TABLE II

PREPARATION OF SOME PHENYL DISUBSTITUTED MALONATES

Disubst. malonic acid[a]	M.p. of acid, °C.	Acid chloride[b]			Diphenyl ester[c]				Anal. of phenyl ester			
		Yield, %	B.p., °C.	Mm.	Yield, %	B.p., °C.	Mm.	M.p., °C.	Calcd. C	Calcd. H	Found C	Found H
Dimethyl[e]	182	90	96–104	150	75	215–225	18	99	71.81	5.67	71.56	5.71
Diethyl[d,f]	125	72	130–135	120	73	159	1–2	...				
n-Butylethyl[d,g]	110	90	145–155	40	80	176–178	1–2	57	74.09	7.11	73.90	7.15
Di-*n*-butyl[d,h]	160	75	160–178	85	66	191–192	1–2	49	74.74	7.84	75.00	7.61
1,1-Dicarboxycyclohexane[i]	182	95	158–170	115	54	.....	..	87	74.07	6.22	73.65	6.40
Phenylethyl[d,j]	...	...	176–185	60	60	190–215	1	78–80	76.50	5.60	76.67	5.56

[a] Obtained by alkaline hydrolysis of ethyl ester. [b] Prepared by action of PCl_5 on the acid. [c] Prepared by treating acid chloride with dry phenol. [d] Obtained as ethyl ester from Eastman Kodak Co. [e] W. Konigs and J. Hoerlin, *Ber.*, **26**, 2049 (1893), m.p. of acid 192–193°. Acid chloride: Franchimont, *Rec. trav. chim.*, **4**, 207 (1885), b.p. 165°. [f] C. Daimler, *Ann.*, **249**, 173 (1888), m.p. of acid, 125°; acid chloride, b.p. 196–197°, E. Fischer and A. Dilthey, *Ber.*, **35**, 844 (1902); phenyl ester, b.p. 215–225° (15 mm.), "Beilstein," Vol. VI (suplmt.), p. 88. [g] Raper, *J. Chem. Soc.*, **91**, 1837 (1907), m.p. of acid, 116°. [h] P. A. Lenene and L. H. Cretcher, *J. Biol. Chem.*, **33**, 505 (1918), m.p. of acid, 163°. [i] A. I. Vogel, *J. Chem. Soc.*, 1487 (1929), m.p. of acid, 179.5°. [j] Tassilly, Belot and Descombs, *Compt. rend.*, **186**, 149 (1928), m.p. of acid, 182.5°.

Equivalent amounts of phenol and the desired acid chloride were heated at about 200° until evolution of hydrogen chloride was virtually complete. The product was purified generally by distillation at reduced pressure followed by recrystallization from a suitable solvent, such as alcohol. Table II lists the phenyl esters prepared and some of their properties along with analytical data.

Since the preparation of phenyl malonates through the route of the acid chlorides involves several steps and is rather tedious, some attempts were made to prepare them by a shorter route. Therefore, the action of phenol on ethyl malonate was studied. In one experiment ethyl malonate was heated at 185° with a large excess of phenol for about 30 hours in the presence of a small amount of litharge. Some low boiling material was removed but this was found to be mostly ethyl acetate along with a little ethanol. Distillation of the reaction mixture yielded no phenyl malonate. This reaction was repeated using concentrated sulfuric acid as catalyst but with the same results. It was therefore concluded that phenyl esters of malonic acids could not be obtained conveniently by this method.

Preparation of Polymers.—The polymers listed on Table I were prepared by the fusion of equivalent quantities of phenyl ester with diamine. Equivalent quantities of diamine and phenyl ester were accurately weighed into glass tubes which were evacuated and then sealed. The sealed tube with the reactants was then heated for a specified length of time at 200–210°. After cooling, the tube was opened and attached to an apparatus so designed that the reactants could be heated in an atmosphere of nitrogen or under reduced pressure. The reactants were then heated in an atmosphere of nitrogen at atmospheric pressure at a temperature of 260–280° for a given length of time, after which the pressure was gradually reduced to 2–3 mm. Agitation was effected by bubbling nitrogen through a capillary tube into the polymer during the reduced pressure cycle. The polymerization conditions for each polymer prepared are given on Table I.

WILMINGTON, DELAWARE RECEIVED NOVEMBER 7, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Studies on Thioaldehydes. I. The Monohalothiobenzaldehydes

BY JAMES A. STANFIELD AND LESLIE B. REYNOLDS, JR.

RECEIVED OCTOBER 15, 1951

Conversion of all of the monochloro-, monobromo- and monoiodobenzaldehydes to the thiobenzaldehyde analogs has been effected using hydrogen sulfide. Each thiobenzaldehyde has been isolated in two geometrical forms. Formation of symmetrically substituted stilbenes by heating the thioaldehyde with freshly precipitated copper powder has been achieved in satisfactory yields.

The simple thioaldehydes have, for the most part, been investigated rather thoroughly. In particular, Wörner[1] has studied these compounds. However, little success has been realized in the study of the conversion of halobenzaldehydes to the corresponding halothiobenzaldehydes.[2] As a result only two halothioaldehydes have been prepared, these being obtained from the corresponding benzaldehyde derivative as white crystalline masses along with some oily products.[1] Conversion of aryl thioaldehydes into stilbene analogs and homologs by heating with copper powder has been reported previously.[3] By use, therefore, of these reactions, it was considered possible to prepare from the halobenzaldehydes the corresponding symmetrical halostilbene derivatives in satisfactory yields. Several of these stilbenes have not been reported. The reactions are shown in the formula chart.

Although several methods are available, the one most widely used for preparing thiocarbonyl compounds involves the action of dry hydrogen sulfide on the corresponding oxo-carbonyl compound.[4] Usually the oxo-compound is dissolved in a suitable solvent such as alcohol or ethyl acetate, the solution saturated with dry hydrogen chloride, and a stream of hydrogen sulfide passed into the solution. The thio-compound usually precipitates. It should be mentioned that the monomeric thioaldehyde is not isolated, but only the trimer or a linear polymer is obtained. No pure monomeric aryl thial has been described. The resulting halothiobenzaldehyde should be obtainable, therefore, in two iso-

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[1] E. Wörner, *Ber.*, **29**, 139 (1896).

[2] C. L. Jackson and J. H. White, *ibid.*, **11**, 1042 (1878).

[3] (a) J. Klinger, *ibid.*, **9**, 1893 (1876); **10**, 1877 (1877); (b) J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton and G. P. Turner, THIS JOURNAL, **63**, 1334 (1941).

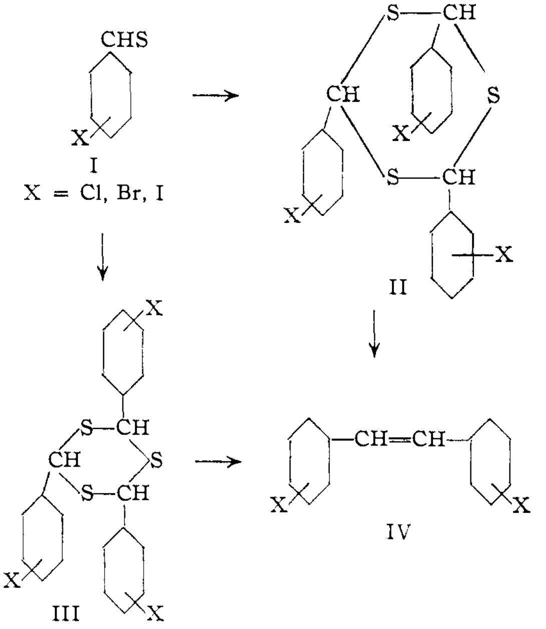
[4] For an excellent review on thiones and thials, see E. Campaigne, *Chem. Revs.*, **39**, 1 (1946).

TABLE I

Thiobenz-aldehyde	Yield of α- and β-isomers	M.p., °C.[a] Alpha	M.p., °C.[a] Beta	Analytical data Halogen, % Calcd.	Halogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Molecular wt. Calcd. for trimer	Found
o-Chloro-	98.7	162.7–163.5	223.9–224.6	22.6	22.9	20.5	20.5	469.9	461.3
m-Chloro-	91.2	115.8–116.4	163.0–163.2	22.6	22.7	20.5	20.5	469.9	463.6
p-Chloro-	94.3	137.4–138.2	189.6–190.4	22.6	22.2	20.5	20.1	469.9	459.6
o-Bromo-	91.6	186.0–186.7[b]	220.6–221.0[c]	39.7	39.5	15.9	15.8	603.3	588.2
m-Bromo-	87.6	141.6–142.3	177.3–177.9	39.7	39.1	15.9	15.6	603.3	591.6
p-Bromo-	88.7	182.2–183.0[d]	205.3–205.9[e]	39.7	39.0	15.9	15.7	603.3	596.1
o-Iodo-	91.4	188.7–189.6	202.0–202.6	51.1	49.9	12.9	12.6	744.3	738.7
m-Iodo-	84.6	196.2–197.4	212.6–213.1	51.1	50.3	12.9	12.7	744.3	740.3
p-Iodo-	78.7	113.6–114.8	211.3–212.1	51.1	50.0	12.9	12.8	744.3	736.5

[a] All melting points were determined in an electrically heated aluminum block using Anschütz thermometers. All melting points have been corrected. [b] Wörner (ref. 1) reported 75° as the melting point. [c] Previously reported 155° (ref. 1). [d] Previously reported 174° (ref. 1). [e] Previously reported 203° (ref. 1).

meric forms, corresponding to II and III. Heating of either of these with copper powder should yield the corresponding stilbene, IV.



The existence of the two isomeric thioaldehydes has been confirmed for each of the thioaldehydes reported in this work. The results of this phase of the investigation are summarized in Table I. The agreement with previously reported melting points for the α-*o*-bromo, the β-*o*-bromo, and the α-*p*-bromo isomers is not good. It is believed that in the cases of these two α-isomers, earlier workers did not have pure samples of these isomers, but rather had achieved only a partial separation of the α-isomer from the β-isomer. It has been noted herein that a small amount of pure β-form has a pronounced effect upon the melting point of the pure α-form. The discrepancy in the melting point of the β-*o*-bromo isomer may be due to the fact observed by Wörner[1] of the presence of a molecule of benzene of crystallization in his sample of this compound. The presence of benzene of crystallization in the sample of β-*o*-bromothiobenzaldehyde obtained by the method described below could not be verified either by extensive warming in vacuum or by methods of analysis.

The formation of the α-isomer (II) is favored by lower hydrogen chloride concentration and low temperatures. In this investigation it has been found that the use of ethyl acetate as a solvent for the reaction also favors the formation of the α-isomer. The β-isomer (III) may be obtained more favorably by using absolute ethanol as the solvent for the oxo-aldehyde. These observations are in agreement with the reported[5] formation of the α-isomer being favored by lower hydrogen chloride concentration since hydrogen chloride would be expected to be more soluble in ethanol than in ethyl acetate. However, in the methods described herein, mixtures of the α- and β-forms were obtained with the β-isomer predominating. These could be separated by either of two means: (1) extraction of the α- by hot ethanol, leaving the β-isomer, or by (2) extraction of the α- by cold benzene, leaving the β-isomer.

TABLE II

THE STILBENES

Stilbene	Yield, %	M.p., °C.[a]	Analytical Data Halogen, % Calcd.	Halogen, % Found	Mol. wt. Calcd.	Mol. wt. Found
2,2′-Dichloro-	78.2	96.4–96.8	28.4	27.9	249.1	240.2
3,3′-Dichloro-	88.0	93.8–94.6	28.4	28.1	249.1	238.4
4,4′-Dichloro-	89.4	154.0–154.4	28.4	27.9	249.1	242.9
2,2′-Dibromo-	64.2	108.0–108.4	47.3	46.9	338.0	329.2
3,3′-Dibromo-	83.4	52.8–53.4	47.3	47.0	338.0	336.1
4,4′-Dibromo-	88.7	205.7–206.5	47.3	46.8	338.0	333.9
2,2′-Diiodo-	47.3	149.5–150.1	58.7	57.4	432.1	426.3
3,3′-Diiodo-	61.6	91.4–92.0	58.7	57.7	432.1	418.7
4,4′-Diiodo-	62.5	259.2–260.0	58.7	57.3	432.1	428.6

[a] All melting points were determined using an electrically heated aluminum block and Anschütz thermometers. All melting points corrected.

Besides the use of copper for the conversion of thials to ethylenic types, iron powder or zinc dust[6] and Raney nickel[7,8] have been reported as being satisfactory. In this work, the thials were readily converted to the stilbenes in satisfactory yields by the use of freshly precipitated copper powder. Under the conditions of the reaction, only one of the geometrical isomers apparently was obtained, this likely being the *trans*-isomer. Such would seem probable since the *trans*-isomer would be the more stable and hence the more likely formed under the high temperatures such as were used in the preparation of the stilbenes. Table II gives data on the stilbenes obtained.

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(5) J. F. Suyver, *Rec. trav. chim.*, **24**, 377 (1905).

(6) K. Kopp, *Ber.*, **25**, 600 (1892).

(7) J. K. Cline, E. Campaigne and J. W. Spies, THIS JOURNAL, **66**, 1136 (1944).

(8) H. Hauptmann and B. Wladislaw, *ibid.*, **72**, 707 (1950).

Experimental

The Oxo-aldehydes.—*o*-Chlorobenzaldehyde was purchased from Distillation Products Industries and the fraction boiling between 209–210°, uncorrected, used. The *p*-chloro-, *m*-bromo- and *p*-iodobenzaldehydes were prepared in yields of 39, 41 and 37%, respectively, from the corresponding toluene derivative by oxidation with CrO_3 in acetic anhydride–acetic acid media followed by hydrolysis of the diacetate. The procedure was that used by Coleman and Honeywell for preparing *p*-nitrobenzaldehyde.[9] The *m*-chlorobenzaldehyde was prepared by the method of Buck and Ide.[10] In a like manner, the *m*-iodoisomer was obtained in 70% yield. *o*-Bromobenzaldehyde was synthesized from *o*-bromotoluene following the procedures of Coleman and Honeywell.[11] The *p*-bromobenzaldehyde was synthesized by Stephen's method[12] from *p*-bromobenzonitrile. The *o*-iodobenzaldehyde was available as a student preparation and its method of synthesis was unknown. It was recrystallized several times from water–alcohol mixtures to give white crystals, m.p. 34.5–35.5°.

The Thioaldehydes. *o*-Chlorothiobenzaldehyde.—All the thioaldehydes were prepared by similar methods, hence the procedure given here may be applied to all. It should be mentioned, however, that in the case of the *p*-chloro isomer, 50 ml. of absolute ethanol was added to the ethyl acetate so as to effect complete solution of the oxo-aldehyde. For those aldehydes which were liquids, 10 ml. was used; for those which were solids, 5 g. was used.

Ten ml. of *o*-chlorobenzaldehyde was dissolved in 125 ml. of absolute ethyl acetate in a 300-ml. erlenmeyer flask. Three tubes were provided in the stopper. The solution was cooled to 2° and dry hydrogen chloride, obtained directly from a cylinder, was bubbled into the solution until saturation was reached. At this point, hydrogen sulfide was bubbled slowly into the solution through a second entry tube. During the entire reaction period hydrogen chloride was continually passed into the solution. It was desirable that the rate of admission of the hydrogen sulfide not be too fast or exceed the rate of introduction of the hydrogen chloride. After two hours, the process was discontinued. Since only a small amount of precipitate appeared at this time, the flask was allowed to stand overnight during which time the temperature of the mixture gradually reached room temperature. *o*-Chlorothiobenzaldehyde (α- and β-isomers) appeared as a white precipitate. After removing the product, the filtrate was returned to the original flask, cooled, and once more saturated with hydrogen chloride followed by addition of hydrogen sulfide for one hour. Upon standing, another precipitate of thioaldehyde appeared. It was removed by filtration and combined with the first portion of product. The total yield was 12.3 g. (10.8 g. from the first precipitation and 1.5 g. from the second). The over-all yield amounted to 98.7%. The product was recrystallized from benzene or ethyl acetate. Analyses were made for sulfur and halogen, using the Parr bomb method. Molecular weight determinations were made by boiling point elevation using ethyl acetate as the solvent. These results are shown in Table I.

Separation of the α- and β-Isomers.—The thioaldehyde from the above procedure consisted mainly of the β-form with some α-present. To separate the isomers, the thioaldehyde was placed in boiling ethanol (95%) for five minutes and then the mixture was filtered while hot. The filtrate, upon addition of water until cloudiness resulted, yielded a white crystalline product when cooled. This, the α-isomer, was recrystallized several times until a pure sample was obtained. The residue from the extraction was dissolved in boiling benzene and recrystallized. After several such recrystallizations, pure β-isomer was obtained. Melting points of the isomers are given in Table I.

A second method was found more practical in the cases of the separation of the two isomers of the *o*-bromo-, *o*-iodo-, *m*-iodo- and *p*-iodothiobenzaldehydes. In these instances, the crude thiobenzaldehyde was placed in contact with a small amount of benzene and permitted to stand overnight. The α-isomer, being much more soluble in the cold benzene, dissolved and left the β-isomer. After filtering the resulting solution, evaporation of the solvent gave the α-isomer. It was recrystallized from ethyl acetate. The residue from the filtration was placed in boiling benzene to which a little iodine was added. Upon cooling, crystals of the β-isomer were obtained. These were washed several times with ether and then dried.

For the chloro and bromo compounds, 20% of the crude halothiobenzaldehydes was the α-isomer. In the cases of the iodo compounds, the amount of the α-isomer was not more than 5% of the total thioaldehyde obtained. These percentages are not quantitative since no precise data were taken. They are accurate probably within 1–2%.

The Stilbenes.—The copper powder used in the preparation of the stilbenes was prepared by dissolving 160 g. (1 mole) of copper sulfate in water and adding 16.5 g. (0.25 mole) of zinc dust slowly and with stirring. The resulting precipitate of copper was filtered, washed twice with ethanol and stored, slightly moist, under nitrogen. The copper was not used if it was more than a few days old.

2,2′-Dichlorostilbene.—Ten grams of *o*-chlorothiobenzaldehyde (α- and β-isomers) was placed in a 250-ml. three-necked flask along with 20 g. of freshly prepared copper powder. The flask was equipped with a copper paddle-type stirrer, an inlet through which nitrogen gas was admitted slowly, an outlet for the nitrogen and volatile material which might be formed, and a thermometer. The outlet tube led to an ice-cooled trap. Nitrogen was passed into the flask for a few moments after which the flask and contents were heated by means of a Glas-Col heater until the thioaldehyde melted. It was important that the mixture was not overheated (*i.e.*, the temperature was no more than 20° above the melting point of the thioaldehyde). Stirring was continued throughout the entire heating time of one hour. During this process, the residual ethanol adhering to the copper surface distilled. A small amount of a heavy oil was also carried over.

After heating, the residue was extracted with several portions of benzene, the combined extracts decolorized with charcoal and concentrated to an oily mass. This was boiled with 350 ml. of 95% ethanol, then filtered. Water was added to the filtrate until the white cloud which formed just disappeared. Cooling in a refrigerator freezing unit gave 6.2 g. of 2,2′dichlorostilbene. Toluene, ligroin, ether and dioxane were not as satisfactory as the above method for recrystallization.

The yellow oil which formed in the receiving trap deposited a few crystals which were found to be 2,2′-dichlorostilbene. The oil itself gave a positive aldehyde test and a positive sulfur test. It became polymeric upon heating. A white mass was obtained on repeated washing with ethanol. This mass melted over a wide range (119–196°) and no further attempt was made to purify it. The appearance of the oil was not observed in all instances.

Other stilbenes of the series were prepared in a similar manner. Only in the case of 4,4′-diiodostilbene were additional precautions needed. In this case, the product was readily sublimable, hence the reaction flask was heated very cautiously and the trap immersed in a Dry Ice–acetone-bath. Full data on the stilbenes will be found in Table II.

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

(10) J. S. Buck and W. S. Ide, *ibid.*, p. 130.

(11) G. H. Coleman and G. E. Honeywell, *ibid.*, p. 89.

(12) H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).