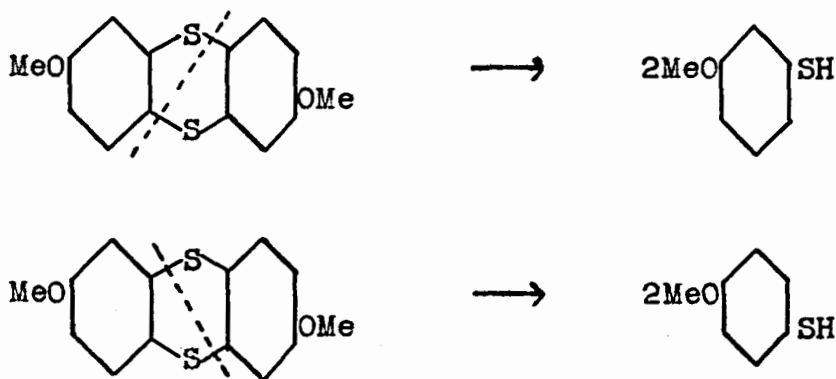
Rây, J. N.; J. Chem. Soc., 119, 1959-67 (1921)

Hale, W. J.; loc. cit.; p. 11

sulfur monochloride with benzene and toluene in their study of the aluminum-mercury couple. With these hydrocarbons, they obtained diphenylene disulfide and ditolylene disulfide respectively, but when they tried higher hydrocarbons they obtained oils which were uncrystallisable and decomposed on distillation. In repeating this experiment, Rây (14) showed that the

(14) J. Chem. Soc., 119, 1961 (1921)

decomposition products in the case of anisole give a clue as to the constitution of the thianthrene derivative. A mixture of two mercaptans was found in the distillate. The following equations were given in explanation:



I. Boeseken (15) tried the action of sulfur

(15) Rec. trav. chim., 24, 209 (1905)

Hale, W. J.; loc. cit.; p. 11

dichloride, sulfur monochloride and sulfur on benzene

in the presence of aluminum chloride. He found that at 10° or lower temperatures the sulfur chlorides yielded diphenyl sulfide. At around 60° with sulfur dichloride, he also obtained thianthrene. At the boiling point of benzene, using sulfur, the products were diphenyl sulfide, thianthrene and hydrogen sulfide. In all cases, he assumed likely that diphenyl sulfide was first formed and this then reacted with free sulfur to form thianthrene. The sulfur dichloride decomposed to give the monochloride and chlorine and ^{the} monochloride liberated sulfur in the course of the reaction.

J. J. B. Deuss in his article (16) on the

 (16) Ber., 41, 2329-31 (1908)

 constitution of thianthrene discusses various reactions for its preparation which might give a clue as to its structure. In an attempt to prove that the sulfur atoms were in the ortho positions, he split thianthrene-disulphone with phosphorus pentachloride to form benzene-o-disulphonylchloride and orthodichlorobenzene. The latter was characterized by preparing the nitro derivative since the boiling points of the dichlorides of the different isomers are very close together. The benzene-o-disulphonylchloride melted at 105°, the meta and para isomers melting at 63° and 131-139° respectively. J. Pollak (17) was not satisfied with

 (17) Monats., 34, 1675 (1913)
 Hale, W. J.; loc. cit.; p. 13

the melting point obtained by Deuss for the benzene-o-di-
 sulphonylchloride, which was given^{by}Holleman and

Pollak (18) as 142°. Heilbron (19) gives it as 143°,

(18) Rec. trav. chim., 29, 416 (1910)
 Hale, W. J.; loc. cit.; p. 13
 (The melting point is not reported in C. A. 5,
 680⁸ (1911), an abstract of Holleman and Pollak's
 article, which gives the melting points of the isomers.)

(19) Dictionary of Organic Compounds; vol. I; p. 126
 (1934)

both values differing widely from Deuss.

Deuss (20) warmed thiophenol in ligroin

 (20) Rec. trav. chim., 27, 145-8
 C. A. 2, 2552² (1908)

solution with aluminum chloride and obtained hydrogen
 sulfide, hydrogen chloride, phenyl sulfide and phenylene
 disulfide, (C₆H₄)₂S₂. Next he (21) added aluminum

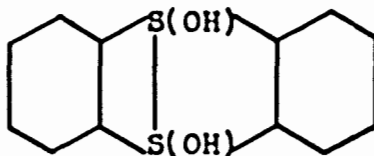
 (21) Rec. trav. chim., 28, 136-41 (1908)
 C. A., 3, 1746⁹ (1909)

chloride in small portions to diphenyl disulfide in
 ligroin and heated. He obtained thianthrene and thio-
 phenol from the reaction mixture. The ortho and para
 thiocresols were found to react with aluminum chloride
 but the meta derivative did not.

K. Fries and W. Volk (22) found that thio-

 (22) Ber., 42, 1170-6 (1909)
 C. A., 3, 2131⁹ (1909)

phenols, when treated with fuming sulfuric acid, give sulfur dioxide and disulfides. On further action, more sulfur dioxide is given off and thianthrenes are formed in from 10 to 20% yield. These authors postulate intermediate oxygen derivatives, giving the following stages — thiophenol, $\text{SH} \longrightarrow$ disulfide, $\text{S}\cdot\text{S}$; disulfoxide, $\text{SO}\cdot\text{SO}$; hypothetical compound (III); monosulfoxide, $>\text{SO}\cdot\text{S}<$; thianthrene.



III

O. Lange, M. W. Widman, and A. Wennerberg,

(23) announced the use of pyrocatechol and phosphorus

(23) Deutsches Reichs-Patent 330, 834 (1920)

Friedlander XIII 263

Hale, W. J.; loc. cit.; p. 25

pentasulfide for preparing thianthrene by another
method.

J. N. Rây (24) modified the Friedel-Crafts'

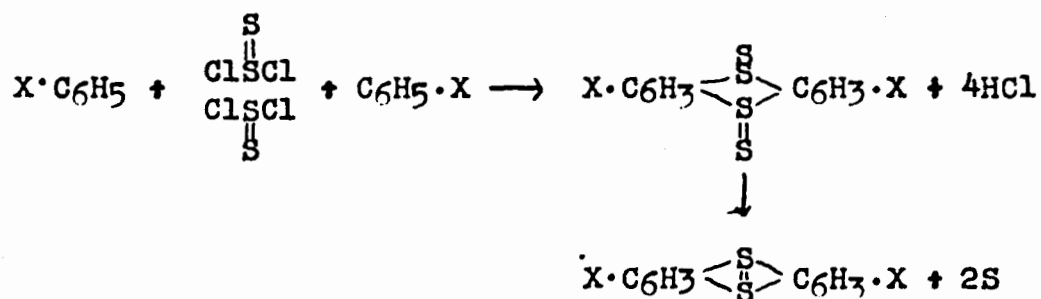
(24) J. Chem. Soc., 117, 1335-9 (1920)

reaction by using metallic aluminum and mercuric
chloride instead of aluminum chloride in the preparation
of thianthrene from benzene and sulfur. He obtained
an 80% yield with one of the highest melting points
for thianthrene recorded in the literature. It melted

at 160° when crystallized from acetone. Ray (25) later

 (25) J. Chem. Soc., 118, 1959-67 (1921)

 applied the aluminum amalgam method to the preparation
 of various thianthrene derivatives by reacting the
 corresponding derivatives of benzene with sulfur mono-
 chloride. In the formation of dichlorothianthrene
 from chlorobenzene, he isolated an intermediate product
 containing twice as much sulfur as the final product.
 His equation for the reaction in general is:



The intermediate compound is very unstable and decomposes readily with moisture, liberating free sulfur. He was not able to condense an acid chloride with a hydrocarbon by means of aluminum amalgam, however, and found that it would not react with acid chlorides in general. It was possible, though, to condense the acid chlorides with sulfur monochloride to give carboxylic derivatives of thianthrene. With the higher hydrocarbons the condensation seems to take place but the product breaks down on distillation. He obtained two dichlorodimethyl derivatives, diacetylaminothianthrene,

dimethoxythianthrene and others.

Kurt Brass and Ludwig Kohler (26) prepared

 (26) Ber., 54B, 594-7 (1921)
 C. A. 15, 2639¹ (1921)

dibenzothianthrenediquinone by the action of sodium sulfide on 2,3-dichloro(or dibromo)- α -naphthoquinone.

The action took place very easily. They later (27)

 (27) Ber., 55B, 2543-68 (1922)
 C. A. 17, 1014-6 (1923)

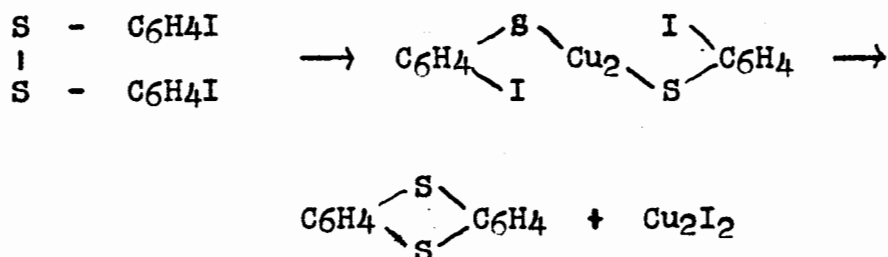
used this same type of reaction to make similar compounds such as dihydrodibenzothianthrenediquinone, dinaphthiophenediquinone and others. They mention the formation of sodium thiophenate in the preparation of the monosodium salt of dihydrodibenzothianthrenediquinone by the action of sodium sulfide out of contact with the air. Some of the compounds formed are not very stable.

S. Krishna (28) contributed to the number of

 (28) J. Chem. Soc., 123, 156-160 (1923)

thianthrene derivatives by forming the first unsymmetrical compounds. He condensed 6-chloro-3-nitrobenzenesulphinic acid with the sodium salt of phenyl mercaptan to give 4-nitro-2-sulphinodiphenyl sulfide (I) which when dissolved in concentrated sulfuric acid and allowed to stand for a time and treated with water, will precipitate out the 3-nitrothianthrene (II). Sulfur dioxide is evolved from the sulfuric acid solution. If

form the cyclic disulfide. They think that copper mercaptides are first formed which subsequently lose cuprous iodide:



This synthesis took place in three cases, and seems capable of wide application.

R. W. Bost and P. Borgstrom (32) in their

 (32) J. Amer. Chem. Soc., 51, 1922-25 (1929)

 study of tin tetraphenyl as a phenylating agent, obtained diphenyl sulfide, diphenyl disulfide and thianthrene when they reacted it with sulfur. Higher temperatures favored formation of thianthrene. They obtained thianthrene when the substances were heated in a sealed tube at 250° for twenty hours, none being obtained at 190°. Hydrogen sulfide was given off in the case of thianthrene formation.

H. B. Glass and E. E. Reid (33) heated benzene

 (33) J. Amer. Chem. Soc., 51, 3428-30 (1929)

 and sulfur together without a catalyst in a closed tube at 350° for 24 hours. Upon opening the bomb, they obtained thiophenol, diphenyl sulfide, diphenyl disulfide, diphenylene disulfide (thianthrene) and

hydrogen sulfide. Iron was not necessary for the reaction since they got the same results in glass. Ethylbenzene reacted very readily at the same temperature to give mostly 2,4-diphenylthiophene instead of thianthrene derivatives. They compared the latter reaction with the action of oxygen on ethylbenzene to form acetophenone and showed that this case bore out the analogy of sulfuration to oxidation.

H. W. Schechten (34) expected to make 2,2' di-

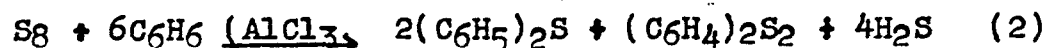
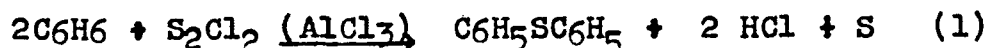
 (34) Ber., 65B, 1608-9 (1932)
 C. A. 27, 70¹ (1933)

thiocyanodiphenyl from the hexathiocyanochromate of tetrazotized 2,2' diamino-diphenyl but obtained chiefly biphenylene sulfide melting at 99.5° and a little of the disulfide melting at 114.5°. The latter is an isomer of thianthrene.

W. W. Hartman, L. A. Smith, and J. B. Dickey
 (35) prepared diphenyl sulfide on a semi-commercial

 (35) Ind. Eng. Chem., 24, 1317-8 (1932)

 scale from benzene by the action of sulfur monochloride and aluminum chloride. Using 4050 grams of aluminum chloride and 3525 grams of sulfur chloride with a total of 10,620 grams of benzene they obtained 4050 grams of purified diphenyl sulfide and 80 grams of thianthrene melting at 155-6°. They give the following as the reactions involved:



In their study on the stereoisomerism of disulfoxides in the thianthrene series, H. Baw, G. M. Bennett and P. Dearn (36) made 2,6-dichlorothianthrene

 (36) J. Chem. Soc., 680-4 (1934)

 in good yield by the action of sulfuric acid on p-chlorophenylthiol. They say the reaction appears to leave no doubt as to its configuration:



N. M. Cullinane and H. J. Padfield (37)

 (37) J. Chem. Soc., 1131-4 (1935)

 heated thiophenol with litharge and obtained thianthrene along with diphenylene sulfide, diphenyl sulfide and diphenyl disulfide.

G. Dougherty and P. D. Hammond (38) made a

 (38) J. Amer. Chem. Soc., 57, 117-8 (1935)

 study of the reaction of sulfur with benzene in the presence of aluminum chloride. Under the conditions used, they obtained only diphenyl sulfide and thianthrene. The ratio of the two was affected markedly by the aluminum chloride content of the reaction mixture. When

250 cc. of benzene, 32 g. of sulfur and aluminum chloride. were refluxed together at 80° for three hours, the optimum yield of thianthrene was obtained when 0.25 mole of aluminum chloride was used. The yield was 0.183 mole of thianthrene under these conditions. When the content of aluminum chloride was increased to 0.5-1.0 moles, diphenyl disulfide alone was the product. They also formed thianthrene from diphenyl sulfide and sulfur in the presence of aluminum chloride. This gave a nearly quantitative yield. Here also, too much aluminum chloride cut the yield.

Work done by M. Prasad, J. Shanker and

B. H. Peermohamed (39) on the crystalline structure of

(39) J. Indian Chem. Soc., 14, 177-87 (1937)

C. A. 31, 8303¹ (1937)

thianthrene by the use of the X-ray, showed that Krafft and Lyons (see above) were correct when they named the compound. These later workers assign the anthracene structure to thianthrene, with the carbon atoms 9 and 10 replaced by sulfur, but the unit cell of thianthrene has four molecules instead of two as found in anthracene.

EXPERIMENTAL PART

The reactions for the preparation of thi-anthrene were carried out in steel tubes of about 300 ml. capacity, the volume in the four tubes varying from 294 ml. to 301 ml. The volumes were measured by filling with water, screwing the plugs in by hand, removing them and pouring out the water into a graduate and measuring it. These tubes were heated in an electric furnace which was thermostatically controlled. The temperature could be kept constant at $360^{\circ} \pm 3^{\circ}$.

When a run was made, the four tubes were washed out thoroughly with soap and water using a fairly stiff brush. They were then rinsed out with distilled water since an analysis for chloride was to be run on the product. The water was allowed to drain out and then the materials to be tested (listed in table of data) were placed in the tubes. A paste of graphite in alcohol was placed on the threads of the plugs, which were then screwed in. The tubes, plugs and washers were all marked and the same plug and washer were used for a particular tube each time. Since the pressure developed is of the order of 2500 lbs./in^2 , the plugs must be securely tightened. This was done quite satisfactorily by means of two large pipe wrenches, as shown by the fact that in

only two cases out of forty were leaks noted.

The furnace was turned on and the temperature allowed to rise to around 370° . The four tubes then were placed in the furnace and the temperature usually fell to about 320° . In about two hours and a quarter to two hours and a half the temperature rose again to 360° . The thermostat was then set and the temperature allowed to remain at 360° for about four hours. The furnace was then turned off and the tubes allowed to remain in the furnace to cool spontaneously.

The tubes were opened after they became cold and the contents were poured into one-liter round bottomed flasks. Steam was then passed into the tubes and the distillate caught in the flasks containing the original contents. The tubes themselves had to be heated with a low flame in order to get any distillate to come over since steel tubes conduct heat rather readily. After the volatile matter had distilled over, this flame was turned off and a few minutes later, the tubes were disconnected from the source of steam. The contents were poured into the round bottomed flasks with the original contents and the tubes were rinsed out two or three times with water into the same containers. While the tubes were still hot, often hot enough to make the benzene boil, they were extracted with benzene.

The extraction was made by shaking with about 150 ml. of benzene added in three portions. The benzene from each tube was poured into a corresponding small stoppered flask and set aside. The steel tubes were set aside also for the next run.

Steam was passed into the liter round bottomed flasks containing the steam distillate from the steel tubes in addition to the original contents of these tubes. To prevent an undue increase in the amount of water in the flasks from the condensed steam, the flasks were heated by burners. The steam distillate was caught and saved for later study. Any phenol, thiophenol, benzene, chlorobenzene, unreacted o-dichlorobenzene, or possibly chlorophenol would be found in this steam distillate along with part of the diphenyl sulfide. In some cases a little thianthrene was found to distill with steam but this was always a very small amount. After the material, volatile with steam, had passed over, the steam distillation was stopped and the flask containing the residue allowed to cool a little. As soon as it was cool enough so that the benzene would not boil out, the benzene used to extract the corresponding steel tube was added to the flask and the whole shaken up thoroughly.

The solution was filtered to remove graphite

and traces of iron sulfide and the benzene layer was separated from the water layer left behind in the steam distillation and was poured into a distilling flask. The aqueous layer was extracted with two more twenty to thirty milliliter portions of benzene which were then added to the contents in the distilling flask. The most of the benzene in the extractions was distilled out of the distilling flask and the remainder (about 15 to 20 ml.) was rinsed into a weighed dish and set aside to evaporate spontaneously. The nonvolatile portion left behind was weighed. The oil present was washed off of the crystals with ether on a small suction funnel leaving fairly pure thianthrene. The crystals were sucked dry, weighed and the melting point determined. The ether was allowed to evaporate off from the oil, which was weighed and then distilled under vacuum, usually between 1 and 2 mm. of Hg. Three or four fractions were separated, weighed and saved for further study. The distillation was a rather difficult one since the amount of oil distilled was often small requiring the use of a very small distilling flask if any distillate was to be obtained. Two flasks of different sizes were made and used. Both were of the Claisen type, one being made from two pyrex test tubes and the other

from a regular type 25 ml. distilling flask. Foaming was especially bad with the small flask and about the only way to distill the material satisfactorily was to boil it fast, as it would bump over if boiled slowly and would foam over if a current of air was passed through it. As a result, the accuracy of the temperatures obtained for the different fractions was not the best in some cases. Melting points were run on the solids in these fractions. A high boiling, slightly dark-colored oil, boiling up as high as 250° at one mm. Hg, was obtained which should be studied further.

The water layer of the residue of the steam distillate, after its separation from the benzene, was made up to a liter and aliquots ^{were} taken for inorganic analysis. The hydroxide ion content was determined by titrating to the methyl orange end-point with standard acid. The titrations for the runs in which calcium acetate was one of the reactants were not very satisfactory since the end-point was indeterminate, very likely due to the buffer action of the acetate ion. The determination of sulfide after the runs was not satisfactory because of interfering substances but qualitative tests showed that there was none in most cases so this did not seriously interfere. The sulfide content of the solutions used for the reaction was

determined, with best results, by adding the sample of sulfide to an excess of standard iodine in sufficient acid to make the resulting solution slightly acid, then back-titrating with standard thiosulfate. The chloride ion content of the solution was determined by the Volhard method as modified by J. R. Caldwell and H. V. Meyer (1).

 (1) Ind. Eng. Chem., Anal. Ed., 7, 38-9 (1935)

They use nitrobenzene instead of filtration to prevent the interference of the silver chloride precipitate in the back-titration with thiocyanate. This worked very satisfactorily except when sulfide was present. In these cases, the sulfide was precipitated with cadmium nitrate and filtered off. The titration was run on the filtrate. An interesting observation was made in this connection. In these cases and in others where a slight trace of sulfide was present, the silver chloride would precipitate out white at first and then when practically all of the chloride had been precipitated, it would darken to gray, sometimes a fairly dark gray. One can almost tell the end-point by this color change. In a great many cases the silver chloride did not darken at all, showing that all of the sulfide was used up, even the last trace. This was true, even in cases where sulfide was added in excess of the amount required, theoretically, to react with the o-dichlorobenzene present although the excess was

sufficient to cut the yield of thianthrene considerably.

Almost invariably an oil separated out and settled to the bottom of the steam distillate. This oil was removed, using an elongated medicine dropper, and measured in a small graduate. It was then shaken vigorously with 2-N sodium hydroxide and allowed to settle if it would. Often an emulsion formed which would not separate on standing. This emulsion could be separated fairly well by centrifuging a few minutes. The two layers were separated and the lower oily layer distilled. Since the amount of this oil was nearly always small, it was usually distilled from a test tube which had a side arm sealed into its side about 4.5 cms. from the bottom. This test tube was placed in a hole in an asbestos board and supported by a clamp. Three other asbestos boards were placed upright around it to protect the tube from draughts. If the heating was done carefully, watching the tube closely, fairly good fractionation could be obtained with fairly accurate boiling points. Fractions were taken at each point where a pause in rise of temperature occurred or there was some other indication of a change in the composition of the distillate such as a change in refractive index, easily seen when a drop of liquid fell into the rest of the distillate. Usually three

or four fractions were obtained. These were set aside in case they are wanted for future study.

The alkali-soluble fraction was acidified and the odor noted. Often it was necessary to get someone else to smell it because after one works with these mercaptans a while one cannot state definitely whether the mercaptan is present or not by its odor. In a few cases, enough mercaptan was set free when the alkali-soluble layer was acidified, to give a sufficient quantity to distill. In most cases where this was expected to occur, the alkali layer was extracted with ether to remove any of the other fraction that might be mixed in with it, before it was acidified. Most of this alkali-soluble oil was thiophenol as shown by its boiling point of around 168° and its odor but there seemed to be a trace of some very high boiling oil, which may or may not have been carried over from the other layer.

Phenol was determined in the aqueous layer of the steam distillate. This was diluted to 500 ml. usually. If much phenol was present, an aliquot was taken; if not, all of it was taken and the phenol precipitated as the tribromide by adding an excess of bromine water. The precipitate was filtered off, dried in air and weighed as the tribromide.

The above was the experimental procedure followed in this work. For various reasons, all of the operations were not done in every case, but they were done in enough representative cases to give a fairly good idea of what would happen in the others.

The results of selected runs are given in tabular form. Many factors are concerned with the yield of thianthrene and not all of these have been worked out satisfactorily. Apparently duplicate runs did not give duplicate results in all cases, but the data should give a satisfactory comparison of reagents and conditions. The yield of thianthrene reported represents a minimum value, especially in the runs with low yields, for thianthrene is somewhat soluble in the oil formed.

TABULATION OF RESULTS

Run No.	2A	2B	2C	3A
No. tube	I	II	III	I
Vol. tube	299 ml.	301 ml.	296 ml.	299 ml.
Temp.	5 hours at 359-360°			3.5 hrs 360°
Time, hrs., (total)	11.5	11.5	11.5	5.3
$\text{o-C}_6\text{H}_4\text{Cl}_2$, g.	14.7	14.7	14.7	14.7
" mol.	0.1	0.1	0.1	0.1
Sulfide	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ - Baker's lot 81133			
" g.	24	24	24	24
" mol.	0.1	0.1	0.1	0.1
Added ---	---	NaOH	NaHCO_3	NaHCO_3
" g.	---	4	8.4	8.4
" mol.	---	0.1	0.1	0.1
Total alkali, mol. (to m. o.)	0.2	0.3	0.3	0.3
H_2O g.	120	120	120	16
H_2O mol.	6.6	6.6	6.6	0.9
$\text{oC}_6\text{H}_4\text{Cl}_2/\text{S}/\text{OH}/\text{H}_2\text{O}$	1/1/2/66	1/1/3/66	1/1/3/66	1/1/3/9
After run:				
Oil in steam distillate, ml.	1.5	0.4	0.6	7.6
Ditto after NaOH extract., ml.	1.2	0.3	0.4	7.5
$\text{C}_6\text{H}_5\text{SH}^*$, g.	0.3	0.1	0.2	0.1
$\text{C}_6\text{H}_5\text{SH}$, mol.	.0027	.0009	.0018	.0009
$\text{C}_6\text{H}_5\text{SH}$, %	2.7	0.9	1.8	0.9

* This is an approximate value.

Run No.	2A	2B	2C	3A
B.P. of oil after $\frac{1}{8}$ ml. at 293-60		---	---	most at 168-72°; few drops 300-100°
NaOH extraction				9
$\text{oC}_6\text{H}_4\text{Cl}_2$, g. rec.	none	---	---	
" mol. used	0.1	---	---	0.04
* Ph_2S , g.	0.6 d.	---	---	trace
Ph_2S , mol.	0.003	---	---	---
Wt. of C_6H_6 extract, g.	5.37	2.28	7.19	1.48
Condition	oily solid	oily solid	many crystals	---
Wt. thianthrene after Et_2O ext., g.	1.26	0.36	2.23	0.01
Thianthrene, mol.	0.0059	0.0018	0.0103	0.00005
% yield	12	4	21	0.1
M. P.	147-50°	---	---	---

Analytical data:

OH^- , mol. rec.	nil.	0.10	0.10	0.22
OH^- , mol. used	0.20	0.20	0.20	0.08
Cl^- , mol. formed	0.18	0.20	0.18	0.06
$\text{S}^=$, mol, recov.	nil.	trace	nil.	present
$\text{S}^=$, mol. used	0.1	0.1	0.1	---
$\text{oC}_6\text{H}_4\text{Cl}_2/\text{S}/\text{OH}/\text{Cl}^{**}$	1/1/2/1.8	1/1/2/2	1/1/2/1.8	1/ /2/1.5

* Ph_2S as given here is approximate, (d.) indicates that it was found in the steam distillate, (E.) given in later runs, indicates that it was found in the distillate from the ether extracted oil. Unless both are given the total amount is not shown.

**Ratio of other materials used to chloride formed.

Run No.	3D	5A	5B	5C
No. tube	IIII	I	II	III
Vol. tube	294 ml.	299 ml.	301 ml.	296 ml.
Temp.	3.5 hrs 360°	4 hrs 20 min. at 360°		
Time, hrs. (total)	5.3	7	7	7
$\text{o-C}_6\text{H}_4\text{Cl}_2$, g.	14.7	14.7	14.7	14.7
" mol.	0.1	0.1	0.1	0.1
Sulfide	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ from Baker's lot 81133			
" g.	24	24	24	24
" mol.	0.1	0.1	0.1	0.1
Added	$\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	HOAc	HOAc	HOAc
" g.	8.8	6	9	12
" mol.	0.05	0.10	0.15	0.20
Total alkali, mol.---		0.10	0.05	0.00
(to m. o.)				
H_2O g.	120	120	120	120
H_2O mol.	6.6	6.6	6.6	6.6
$\text{oC}_6\text{H}_4\text{Cl}_2/\text{S}/\text{OH}/\text{H}_2\text{O}$	1/1/ /66	1/1/1/66	1/1/.05/66	1/1/0/66
After run:				
Oil in steam				
distillate, ml.	0.9	0.7	1.2	5.6
Ditto after				
NaOH extract. ml.	0.8	0.6	1.0	5.5
$\text{C}_6\text{H}_5\text{SH}$, g.	0.1	0.1	0.2	0.1
$\text{C}_6\text{H}_5\text{SH}$, mol.	.0009	.0009	.0018	.0009
$\text{C}_6\text{H}_5\text{SH}$, %	0.9	0.9	1.8	0.9

Run No.	3D	5A	5B	5C
	2-3			3.8ml.
B. P. of oil after drops	180-5 ⁰ ;	275-82 ⁰	265-82 ⁰	176 ⁰ ;
NaOH extraction	2-3 drops			rest at
	240-50 ⁰			286-62 ⁰
$\text{oC}_6\text{H}_4\text{Cl}_2$, g. rec.	trace	none	none	5
" mol. used	0.1	0.1	0.1	0.07
* Ph_2S , g.	---	0.7 d.	d&E 3.3	3 d&E
Ph_2S , mol.	---	.004	0.018	0.016
Wt. of C_6H_6 extract, g.	6.11	6.24	7.42	4.53
Appearance	---	oily solid	consid. oil	much oil
Wt. thianthrene after Et_2O ext., g.	4.34	2.48	1.32	0.45
Thianthrene, mol.	.020	.012	.006	.002
% yield	40	23	12	4
M. P.	---	142-8 ⁰	151-4 ⁰	---
Analytical data:				
OH^- , mol. rec.	.096	---	---	---
OH^- , mol. used	---	---	---	---
Cl^- , mol. formed	0.16	0.18	0.18	0.08
S^- , mol. recov.	nil	nil	nil	trace
S^- , mol. used.	0.1	0.1	0.1	0.1
$\delta\text{C}_6\text{H}_4\text{Cl}_2/\text{S}/\text{OH}/\text{Cl}$	1/1/ /1.6	1/1/ /1.8	1/1/ /1.8	1/1.4/ /1.1

*See above

Run No.	5D	6A	6B	6C
No. tube	IIII	*	I	II
Temp.	4.3 hrs at 360°	4.5 hrs. at 360-362°		
Time, hrs. (total)	7	6.5	6.5	6.5
o-C ₆ H ₅ Cl ₂ , g.	14.7	29.4	73.5	29.4
" mol.	0.1	0.2	0.5	0.2
Sulfide	Baker's Na ₂ S·9H ₂ O	Na ₂ S·9H ₂ O (Mallinckrodt)		
" g.	24	48	120	48
" mol.	0.1	0.2	0.5	0.2
Added	Ca(OAc) ₂	NaHCO ₃	NaHCO ₃	NaHCO ₃
" g.	35.2	16.8	42	16.8
" mol.	0.2	0.2	0.5	0.2
Total alkali, mol. --- (to m. o.)		0.4	1.0	0.4
H ₂ O g.	120	32	80	82
H ₂ O mol.	6.6	1.8	4.5	4.5
oC ₆ H ₅ Cl ₂ /S/OH/H ₂ O	1/1/ /66	1/1/2/9	1/1/2/9	1/1/2/22
After run:				
Oil in steam distillate, ml.	1.1	6.1	7.5	4.6
Ditto after NaOH extr., ml.	0.9	---	---	---
C ₆ H ₅ SH, g.	0.2	odor of C ₆ H ₄ (OH)Cl	strong odor	phenol odor
C ₆ H ₅ SH, mol.	.0018	none	trace	none
C ₆ H ₅ SH, %	1.8	---	---	---

* This run was made in an old tube, which was rotated during the period of heating. It had a volume of 280 ml. as compared with 300 ml. for the regular tubes.

Run No.	5D	6A	6B	6C
B. P. of oil after NaOH extraction	0.3 ml. at 170-80°; rem. at 278-84°	trace 80°; 4.8 145-80°; 1 ml. at 260-90°	1.5 ml. 145-50°; 4.4 at 168-79°; 1.2 ml. 295-318°	1.9 ml. 135-47°; 1.6 ml. 168-79°; 0.7 ml. 285-95°
oC ₆ H ₄ Cl ₂ , g.rec.	0.4	4.8 approx.	5.7	2.1
" mol. used	0.095	0.17	0.46	0.19
*Ph ₂ S, g.	0.7 d.	1 d.	1.2 d.	0.8 d.
Ph ₂ S, mol.	0.004	0.0054	0.0065	0.004
Wt. of C ₆ H ₆ extract, g.	7.87 little oil in needles	12.72 mostly oil	40.55 consid. oil	12.12 some oil reddish color
Appearance				
Wt. thianthrene after Et ₂ O ext. g.	3.21	0.97	11.70	3.03
Thianthrene, mol.	0.015	0.0045	0.054	0.014
% yield	30	4.5	22 136-144**	14
M. P.	145-51°	150-3°	148-52°	134-47°
Analytical data:				
OH ⁻ , mol. rec.	0.35	---	---	---
OH ⁻ , mol used	---	---	---	---
Cl ⁻ , mol. formed	0.16	0.26 slight trace	0.77	0.29 slight trace
S ⁼ , mol. recovered	nil	trace	none	trace
S ⁼ , mol. used	0.1	0.2	0.5	0.2
*oC ₆ H ₄ Cl ₂ /S/OH/Cl	1/1.05/ /1.7)	(1/1.2/ /1.5)	(1/1.1/ /1.7)	(1/1.05/ /1.5)

* See above.

** This sample was crystallized from benzene, and was slightly sticky. Other sample from ether.

Run No.	6D	7A	7B	7C
B. P. of oil after NaOH extraction	spilled, evidently similar to others of series 6	1.8 ml. 275-86°; 0.2 ml. 300-5°	1.4 ml. 281-90°; 0.1 ml. around 300°	3.4 ml. 168-88°; 0.8 ml. 291-303°
$\text{oC}_6\text{H}_4\text{Cl}_2$, g.rec.	---	none	none	4.5?
" mol. used	---	---	---	0.17
* Ph_2S , g.	---	2.1 d.	1.7 d.	0.95 d.
Ph_2S mol.	---	0.011	0.009	0.005
Wt. of C_6H_6 extract g.	14.17	13.04	14.41	12.85
Appearance	quite oily	oily, light colored solid	oily, light colored solid	mostly light colored oil
Wt. thianthrene after Et_2O ext. g.	3.62	3.72	6.20	0.94
Thianthrene, mol.	0.017	0.017	0.029	0.004
% yield	17	17	29	4
M. P.	149-52°	145-50°	135-46°	141-50°
Analytical data:**				
Cl^- , mol. formed	0.34 slight	0.39	0.39	0.30
S^- , mol. recov.	trace	none	none	none
S^- , mol. used	0.2	0.24	0.20	0.24
$\text{oC}_6\text{H}_4\text{Cl}_2/\text{S}/\text{Cl}$	1/1/1.7	1/1.2/2.0	1/1/2.0	1/1.4/1.8

* See above.

** The hydroxyl ion was not determined on these and later runs.

Run No.	7D	8A	8B	8C
No. tube	IIII	I	II	III
Temp.	4 hrs. 360-3°	4 hours and a half at 360°		
Time, hrs. (total)	6 $\frac{3}{4}$	6.8	6.8	6.8
$\text{o-C}_6\text{H}_4\text{Cl}_2$, g.	29.4	29.4	29.4	73.5
" mol.	0.2	0.2	0.2	0.5 (Mall.)
Sulfide	NaSH solution (Baker's)			$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$
" g.	10.2*	10.2*	10.2*	120
" Mol.	0.2	0.2	0.2	0.5
Added	$\text{Ca}(\text{OAc})_2$	freshly prepared $\text{Ca}(\text{OH})_2$		$\text{Ca}(\text{OAc})_2$
" g.	17.6	7.4	7.4	44
" mol.	0.1	0.1	0.1	0.25
Total alkali, mol. (to m. o.)	---	0.44	0.44	---
H_2O g.	60	60	135	84
H_2O mol.	3.3	3.3	7.5	4.7
$\text{oC}_6\text{H}_4\text{Cl}_2/\text{S}/\text{OH}/\text{H}_2\text{O}$	1/1/ /17	1/1/2 $\frac{3}{17}$	1/1/2 $\frac{3}{38}$	1/1/ /9.4
After run:				
Oil in steam distillate, ml.	7.6	3.8	3.6	33.5
Ditto after NaOH extr. ml.	6.2	2.2	1.9	32.5
$\text{C}_6\text{H}_5\text{SH}$ g.	1.4	1.6	1.7	1.0
" mol.	0.013	0.014	0.015	0.009
" %	6.5	7	7.5	1.8

* Grams NaSH

Run No.	7D	8A	8B	8C
B. p. of oil	5.4 ml.	0.5 ml.	1.2 ml.	1.6 ml.
after NaOH	168-77°;	145-85°;	280-94°;	118-300°;
extraction	0.6 ml.	1.0 ml.	0.1 ml.	28.1 ml.
	276-80	285-94°;	294-300°	168-81°;
		0.1 ml.		0.8 ml.
		305-90		197-309°
$\text{oC}_6\text{H}_4\text{Cl}_2$, g. rec.	7.1	trace	none	36.5
" mol. used	0.15	0.2	0.2	0.25
* Ph_2S , g.	0.7 d.	4.5 d&E	4.2 d&E	trace
Ph_2S , mol.	0.004	0.024	0.022	---
Wt. of C_6H_6	12.31	15.06	14.73	11.20
extract, g.	mostly		more	
Appearance	light	slightly	oily	reddish
	colored	oily	than	oil
	oil		8A	
Wt. thianthrene	1.16	7.49	8.10	none
After Et_2O ext.g.				
Thianthrene, mol.	0.0054	0.035	0.038	0
% yield	5.4	35	38	0
M. P.	149-153°	145-150°	134-144°	---
Analytical data:				
Cl^- , mol. formed	0.25	---	---	---
S^- , mol. recov.	none	---	---	---
S^- , mol. used	0.2	---	---	---
* $\text{oC}_6\text{H}_4\text{Cl}_2/\text{S}/\text{Cl}$	1/1.3/1.7	---	---	---

* See above.

The ether-extracted oil from 8A distilled at 1-2 mm. Hg as follows: 3.3 g., 126-40°; 0.73 g., 140-70°; 1.16 g., 170-220°; 1.34 g., 220-80°; residue, 0.31 g. The first fraction was distilled at atmospheric pressure and gave fractions at 250-65°; 265-90° and 290-315°. When oxidized with chromic acid in acetic acid solution, solids were obtained melting at 123-4° and 122-4° for the first two fractions of the last distillation. Pure diphenylsulfone melts at 129°.

Run No.	9A	9C	9D	10D
No. tube	I	III	IIII	IIII
Temp.	four and a quarter hrs. 360°			3 1/4 hrs 360°
Time, hrs. (total)	6.3	6.3	6.3	5.3
$\text{o-C}_6\text{H}_4\text{Cl}_2$, g.	24.9 g.	11 g. thi-		
$\text{o-C}_6\text{H}_4(\text{OH})\text{Cl}$		anthrene	29.4	29.4
" mol.	0.2	0.05	0.2	0.2
Sulfide	none	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	fresh NaSH from 8 g. NaOH	fresh NaSH from 0.1 Na_2S
" g.	---	24	10.2?	10.2?
" mol.	---	0.1	0.2	0.2
Added	NaOH	none	$\text{Ca}(\text{OH})_2$ (fresh)	$\text{Ca}(\text{OH})_2$ (com.)
" g.	8	---	before H_2S 7.4	after H_2S 7.4
" mol.	0.2	---	0.1	0.1
Total alkali, mol. (to m. o.)	0.2	0.2	0.4	0.4
H_2O g.	75	44	120	120
H_2O mol.	4.2	2.4	6.6	6.6
$\text{oC}_6\text{H}_4\text{Cl}_2/\text{S}/\text{OH}/\text{H}_2\text{O}$	---	---	1/1/2/33	1/1/2/33
Wt. C_6H_6 extr. g.	2.47	9.24	15.51	17.92
Appearance	Viscous black oil	dry, mostly white	almost complete dryness	almost white solid
Wt. thianthrene after Et_2O ext. g.	0	8.23	11.99	10.40
Thianthrene, mol.	0	0.038	0.0556	0.048
% yield	0	75	55.6	48
M. P.	---	154-5°	141-50°	---

* Solution was not shaken much during addition of hydrogen sulfide.

DISCUSSION

In the reaction to form thianthrene from o-dichlorobenzene and sodium hydrogen sulfide, equimolar quantities of the aromatic halide and sulfide react. Also, the amount, form in which it is added, and the concentration of the hydroxide ion play an important part. The results obtained indicate that sufficient potential hydroxide should be present to react with all of the hydrogen chloride set free by the reaction, but that the hydroxide ion concentration should never be large.

Calcium hydroxide is a fairly strong alkali but is relatively insoluble at room temperature and is even less soluble at higher temperatures, at least for the range in which the data are available (1). There-

 (1) Lange's Handbook of Chemistry (1st ed., p. 129) gives the solubility of calcium hydroxide at 0° as 0.185 parts in 100 parts of water, by weight, and at 100° as 0.077 parts per 100.

 fore, calcium hydroxide should be an ideal source of hydroxide ions to remove the hydrogen chloride from the field of action, and to keep the alkalinity relatively low at all times. The results from run number 9D, which gave the best yield of thianthrene obtained, show that calcium hydroxide is an ideal reagent for this purpose. This run contained equimolar quantities of o-dichloro-

benzene and sodium hydrogen sulfide, freshly prepared, and a one-half molar quantity of freshly precipitated calcium hydroxide. The calcium hydroxide was made from pure sodium hydroxide and calcium acetate. The supernatant liquid was filtered off to decrease the concentration of ions not needed in the reaction. The calcium hydroxide was added to the sodium hydroxide solution from which the sodium hydrogen sulfide was prepared, before the hydrogen sulfide was introduced but the solution was shaken very little, so that the calcium hydroxide likely did not react much with the hydrogen sulfide. This solution had a very low concentration of ions other than those of sodium, calcium, sulfide, and hydroxide. The next best yield was obtained in run 10D by using a half molar quantity of commercial purified calcium hydroxide with a solution molar in sodium hydrogen sulfide. This was made by saturating a solution containing a half molar quantity of sodium sulfide with hydrogen sulfide. The mixture containing the calcium hydroxide and the sodium hydrogen sulfide was added to a molar quantity of o-dichlorobenzene. This gave a 48% yield instead of 55.6% for the best one. The calcium hydroxide used had been prepared for some time and probably contained considerable carbonate if nothing else.

Using equimolar quantities of o-dichlorobenzene and Baker's sodium hydrogen sulfide, which contained approximately 18% excess alkali, in runs 8A and 8B with half molar quantities of freshly precipitated calcium hydroxide, the yield was cut to 35% and 38% of the theoretical. Run 8B contained 75 ml. more water than 8A, which may account for the higher yield in 8B. These runs also bear out the conclusion that any increase in the concentration of the alkali is harmful. The interference of other ions is shown by the fact that when calcium acetate was used instead of calcium hydroxide in run 7D, where the other conditions were the same as in 8A, the yield was cut to 5.4%. This mixture evidently did not give sufficient reserve alkalinity. When equimolar quantities of o-dichlorobenzene, Baker's sodium hydrogen sulfide and sodium bicarbonate were used in 7B with the same conditions as in 7D except that the bicarbonate was used in place of the calcium acetate, the yield was 29%. When sodium sulfide was used as the source of sulfide, the differences in the action of calcium acetate and the sodium bicarbonate were not as definite. In most cases, the sodium bicarbonate seemed to give better results, but in one case, run 3D, a yield of 40% thianthrene was obtained, using equimolar quantities of o-dichlorobenzene and sodium sulfide with

a half molar quantity of calcium acetate and about a 66 molar quantity of water. The period of heating here was slightly shorter than usual, which may have had something to do with the result obtained.

Several runs were made using sodium sulfide and o-dichlorobenzene to show the effects obtained with various substances added to vary the alkalinity of the solution. When equimolar quantities of sodium sulfide and o-dichlorobenzene with water alone were used, run 2A, the yield of thianthrene was cut to 12%, and when an equimolar amount of sodium hydroxide was added, run 2B, it was cut to 4%.

The effect of acetic acid was also tried. The acid was sealed into test tubes and placed in the steel tubes, which were sealed up before the glass tubes were broken by shaking the steel tubes. This was done to prevent the loss of hydrogen sulfide when the acid came in contact with the sulfide present. When an equimolar quantity of acetic acid was added to equimolar quantities of o-dichlorobenzene and sodium sulfide, a 23% yield of thianthrene was obtained in run 5A. In run 5B, the acetic acid was increased to a one and a half molar quantity, cutting the yield to 12%. In the run 5C, two moles of acetic acid were used to one of sodium sulfide, which gave hydrogen sulfide in the

presence of sodium acetate. This run gave a yield of 4%. In the fourth tube of this series, run 5D, two moles of calcium acetate per mole of sulfide were added, which gave a yield of 30% thianthrene as compared with run 3D which gave a 40% yield when one-half mole of calcium acetate was added for each mole of sulfide.

An excess of alkali and sulfide above the amount theoretically required to react with the o-dichlorobenzene cuts the yield of thianthrene. This is shown in series 7, where 7A and 7C contained 0.2 mole each excess of alkali (sodium bicarbonate and calcium acetate, respectively) and sulfide per mole of dichlorobenzene. The yields were 17% and 4% respectively, which are to be compared with 7B and 7D, containing equivalent quantities, and giving yields of 29% and 5%, respectively. It may be of interest to note that none of this series contained sulfide ion in the reaction mixture after the reaction had occurred.

The amount of water present seems to have considerable effect on the reaction. In run 2C, the 300 ml. tube contained 0.1 mole each of sodium sulfide, sodium bicarbonate and o-dichlorobenzene with 120 ml. of water. The yield of thianthrene was 21%. In 3A, which contained no water but the water of crystallization in $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, but had the same amounts of the other

materials, the yield was cut to 0.1%. This was increased to 4.5% in 6A by doubling the quantities of all the reactants in the tube. Adding 50 ml. of water in run 6C increased the yield to 14%. Adding 100 ml. of water in 6D, keeping the other quantities the same, raised the percentage to 17%. Using one-half mole each of sodium sulfide, sodium bicarbonate and o-dichlorobenzene with no water except the water of crystallization (81 grams), in 6B, the yield was increased to 22%. Thus, it seems that better yields are obtained by loading the tubes more heavily, but there is a limit to the loading of the tubes because if no space is left for gas to form, the tubes will explode. It is well to take no chances for an explosion would be exceedingly dangerous.

Run 9C was made in order to see whether thianthrene would decompose under the conditions of the reaction, although the preparation by various methods at high temperatures would show it to be quite stable. The tube was loaded with 11 grams of fairly pure thianthrene and 50 ml. of sodium sulfide solution containing 0.1 mole of sulfide. After heating for four hours and a quarter at 360° , 8.23 grams of ether-washed crystals of thianthrene were recovered along with 0.88 gram of ether extracted oil. This result shows that thianthrene does decompose slightly under conditions a little more

drastic than those under which the reaction is ordinarily carried out. It may be of interest to note that a deep green color appeared in the residue of the steam distillation, which filtered out. This material did not seem to have any tendency to melt or burn as the usual organic product would do. The decomposition observed may account in part for the low yields obtained, but side reactions present must be partially responsible.

The chloride in o-dichlorobenzene may be replaced by aqueous sulfide solution with hydrogen(-H), hydroxyl(-OH), mercapto or sulfhydryl(-SH) and sulfide (-S-). The isolation of phenol, thiophenol, diphenyl sulfide and thianthrene from the reaction mixture shows this to be true. Some other possibilities are o-chlorophenol, o-chlorothiophenol and chlorobenzene but none of these have been isolated. In 6A, the odor of chlorophenol was noted, however. Also the oil from the steam distillate in 8C contained a fraction of 1.6 ml. boiling from 118-130° which may have contained chlorobenzene (b. p. 132.1°). A 1.9 ml. fraction was obtained from 6C which came over at 135-147°. It is very probable that the last named three compounds react very readily to form more stable products thus making it difficult to isolate them.

M. Tomita (2) prepared diphenylene dioxide

(2) J. Pharm. Soc. Japan, 52, 429-32 (1932)(in German
49-51)

C. A. 26, 4589⁹ (1932)

(m. p. 119°) by the condensation of o-bromophenol.

This compound is similar to thianthrene, having oxygen atoms in place of the sulfur atoms in thianthrene, and might be formed in the preparation of thianthrene. Run 9A was made using an aqueous solution of sodium chlorophenate, to see if the conditions used in these runs might be expected to yield appreciable amounts of diphenylene dioxide. The product obtained after heating for four hours and a quarter at 360°, when vacuum distilled, yielded solids in three fractions. These solids melted at 50-55°, 60-80° and 240-52°, but nothing melting around 119° was found. In addition, the first fraction obtained, contained a solid which took up water from the air very readily, which was soluble in ether and which looked and smelled like phenol. This run indicates the complexity of the products that may be expected from the preparation of thianthrene in the light of the number of products obtained from a minor intermediate byproduct. It indicates also the difficulties that will be encountered in the isolation of all the byproducts in the reaction of sodium hydrogen sulfide and o-dichlorobenzene.

SUMMARY

The most successful method for the preparation of thianthrene was that in which sufficient hydrosulfide was present to react with all of the o-dichlorobenzene (an excess is detrimental) with a sufficient amount of base present to remove the hydrogen chloride as it is formed, but keeping the hydroxide ion concentration low at all times. Calcium hydroxide was used since it does not give a very high hydroxyl ion concentration because of its relative insolubility, but it is a sufficiently strong alkali to remove the hydrogen chloride formed very readily. Best results were obtained when freshly prepared hydrosulfide (made by saturating the sulfide or hydroxide with hydrogen sulfide) and freshly precipitated calcium hydroxide were used. Should uses be developed for thianthrene, this method of synthesis should prove the best commercial method, since all materials used are relatively cheap. However, it probably will not be popular as a laboratory method for the preparation of small quantities unless the necessary equipment is available.

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AUTOBIOGRAPHY

I, Eugene Alton Talley, was born at Glen Allen, Virginia on June 5, 1911. The following year my parents moved to New Kent County, Virginia where they reside at the date of this writing. I attended the public schools of New Kent and Charles City counties, graduating from The Charles City High School in June, 1927. I entered The College of William and Mary in September 1932 and was awarded a Bachelor of Chemistry Degree by that institution in June, 1936. In September, 1936 I entered The University of Richmond on a graduate assistantship and began work leading to a Master of Science degree.

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