A STUDY ON THE REACTION OF SOME

MONOHALOTHIOBENZALDEHYDES WITH

COPPER POWDER

A THESIS

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by

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I should also like to thank the staff of the School of Chemistry
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her unceasing encouragement and infinite patience should properly
be designated co-author of this thesis.

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ABSTRACT

The following compounds were obtained or prepared in order to make the thio derivatives: o, m, and p-chlorobenzaldehyde, o, m, and p-bromobenzaldehyde, and o, m, and p-iodobenzaldehyde.

Each of these compounds was dissolved in ethyl acetate, saturated with hydrogen chloride gas at 0° C., and converted to the corresponding thioaldehyde by bubbling hydrogen sulfide through the solution. Of the nine resulting thioaldehydes, seven are new compounds. Their melting points were determined and their formula confirmed by quantitative analysis for sulfur and halogen. They were shown to exist as trimers by molecular weight studies. Each of them was isolated in two forms which are thought to correspond to the cis and trans stereochemical configurations.

The reactions of each of these nine thiobenzaldehydes was studied by heating them above their melting points in the presence of freshly precipitated copper powder. The resulting dihalostilbenes were purified. Their melting points were determined, they were analyzed for halogen, and their molecular weights were determined to confirm their formula. Only one of the two theoretical stereoisomers was observed. Of the nine stilbenes, four are new compounds.

CHAPTER I

INTRODUCTION

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CHAPTER I

INTRODUCTION

The preparation of thioaldehydes from aldehydes by treatment

with hydrogen sulfide has been known for more than a century, but

the techniques for doing this have varied greatly. The method of

Bost and Constable,[1] which involves passing hydrogen sulfide through

a solution of the aldehyde in concentrated ethanolic hydrogen chloride,

seems to be the most used at the present. The resulting thioaldehyde

is obtained as a trimer. Consequently, stereochemical considerations

show that both a cis and trans configuration is possible.

It has been stated that an extensive study of the monohalo-

thiobenzaldehydes has not been made,[2] and of the nine isomers of the

chloro, bromo, and iodothiobenzaldehydes, only two have been reported,

the o-bromo and the p-bromo.

Various thioaldehydes have been reduced with copper powder,[3]

[1]Bost, R. W. and E. W. Constable, Organic Syntheses, Coll.
Vol. II (New York: John Wiley and Sons, Inc., 1943) p. 610.

[2]Campaigne, E., Chem. Rev., 39, 1 (1946).

[3]Klinger, H., Ber., 10, 1877 (1877).

with iron powder or zinc dust,[4] and with Raney nickel[5] to give the corresponding stilbenes.
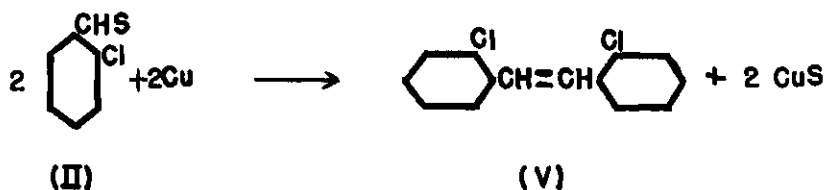
The present work was undertaken in order to prepare the nine monohalothiobenzaldehydes referred to above and to determine some of their physical constants. It was also proposed to study their reaction with copper powder and to determine the physical constants of any stilbenes resulting from this reaction.

Typical of the reactions proposed is that of o-chlorobenz-aldehyde (I) which is treated at 0° C. with hydrogen sulfide in a suitable solvent saturated with hydrogen chloride. The resulting o-chlorothiobenzaldehyde (II) may then be separated into two isomers, cis-tri-o-chlorothiobenzaldehyde (III) and trans-tri-o-chlorothio-benzaldehyde (IV). Heating these products with copper powder gives 2,2'-dichlorostilbene (V).

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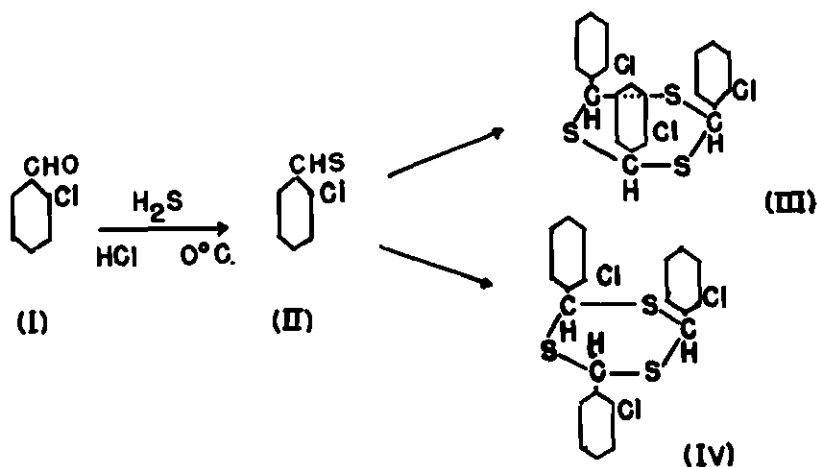
[4]Kopp, K., Ber., 25, 600 (1892).

[5]Hauptmann, H. and B. Wladislaw, J. Am. Chem. Soc., 72, 707 (1950).

$$2 \underset{(II)}{\overset{CHS}{\underset{Cl}{\bigcirc}}} + 2Cu \longrightarrow \underset{(V)}{\overset{Cl}{\bigcirc} CH=CH \overset{Cl}{\bigcirc}} + 2\ CuS$$

Of the nine stilbenes, five have been reported, three of which have been isolated in both _cis_ and _trans_ stilbene configurations.

All of the monohalobenzaldehydes which are used as the starting materials have been reported previously and are easily made.

Thus, this investigation has the following purposes:

1. To study the preparation of each of the three isomers of the chloro, bromo, and iodothiobenzaldehydes.

2. To separate the stereoisomers of each of these and to determine their physical constants.

3. To study the reaction of copper powder on the thiobenzaldehydes and to determind the nature and properties of the main products.

CHAPTER II

HISTORICAL

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HISTORICAL

A. The Monohalothiobenzaldehydes

In 1841 Laurent[1] treated benzaldehyde with ammonium sulfide
and isolated eight compounds, of which one was assigned the formula
$(C_7H_6S)_n$ and melted at 80-90° C. Twenty-five years later, Fleischer[2]
made thiobenzaldehyde from benzal chloride and potassium bisulfide.
He reported white needles melting at 68-70° C. The first trithio-
aldehyde was isolated by Klinger in 1876 when he found both the
alpha and beta forms of trithioacetaldehyde by treating acetaldehyde
with hydrogen sulfide and acidifying the resulting mass.[3]

Baumann and Fromm[4,5] studied the compounds obtained when an
ethanolic solution of benzaldehyde was treated with hydrogen sulfide
and various concentrations of hydrogen chloride. It was noted that
the amount of the beta isomer was greatly increased as the temperature
of the reaction and the concentration of hydrogen chloride increased.
Among the products obtained were the two trimers, α-trithiobenzalde-
hyde, m. p. 166-167° C., and β-trithiobenzaldehyde, m. p. 225-226° C.

[1]Laurent, A., Ann., 38, 320 (1841).

[2]Fleischer, M., Ann., 140, 234 (1866).

[3]Klinger, H., Ber., 9, 1893 (1876).

[4]Baumann, E., and E. Fromm, Ber., 22, 2600 (1889).
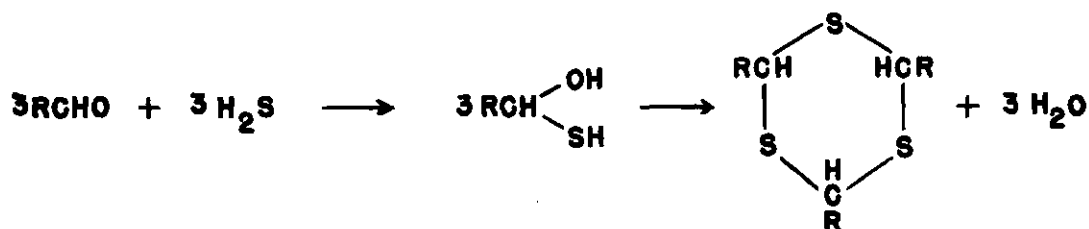
[5]Baumann, E. and E. Fromm, Ber., 24, 1431 (1891).

Another product, previously called ɣ-trithiobenzaldehyde, which melted at 83-85° C., was shown to be the same as Laurent's thioaldehyde which melted at 80-90° C.[6] Suyver[7] also made a careful study of the two isomers, determining the solubilities and extent of conversion of the <u>alpha</u> into the <u>beta</u> form by treatment with catalysts. The <u>alpha</u> form could be prepared in high yield by diluting a 95% ethanolic solution of benzaldehyde with one-fourth its volume of ethanol saturated with hydrogen chloride. After cooling the mixture to -15° C., the whole solution was saturated with hydrogen sulfide, whereupon the <u>alpha</u> isomer precipitated. The <u>beta</u> form was obtained by saturating an ethanolic solution of benzaldehyde with hydrogen chloride and hydrogen sulfide at 0° C. If the α-trithiobenzaldehyde was heated alone, only a small amount of the <u>beta</u> isomer was formed, but if it was heated with acid catalysts such as acetyl chloride, hydrogen chloride, sulfur trioxide, or iodine, it was largely converted to the more stable <u>beta</u> isomer. The <u>alpha</u> isomer is 55 times more soluble in chloroform and 435 times more soluble in benzene than the <u>beta</u> isomer.

Baumann and Fromm[8] have proposed a mechanism for the reaction as one in which hydrogen sulfide is added and water is given off:

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[6]Laurent, A., <u>op. cit.</u>, p. 321.

[7]Suyver, J. F., <u>Rec. trav. chim.</u>, <u>24</u>, 377 (1905).

[8]Baumann, E. and E. Fromm, <u>op. cit.</u>, p.1457.

$$3 \text{RCHO} + 3 \text{H}_2\text{S} \longrightarrow 3 \text{RCH} \underset{\text{SH}}{\overset{\text{OH}}{<}} \longrightarrow$$

[structure: six-membered ring with alternating S and CHR/HCR groups] $+ 3 \text{H}_2\text{O}$

Into a cooled ethanolic solution of o-bromobenzaldehyde,
Wörner bubbled hydrogen chloride gas and hydrogen sulfide, with the
resultant formation of a "white crystalline mass along with some oily
products."[9] The crystals and oil were placed in a boiling ethanol-
chloroform mixture and the product precipitated upon addition of
water. Wörner called the product, a white crystalline powder melting
at 75° C., ∝-tri-o-bromothiobenzaldehyde.

Part of the thioproducts was insoluble in hot ethanol. These
were dissolved in hot benzene and gave white needles on cooling.
They melted at 155° C. and were called β-tri-o-bromothiobenzaldehyde.
Wörner stated that the alpha form could be changed to the beta form
by heating the former in benzene with a little iodine. In his
report he states that the beta form has a molecule of benzene of
crystallization. Quantitative analysis was used to substantiate
his assertions. None of his methods for these determinations is
given. He also stated that accurate yields could not be calculated
because of the unavoidable loss in the purification of the alpha
compound.

[9]Wörner, E., Ber., 29, 139 (1896).

Wörner also prepared p-bromothiobenzaldehyde by a procedure similiar to that given for the ortho isomer. In separating the isomers he observed that the alpha compound was soluble in cold benzene while the beta product was soluble only in hot benzene. The α-tri-p-bromo-thiobenzaldehyde melted at 174° C. while the beta isomer melted at 203° C. The ratio of alpha to beta was approximately 1:4. Wörner also noted that when positive groups are on the benzene ring of aldehydes, treatment gives the two isomeric trithials, but when negative groups are present only the beta form is obtained and the tendency to make high polymers is noted.

Jackson and White[10] treated ethanolic solutions of p-chloro-benzaldehyde, p-bromobenzaldehyde, and p-iodobenzaldehyde with hydrogen sulfide and obtained reddish white gummy compounds. No identification of these was attempted.

B. The Stilbenes

Trithiobenzaldehyde was readily converted to stilbene by Klinger[11] as far back as 1877 by heating it with copper powder. However, other workers[12] prepared substituted stilbenes simply by heating the appropriate thiobenzaldehyde. Benzaldehyde has been treated with sulfur to give stilbene and some benzoic acid, but the

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[10]Jackson, C. L. and J. H. White, Ber., 11, 1042 (1878).

[11]Klinger, H., Ber., 10, 1877 (1877).

[12]Baumann, E. and E. Fromm, op. cit., p. 1441.

thiobenzaldehyde was detected and thought to be an intermediate in the reaction.[13] Kopp found that substituted thiobenzaldehydes heated alone gave tetraarylthiophenes, but when heated with iron powder or zinc dust, the stilbene derivative was the chief product.[14] Two years later, another of his papers[15] stated that the heating of thials far above their melting points gave the respective stilbene derivatives.

Recently Wood used freshly reduced copper powder to react with the various trithiobenzaldehydes to give stilbenes,[16] whereas Hauptman and Wladislaw used "hydrogen-free" Raney nickel to obtain stilbenes from thiobenzaldehydes.[17]

Gill heated 25 g. o-chlorobenzalchloride with 35 g. copper powder and 35 g. sand at 105° C.[18] The primary product was 2,2'-dichlorostilbene which melted at 97° C. The yield was 3 g. or 19% theoretical.

Pascal and Normand[19] found that decomposition by heat of

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[13]Barbaglia, G. A. and A. Marquardt, Ber., 24, 1881 (1891).

[14]Kopp, K., Ber., 25, 600 (1892).

[15]Kopp, K., Ann., 277, 339 (1894).

[16]Wood, J. H., J. A. Bacon, A. W. Meibohm, W. H. Throckmorton, and G. P. Turner, J. Am. Chem. Soc., 63, 1334 (1941).

[17]Hauptman, H. and B. Wladislaw, J. Am. Chem. Soc., 72, 707 (1950).

[18]Gill, A. H., Ber., 26, 649 (1893).

[19]Pascal, P., and L. Normand, Bull. Soc. Chim. Fr., (4)9, 1062 (1911).

4,4'-dichlorobenzaldazine above 284° C. gives 4,4'-dichlorostilbene.
This was crystallized from ethanol and melted at 153.8° C. Bromination
in ether at 0° C. gives a dibromide with a melting point of 195-197° C.
Späth made the product by boiling p-chlorophenyl magnesium bromide and
the ethyl acetal of chloroacetaldehyde for two hours with 40% sulfuric
acid.[20] It crystallized from a chloroform-ethanol mixture to give
plates melting at 177° C. Bromination in chloroform gave a dibromide,
melting point 226-227° C. Heating the vapor of p-chlorotoluene was
the method used by others[21] to obtain 4,4'-dichlorostilbene. They
reported needles from ethanol melting at 168-171° C. Anschütz made
the product by heating "Fumarsaüre-bis-(4-chlor-phenylester)". His
product melted at 170° C.[22]

From the potassium salt of 2-bromophenylnitroacetonitrile,
2,2'-dibromostilbene was made by heating with a dilute solution of
sodium hydroxide in a sealed tube.[23] A low melting form (m. p. 186° C.)
appeared from cool ethanol, while the high melting form (m. p. 206° C.)
was obtained from boiling ethanol. With bromine and glacial acetic
acid the dibromide formed melted at 225° C.

In studying the condensation of ethyl nitrate with p-bromobenzyl-

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[20]Späth, E., Monatsh., 35, 463 (1914); Chemical Abstracts, 8, 2365[8] (1914).

[21]Meyer, H. and A. Hofmann, Monatsh., 38, 141 (1917).

[22]Anschütz, R., Ber., 60, 1321 (1917).

[23]Wislicenus, W. and M. Fischer, Ber., 43, 2239 (1910).

chloride, Wislicenus also made studies of the reaction of the con-
densation products with sodium hydroxide.[24] When sodium p-bromophenyl-
isonitroacetonitrile and sodium p-bromophenylisonitromethane were
heated at 150-156° C. with sodium hydroxide, 4,4'-dibromostilbene
resulted. It crystallized as lustrous plates from ethanol (m. p. 208-
210° C.). In 1927, Anschütz made the same product by heating "Fumar-
saüre-bis-(4-brom-phenylester)" to 240-245° C.[25] His product melted
at 210-211° C.

Meyer and Hofmann found that by heating p- iodotoluene, they
obtained aniline, stilbene, bibenzyl, and 4,4'-diiodostilbene.[26]
The final product was crystallized from ethanol and toluene to give
a sublimable product which did, however, melt at 257-259° C. The
same product has also been prepared by subliming 4,4'-diiodobenzald-
azine.[27]

In most of the preparations reported above, the various authors
differ with respect to the melting point of the same compound.
Therefore some doubt must be cast on either the validity of their
conclusions or the accuracy of their experiments.

[24]Wislicenus, W., Ber., 41, 4121 (1908).

[25]Anschütz, R., loc. cit.

[26]Meyer, H. and A. Hofmann, loc. cit.

[27]Sah, P. P. T., J. Am. Chem. Soc., 64, 1487 (1942).

CHAPTER III

EXPERIMENTAL

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EXPERIMENTAL

A. The Starting Materials

1. o-Chlorobenzaldehyde

This material was obtained from Eastman Kodak Company, No. 737.
Its boiling point was 209-210° C.

2. m-Chlorobenzaldehyde

m-Chlorobenzaldehyde was made from m-nitrobenzaldehyde by the
following procedure adapted from Buck and Ide:[1]

Into a three-liter beaker provided with a stirrer and cooled in
an ice bath was placed 600 ml. concentrated hydrochloric acid and
450 g. (2 moles) stannous chloride. When the temperature had fallen
below 5° C., 100 g. (0.66 mole) of m-nitrobenzaldehyde was added in
one portion. The temperature rose slowly at first - to 30° C. -
and then rose rapidly to 100° C. A cherry red solution resulted
which changed to an orange paste on cooling to room temperature.
Through a funnel, placed so that the stem was below the surface of
the paste, 46 g. (0.76 mole) sodium nitrite in 150 ml. water was
added until the mixture showed a positive starch iodide test for
nitrous acid.

In a five-liter flask, 189 g. (0.75 mole) of powdered copper
sulfate and 161 g. sodium chloride were dissolved in 600 ml. of hot

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[1]Buck, J. S. and W. S. Ide, Organic Syntheses, Coll. Vol. II,
(New York: John Wiley and Sons, Inc., 1943) p. 130.

water. To this was added a solution of 23.16 g. (0.22 mole) of sodium
bisulfite and 27 g. (0.67 mole) sodium hydroxide in 300 ml. water. To
the resulting hot cuprous chloride solution, the diazonium solution
was added. After the solutions were thoroughly mixed, 840 ml. con-
centrated hydrochloric acid was added and the mixture allowed to stand
overnight. It was then subjected to steam distillation until 2.5
liters of distillate was collected. Extraction of m-chlorobenzaldehyde
was effected with two 150 ml. portions of ether. The ether was dried
with calcium chloride and decanted. Fractional distillation gave
the product, a liquid at room temperature, which boiled at 208-210° C.
The yield was 51.1 g. or 55.3%.

3. p-Chlorobenzaldehyde

This material was made from p-chlorotoluene by the following
procedure adapted from Coleman and Honeywell:[2]

Into a five-liter, three-necked flask fitted with a mechanical
stirrer and thermometer, were placed 1150 ml. (1200 g.) glacial acetic
acid, 1225 ml. (1224 g. or 12 moles) acetic anhydride, and 88 ml.
(94 g. or 0.74 mole) p-chlorotoluene. After the flask had been cooled
in an ice bath to 0° C., 170 ml. of concentrated sulfuric acid was
added slowly. Two moles (200 g.) chromium trioxide was added over a
period of four hours such that the temperature did not rise above
10° C. Upon completion of this addition, the contents of the flask

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[2]Coleman, G. H. and G. E. Honeywell, Organic Syntheses, Coll.
Vol. II (New York: John Wiley and Sons, Inc., 1943) p. 442.

were poured into six two-liter beakers, each two-thirds filled with ice. The precipitate which resulted was filtered with suction and washed with cold water until the green color of the chromium ion was not evident. It was next suspended in 1500 ml. of a 2% sodium carbonate solution and stirred. The product was again collected by filtration, washed with cold water, and dried in a desiccator. Acidification of the filtrate recovered the p-chlorobenzoic acid. Recrystallization from ethanol and ether yielded 25.2 g. of the acid.

The solid p-chlorobenzal acetate was hydrolyzed according to the formula: "For every 45 g. use 100 ml. water, 150 ml. ethanol, and 10 ml. concentrated sulfuric acid." Thus for 142 g. of the acetate, 315 ml. water, 473 ml. ethanol, and 32 ml. concentrated sulfuric acid were used. This was refluxed for six hours. After cooling, the solid was removed by suction filtration. The filtrate was diluted with water as long as product precipitated, and this was also removed by filtration. The aldehyde was recrystallized from ethanol-water mixture, giving a yield of 40.0 g. or 38.5% theoretical. The melting point was 48-49° C.

4. o-Bromobenzaldehyde

o-Bromobenzaldehyde was made from o-bromotoluene by the method of Coleman and Honeywell:[3]

In a two-liter, three-necked flask, a stirrer, dropping funnel,

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[3]Coleman, C. H. and C. E. Honeywell, op. cit., p. 89.

and a reflux condenser were fitted. A thermometer was suspended in the reflux condenser and the top of the condenser was connected to a sodium hydroxide gas trap. One-hundred grams (0.58 mole or 70.3 ml.) of o-bromotoluene was placed in the flask and heated to 105° C. An unfrosted 100 watt tungsten lamp was mounted so that it illuminated the inside of the flask. Through the funnel 62 ml. (1.23 moles or 197 g.) of bromine was dropped into the solution, half the total amount in 1.5 hours and the remaining in 7.5 hours since faster addition than this caused loss of bromine through vaporization. When all the bromine was added, the temperature was increased to 150° C., after which the mixture was allowed to cool. The product was mixed with 200 g. of powdered calcium carbonate and 300 ml. water and re-fluxed for 15 hours. Steam distillation gave a water insoluble yellow liquid. It was separated and stirred with a 40% ethanolic sodium bisulfite solution. The resulting white precipitate was filtered and again steam distilled. The resulting faint yellow liquid, subjected to fractional distillation, yielded 53.6 g. or 49.5% theoretical. The melting point was 20-22° C.; the boiling point 230-234° C.

5. m-Bromobenzaldehyde

m-Bromobenzaldehyde was prepared by Ralph H. Earle, of this laboratory, from m-bromotoluene by chromic acid oxidation. The product distilled at 119-125° C. at 11 mm.

6. p-Bromobenzaldehyde

This product was prepared by the method of Henry Stephen

with no deviations from his method.[4] The yield was less than that expected – 69.3%, probably because none of the intermediate products were purified. The product melted at 55–56° C.

7. o-Iodobenzaldehyde

This material was a student preparation of unknown origin. It was obtained in a very crude form and recrystallized from alcohol-water mixture until the melting point was 34–36° C.

8. m-Iodobenzaldehyde

m-Iodobenzaldehyde was made by Ralph H. Earle from m-nitro-benzaldehyde by a method similiar to that used to make m-chlorobenz-aldehyde mentioned previously. The melting point was 53–55° C.

9. p-Iodobenzaldehyde

p-Toluidine hydrochloride was made by using 40 g. of a student preparation of p-toluidine in 140 ml. concentrated hydrochloric acid and adding enough boiling water to effect solution.[5] It was then cooled to 0° C. and a solution of 28 g. of sodium nitrite in 300 ml. ice water was stirred into the mixture. Stirring continued and more sodium nitrite was added until the mixture gave a persistant test for nitrous acid with starch iodide paper. While stirring manually, 62 g. potassium iodide dissolved in sufficient water to effect solution was added to the mixture. A deep brown solid resulted. This was allowed to stand overnight and then removed by filtration. The

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[4]Stephen, H., J. Chem. Soc., 127, 1874 (1925).

[5]Cumming, W. M., I. V. Hopper, and T. S. Wheeler, Systematic Organic Chemistry (London: Constable and Company, Ltd., 1931) p. 341.

precipitate was recrystallized from ethanol. The product, p-iodotoluene, was highly colored, hence many recrystallizations were necessary to give the final yield of 30.2 g., or 37.2% theoretical, of pure material.

p-Iodotoluene was converted to the aldehyde in the same manner as the p-chlorotoluene previously mentioned was converted to p-chloro-benzaldehyde. The yield of p-iodobenzaldehyde resulting was 11.2 g. or 36.5% theoretical and the melting point was 76-77° C.

B. The Monohalothiobenzaldehydes

1. o-Chlorothiobenzaldehyde

Ten ml. of o-chlorobenzaldehyde was dissolved in 125 ml. of absolute ethyl acetate in a 300 ml. Erlenmeyer flask and cooled to less than 2° C. Hydrogen chloride gas was bubbled directly from a tank into the solution until saturation was reached. Saturation was indicated by the failure of the solution to rise in the admitting tube when the gas flow was discontinued. As soon as saturation was complete, hydrogen sulfide gas was bubbled into the solution while hydrogen chloride gas continued to be introduced at about the same rate. If the hydrogen sulfide was bubbled too fast or far exceeded the rate of admission of hydrogen chloride, the solution became sky blue in color due to colloidal sulfur. This could be corrected by slowing down the rate of hydrogen sulfide entry. The exact rate of administration of these gases was not measured, but after about two hours the process was discontinued. Since there was only a small amount of precipitate present, the flask was placed under a hood and allowed to stand overnight, or until the solution had warmed to room

temperature and all the excess gases bubbled off. Crude o-chloro-
thiobenzaldehyde, the white powdery precipitate which appeared, was
removed by filtration, washed with diethyl ether, and dried in a
desiccator.

The filtrate was placed back in the original flask, and after
cooling, was saturated with hydrogen chloride. The above process was
repeated for one hour. On warming, another precipitate appeared, which
was filtered, washed with ether, dried, and added to the crude o-chloro-
thiobenzaldehyde.

The theoretical yield was 12.5 g. The first precipitation
gave 10.8 g. or 87.3%, and the second gave 1.5 g., bringing the total
yield to 98.7%. It is thought that the process can be continued on
the filtrate to approach 100% yield.

If absolute ethanol is used as a solvent, there results a
smaller initial yield (42.8%). However, successive treatments bring
this also to a quantitative yield. Whereas the ethyl acetate solvent
gives a uniform powdery precipitate, ethanol gives translucent gummy
masses as well as the powder. These masses have been shown to be
almost pure β-tri-o-chlorothiobenzaldehyde.

Quantitative analyses were performed on the crude product using
a Parr electric ignition bomb. One gram of sucrose, one Parr measure
of sodium peroxide, and approximately 0.25 g. crude o-chlorothiobenz-
aldehyde was ignited. The residue was dissolved in 200 ml. distilled
water and the bomb washed thoroughly, placing the washings in the
solution with the residue. Barium nitrate solution removed the

sulfur as barium sulfate. This was separated by gravity filtration through Swedish filter paper, and after washing with dilute (1:4) nitric acid and igniting, the barium sulfate was weighed.

The filtrate was heated to boiling and 2 ml. of hydrazine hydrate was added to reduce all chlorine present to chloride ions. On cooling, a concentrated solution of silver nitrate was added to precipitate the chloride as silver chloride. This was filtered on a weighed, sintered glass filter and dried in an oven at 90° C. to a constant weight.

Analysis:

Theoretical % S: 20.47   Observed: 21.10

Theoretical % Cl: 22.64   Observed: 22.90

Molecular weight determinations by freezing point depression were attempted in benzene and ethylene dibromide, but the product was insufficiently soluble to give good results. Boiling point elevation in carbon tetrachloride was not satisfactory, but ethyl acetate gave fair results by this method. The elevation constant used was 2.77. The theoretical molecular weight for a trimer of o-chlorothiobenzaldehyde is 469.9. A boiling point apparatus using a Cottrell pump was modified so that a Beckmann thermometer could be bathed with the boiling liquid and yet use only 5 ml. of solvent. The observed molecular weight was 461.3 indicating that the trimer was present.

Fractional crystallization of the crude product in ethyl acetate was done to separate the isomers. While this met with some degree of success, because of the time involved it was abandoned

in favor of separation by other means.

Some of the crude thioaldehyde was placed in boiling ethanol (95%) for five minutes and the solution filtered hot. The filtrate, on addition of water and cooling, yielded a white crystalline product, α-tri-o-chlorothiobenzaldehyde, which, after several recrystallizations, melted at 162.7-163.5° C. As in all cases, melting points were effected using an electric block and Anschütz thermometers. Correction for stem exposure was applied.

The residue was dissolved in boiling benzene, and after several recrystallizations, gave a product of white needles which melted at 223.9-224.6° C. This was the β-tri-o-chlorothiobenzaldehyde.

The alpha form was found to be soluble in benzene, ethyl acetate, carbon disulfide, dioxane, and hot 95% ethanol. It was slightly soluble in hot ligroin, hot petroleum ether, hot carbon tetrachloride, and ethylene dibromide. The beta or high melting form was soluble in hot benzene, ethyl acetate, carbon disulfide, and dioxane. It was slightly soluble in hot ligroin, hot petroleum ether, and hot carbon tetrachloride. It was insoluble in diethyl ether, 95% ethanol, water, and 10% sodium hydroxide.

2. m-Chlorothiobenzaldehyde

This compound was prepared using ethyl acetate as a solvent in a manner exactly analogous to the preparation of the o-chloro isomer. The only difference noted was that on each of three runs, the crude mixture resulting had a slight pink color and small

monoclinic crystals could be seen sparkling throughout the powder. The yield, based on the collection of the precipitate only two times, was 91.2%.

Analysis:

Theoretical % S: 20.47   Observed: 20.52

Theoretical % Cl: 22.64   Observed: 22.73

Molecular weight by boiling point elevation of ethyl acetate gave a value of 463.6. Theoretical is 469.9.

Separation of the stereoisomers by solubility difference in ethanol and benzene as described above gave the α-tri-m-chlorothiobenzaldehyde with a melting point of 115.8-116.4° C., and the β-tri-m-chlorothiobenzaldehyde with a melting point of 163.0-163.2° C.

3. p-Chlorothiobenzaldehyde

This compound was prepared in a manner analogous to that used for the o-chloro isomer. Since 10 g. p-chlorobenzaldehyde did not dissolve in the 150 ml. ethyl acetate, 50 ml. absolute ethanol was added to effect solution. As soon as hydrogen chloride gas was introduced, a fine granular material separated out. The procedure was continued, and after hydrogen sulfide was added, the precipitate changed from granular to fluffy. Collection of two successive precipitations gave a yield of 94.3%.

Molecular weight determinations by boiling point elevation of ethyl acetate gave a value of 459.6. The theoretical molecular weight of the trimer is 469.9.

Analysis:

Theoretical % S: 20.47   Observed: 20.09

Theoretical % Cl: 22.64   Observed: 22.20

Separation of isomers by solubility difference in ethanol and
benzene gave α-tri-p-chlorothiobenzaldehyde melting at 137.4-138.2° C.,
and the β-tri-p-chlorothiobenzaldehyde melting at 189.6-190.4° C.

4. o-Bromothiobenzaldehyde

o-Bromothiobenzaldehyde was prepared using 10 ml. o-bromo-
benzaldehyde to 100 ml. absolute ethyl acetate, and obtained as in
the preparation of the o-chloro isomer. The blue color of colloidal
sulfur seemed to appear much more readily with this bromo isomer.
The reaction was discontinued after one hour since the large quantity
of precipitate interfered with the introduction of gases. The yield
for two precipitations in this manner was 91.6%.

Analysis:

Theoretical % S: 15.94   Observed: 15.83

Theoretical % Br: 39.51   Observed: 39.51

Molecular weight by boiling point elevation of ethyl acetate
was 588.2. Theoretical is 603.3.

Separation of the stereoisomers was more successful in this
case by placing the crude product in cold benzene, allowing it to
stand overnight, and filtering. Evaporation of the filtrate at room
temperature gave white crystals which needed only one recrystallization
to give α-tri-o-bromothiobenzaldehyde which melted at 186.0-186.7° C.

The residue from the filtration was placed in boiling benzene to which a little iodine had been added. Cooling yielded needles of β-tri-o-bromothiobenzaldehyde, which after washing twice with ether and drying, melted at 220.6–221.0° C.

5. m-Bromothiobenzaldehyde

m-Bromothiobenzaldehyde was prepared by using 10ml. of m-bromobenzaldehyde in 100 ml. ethyl acetate as in the preparation of the o-chloro isomer. The runs lasted one and one-fourth hours. The yield for two precipitations was 87.6%.

Analysis:

Theoretical % S: 15.94   Observed: 15.62

Theoretical % Br: 39.51   Observed: 39.08

Molecular weight by boiling point elevation of ethyl acetate was 591.6; theoretical is 603.3.

Separation of the stereoisomers by use of ethanol and benzene gave α-tri-m-bromothiobenzaldehyde with a melting point of 141.6–142.3° C., and β-tri-m-bromothiobenzaldehyde with a melting point of 177.3-177.9° C.

6. p-Bromothiobenzaldehyde

Five grams of p-bromobenzaldehyde was dissolved in 100 ml. ethyl acetate and subjected to treatment in the same manner as the o-chloro isomer. The large volume of solvent used was merely as a convenience to the size of the apparatus. The runs lasted for two hours, and the precipitate appeared only on standing - probably due to

the excessive volume of solvent. The yield for two precipitations was 88.7%.

After the final precipitation, the filtrate was allowed to evaporate at room temperature. Needle-like crystals appeared in a small amount of brown oil which gave a positive aldehyde test with Fuschin aldehyde reagent, and a positive test for both organic and inorganic sulfur. The oil and crystals were placed in three times their volume of glacial acetic acid, and allowed to stand. After three days, the oil had gone into solution and the thioaldehyde was filtered off. This additional yield of 0.2 g. was not added to the yield stated above.

Analysis:

Theoretical % S: 15.94   Observed: 15.71

Theoretical % Br: 39.51   Observed: 38.98

Molecular weight determination by boiling point elevation of ethyl acetate was 596.1; theoretical is 603.3.

Separation of the stereoisomers by use of ethanol and benzene gave the α-tri-p-bromothiobenzaldehyde melting at 182.2-183.0° C., and the β-tri-p-bromothiobenzaldehyde melting at 205.3-205.9° C. The beta form was purified easily by addition of a little iodine to the benzene from which it was crystallized.

7. o-Iodothiobenzaldehyde

Five grams of o-iodobenzaldehyde was dissolved in 100 ml. ethyl acetate and treated in the same manner as the o-chloro isomer. The volume of solvent used was for the convenience of the apparatus.

The runs lasted for two hours and after standing gave a yield of 91.4% for two precipitations.

Analysis was performed in a darkroom under photographic conditions because of the rapid decomposition of the silver iodide formed in the analysis for iodine.

Theoretical % S: 12.94   Observed: 12.61

Theoretical % I: 51.16   Observed: 49.90

Molecular weight determinations by boiling point elevation of ethyl acetate was 738.7; theoretical for the trimer is 747.4.

Separation of the stereoisomers by cold benzene gave α-tri-o-iodothiobenzaldehyde which melted at 188.7-189.6° C. Boiling benzene with a little iodine dissolved the material remaining to give the β-tri-o-iodothiobenzaldehyde on cooling. This melted at 202.0-202.6° C. In all of the iodo isomers, the alpha form comprised less than one-twentieth of the total thioaldehyde.

8. m-Iodothiobenzaldehyde

Five grams of m-iodobenzaldehyde was dissolved in 100 ml. ethyl acetate and treated in the same manner as the o-chloro isomer. The runs lasted for two hours and gave a yield for two precipitations of 84.6%.

Analysis:

Theoretical % S: 12.94   Observed: 12.73

Theoretical % I: 51.16   Observed: 50.29

Molecular weight determinations by boiling point elevation of ethyl acetate was 740.3; theoretical is 747.4.

Separation of the stereoisomers by cold benzene gave the
α-tri-m-iodothiobenzaldehyde which melted at 196.2-197.4° C.
By using hot benzene with iodine, the β-tri-m-iodothiobenzaldehyde
was obtained having a melting point of 212.6-213.1° C.

9. p-Iodothiobenzaldehyde

This product was made by dissolving 5 g. p-iodobenzaldehyde
in 100 ml. ethyl acetate and treating the solution in the same manner
as the o-chloro isomer. However, the run lasted for one and one-half
hours. The yield for two precipitations was 78.7%.

Analysis:

Theoretical % S: 12.94   Observed: 12.80

Theoretical % I: 51.16   Observed: 50.03

Molecular weight determination by boiling point elevation of
ethyl acetate was 736.5; theoretical is 747.4.

The stereoisomers were separated by different solubilities in
hot and cold benzene as outlined above. The γ-tri-p-iodothiobenz-
aldehyde melted at 113.6-114.8° C. and the β-tri-p-iodothiobenzalde-
hyde melted at 211.3-212.1° C.

TABLE I

THE MONOHALOTHIOBENZALDEHYDES: SUMMARY OF DATA

Name of Compound	Percentage yield ++	Melting points: alpha isomer	beta isomer
o-Chlorothiobenzaldehyde	98.7	162.7-163.5 +	223.9-224.6 +
m-Chlorothiobenzaldehyde	91.2	115.8-116.4 +	163.0-163.2 +
p-Chlorothiobenzaldehyde	94.3	137.4-138.2 +	189.6-190.4 +
o-Bromothiobenzaldehyde	91.6	186.0-186.7	220.6-221.0
m-Bromothiobenzaldehyde	87.6	141.6-142.3 +	177.3-177.9 +
p-Bromothiobenzaldehyde	88.7	182.2-183.0	205.3-205.9
o-Iodothiobenzaldehyde	91.4	188.7-189.6 +	202.0-202.6 +
m-Iodothiobenzaldehyde	84.6	196.2-197.4 +	212.6-213.1 +
p-Iodothiobenzaldehyde	78.7	113.6-114.8 +	211.3-212.1 +

+ New compounds

++ Yield based on collecting compound from two successive precipitations of the same solution.

C. The Stilbenes

Copper powder was prepared by dissolving 160 g. (1 mole) of copper sulfate in sufficient water and adding 16.5 g. (0.25 mole) zinc dust. The resulting precipitate, finely divided copper, was filtered off, washed twice with 95% ethanol and stored, slightly wet with ethanol, under nitrogen. It was not used if it was more than a week old.

Ten grams of o-chlorothiobenzaldehyde, alpha and beta isomers in the crude mixture, were placed in a 250 ml. three-necked flask with 20 g. fresh copper powder. The flask was equipped with a copper metal stirrer, an inlet through which nitrogen gas was admitted slowly, and an outlet for the nitrogen such that any material which should distil might be caught in an ice-cooled test tube.

With constant stirring, the mixture was heated with a Glas-Col heater until the white thioaldehyde melted. If the reaction was overheated, i.e., if it was heated more than about 20° above the melting point of the thioaldehyde, discoloration of the final material and some decomposition occurred. The material was heated for one hour. During the process, some of the residual ethanol on the copper powder came over into the tube for receiving distillate, and with it came about 3 ml. of a yellow oil. Small needles were also seen.

The copper-containing residue was boiled in 400 ml. benzene, filtered and extracted with 100 ml. portions of benzene until the benzene was no longer discolored. The filtrates were combined, de-

colorized by boiling with charcoal, and the benzene was allowed to evaporate from a large watch glass placed in the draft of a hood. There resulted an oily mass.

The oily mass was placed in a 500 ml. beaker and boiled in 350 ml. 95% ethanol. The insoluble matter was filtered off and discarded, and water added dropwise to the filtrate of boiling alcohol until a white cloud which formed just disappeared. The solution was then placed immediately in the freezing section of the refrigerator. A white powder, 2,2'-dichlorostilbene, resulted which weighed 6.2 g., giving a 78.2% yield.

The compound added bromine in chloroform, indicating a double bond. Qualitative tests showed the presence of chlorine while tests for organic sulfur were negative.

Recrystallization was attempted from toluene, benzene, diethyl ether, benzene-ethanol, xylene, dioxane, petroleum ether, and ethylene dibromide. In each case an oil resulted. However, if a solution of the compound in benzene was heated until the solution was saturated, placed in a closed container, and allowed to stand, very large (3 cm.) hexagonal crystals of the compound could be formed. These, however, were far from pure.

While ethanol-water was not always satisfactory for recrystallization, it was the best method found. Several recrystallizations gave a light tan crystalline product with a melting point of 96.4-96.8° C.

The yellow oil in the distillate of the original reaction was separated from the ethanol which had come over in the test tube with

it with a separatory funnel. It gave a positive test for an aldehyde with Fuschin aldehyde reagent. It also gave a positive qualitative test for sulfur. The components became polymeric as the liquid was heated and could not be separated by fractional distillation. Sodium peroxide had no effect on its polymerization. Washing the oil repeatedly with absolute ethanol gave a white mass which was found impossible to purify. It melted at 119-196° C.

The needles in the distillate had a melting point of 93-95° C., without purification. Using the method of mixed melting points, this product was shown to be the 2,2'-dichlorostilbene.

Bromine was added to the compound in chloroform solution and gave a dibromide melting at 221.3-221.8° C. Bromine added to the needles in the distillate to give a very small amount of a compound whose melting point was 221.2-222.0° C. A mixed melting point showed these two dibromides to be the same product.

Quantitative analysis for chlorine was performed on 2,2'-dichlorostilbene using a Parr bomb as in the analysis for the thioaldehydes.

Theoretical % Cl: 28.41   Observed: 27.73

Molecular weight was determined by the boiling point elevation of carbon tetrachloride solution (K_b: 5.03) in the same apparatus used in the thioaldehyde determinations. Theoretical is 249.13; observed was 240.2.

Attempts to distill the stilbene were not very successful because of the tendency to decompose on overheating. It boiled at

155-157° C. at 1 mm.

All the other thioaldehydes were reacted in the same manner using at least 4 moles of copper powder to one mole of the thioaldehyde. The differences observed were insignificant, except in the case of 4,4'-diiodostilbene mentioned below. Therefore all the pertinent data is summarized in Table II.

4,4'-Diiodostilbene is easily sublimable, so that the reaction flask was heated more cautiously, and the collection tube was immersed in a dry ice-acetone bath. In spite of this, some loss was unavoidable.

TABLE II

THE STILBENES: SUMMARY OF DATA

Compound	Percentage yield	Melting point	Molecular Weight Calc.	Obs.	Analysis for halogen Calc.	Obs.
2,2'-Dichlorostilbene	78.2	96.4-96.8	249.13	240.2	28.41	27.73
3,3'-Dichlorostilbene +	88.0	93.8-94.6	249.13	238.4	28.41	28.11
4,4'-Dichlorostilbene	89.4	154.0-154.4	249.13	242.9	28.41	27.91
2,2'-Dibromostilbene	64.2	108.0-108.4	338.05	329.2	47.28	46.91
3,3'-Dibromostilbene +	83.4	52.8-53.4	338.05	336.1	47.28	47.03
4,4'-Dibromostilbene	88.7	205.7-206.5	338.05	333.9	47.28	46.82
2,2'-Diiodostilbene +	47.3	149.5-150.1	432.06	426.3	58.75	57.42
3,3'-Diiodostilbene +	61.6	91.4-92.0	432.06	418.7	58.75	57.71
4,4'-Diiodostilbene	62.5	259.2-260.0	432.06	428.6	58.75	57.25

+ New compounds

CHAPTER IV

DISCUSSION OF RESULTS

CHAPTER IV

DISCUSSION OF RESULTS

The advantage of using absolute ethyl acetate as a solvent for the conversion of the benzaldehyde to the thiobenzaldehyde rather than absolute ethanol is that it gives the more nearly reproducible results. This may be due to the fact that ethyl acetate has a lower concentration of hydrogen chloride in a saturated solution than does ethanol, and thus the saturation of ethyl acetate is more readily attainable. Baumann and Fromm[1] have stated that the amount of the beta stereoisomer is increased as the concentration of hydrogen chloride is raised. This would also explain the presence of the masses of beta compound in the ethanol solution which do not appear in the ethyl acetate solution.

When the precipitate resulting from the conversion of the aldehyde to the thioaldehyde is removed and the filtrate subjected to the same treatment again, more precipitate appears. This was repeated five times with the o-chloro isomer, each time with a small amount of precipitate resulting. Generally, two precipitations give better than an 85% yield, and as the process continues, a quantitative yield is approached. It will be noted that the yields of the meta isomers for the two precipitations are lower than for the ortho and

[1]Baumann, E. and E. Fromm, Ber., 24, 1431 (1891).

para ones; this is indicative only of the rate of the reaction since all yields approach 100%.

In separating the thioaldehyde stereoisomers, the method is purely empirical, since all of them respond to either method. The chloro isomers seemed best separated by removing the alpha form with ethanol and recrystallizing the beta form from benzene. The bromo and iodo isomers seemed to respond to separation of the alpha form by cold benzene and recrystallization of the beta form from hot benzene to which a little iodine had been added. Wörner observed[2] that iodine converted any alpha present to the beta form. Thus the beta form was more readily obtained in a high state of purity.

The low melting form of the thio compound probably corresponds to the cis configuration stated in the proposed reaction, but since nothing was done to demonstrate this, the lower melting isomer was called the alpha form, and the high melting isomer, representing the trans configuration, was called the beta form. These can be determined, however, by oxidizing the trimer to a trisulfone.[3] Treatment of the trisulfone with methyl iodide and sodium hydroxide adds two methyl groups in the case of the cis configuration and three in the case of the trans configuration.

In the case of the preparation of the p-bromothiobenzaldehyde, the oil which appeared on evaporation of the solvent after the second

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[2]Wörner, E., Ber., 29, 139 (1896).

[3]Baumann, E. and R. Camps, Ber., 39, 69 (1890).

filtration seemed very similiar to the liquid which was distilled in making 4,4'-dibromostilbene. In the latter case the oil was saturated with the stilbene. Both liquids give positive tests for the presence of organic sulfur and the aldehyde group. Both resisted fractionation by distilling, and both polymerized on heating. Baumann and Fromm,[4] in making the thioderivatives of some acetaldehydes, observed that the trimeric ring could be opened through the addition of water giving $HS-CH_2-S-CH_2-S-CH_2OH$. They also reported such compounds as $HS(CH_2S)_xH$, $HS(CH_2O)_x(CH_2S)_yH$, and $HO(CH_2O)_x(CH_2S)_yH$ as being present. It is believed that both the oils mentioned consist of polymers such as these. Their presence can easily be accounted for in the case of the thioaldehydes, and in the case of the stilbenes, their presence would be expected since the copper powder was probably contaminated by both water and copper oxide.

Wörner has said that the **beta** isomer of the thioaldehyde has a molecule of crystallization of benzene when it is recrystallized from that solvent. Molecular weight studies in ethyl acetate and benzene by boiling point elevation give no indication of the additional benzene molecule. It is not clear from Wörner's work why he thought his analyses indicated this.

There was only one form of the stilbenes observed. This is

[4]Baumann, E., and E. Fromm, op. cit., p. 1457.

[5]Wörner, E., loc. cit.

probably the trans form since the cis form of ethylenic linkages is generally supposed to be the less stable of the two. Studies using Fischer-Hirschfelder models show that in the case of the 2,2'-dichlorostilbene, the cis form is unlikely due to steric hindrance of the chlorine and the hydrogen on the ethylenic carbon. In the 2,2'-dibromo and 2,2'-diiodo stilbenes, the cis form is impossible in a stable molecule. While the meta and para substituted forms do not show this same hindrance, the fact that unsubstituted cis-stilbene is less stable than trans-stilbene suggests that these products also may exhibit this instability. Probably the prolonged heating of the material in making the stilbene would convert any of the cis form to trans. In addition, the boiling benzene in which the product was extracted would also tend to convert any cis present to the trans form.

CHAPTER V

SUMMARY

CHAPTER V

SUMMARY

The following compounds were obtained or prepared in order to make the thio derivatives: o, m, and p-chlorobenzaldehyde, o, m, and p-bromobenzaldehyde, and o, m, and p-iodobenzaldehyde.

Each of the above compounds was converted to the corresponding thiobenzaldehyde. Of these nine, seven are new compounds. Their melting points were determined, and their formula confirmed by quantitative analysis for the sulfur and halogen. They were shown to exist as trimers by molecular weight studies. Each of them was isolated in two forms which are thought to correspond to the cis and trans stereochemical configurations.

The reactions of each of these nine thiobenzaldehydes with copper powder was studied, and the resulting stilbenes were purified. Their melting points were determined, they were analyzed for halogen, and their molecular weights were determined to confirm their formula. Only one of the two theoretical stereoisomers was observed. Of the nine stilbenes, four are new compounds.

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