

The 1.3 g. of soluble material gave 82.2% furoic acid on standing for twenty-four hours with the sodium alcoholate solution (values from other experiments were 83.5 and 81.6%).

Calculated saponification values: trifuroate, $C_6H_7O_2(OOCC_4H_5O)_3 = 75.75\%$ of C_6H_5OCOOH ; difuroate, $C_6H_5O_3(OOCC_4H_5O)_2 = 64.0\%$.

Summary

1. Cellulose di- and trifuroates have been prepared by treating standard cellulose with furoyl chloride in the presence of pyridine. The esters were fibrous, dark colored and insoluble in the usual solvents for cellulose esters.

2. A considerable degradation of cellulose takes place during the reaction with the production of furoylated degradation products of cellulose which are black amorphous substances.

3. The analysis of cellulose trifuroate by saponification shows very clearly the fundamental difference of two of the alcoholic hydroxyl groups in the hexose residue from the third or primary hydroxyl and thus confirms the present accepted structure of the hexose residue.

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[CONTRIBUTION FROM THE E. F. HOUGHTON & CO. RESEARCH LABORATORIES]

SOME HETEROCYCLIC DERIVATIVES OF DIPHENYL

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The production on a large scale of diphenyl in order to supply the demand for this very useful heat-transfer medium has already resulted in the price of this material being brought down to a figure comparable with that of any of the polynuclear hydrocarbons, except naphthalene.

Its applications in the chemical industry for synthetic purposes are in consequence destined to become of increasing importance, especially as it appears likely that the price can be further reduced.

The recent work by Jenkins, McCullough and Booth¹ has indicated for instance that the simple mono-chloro, nitro and amino derivatives can be produced readily on a commercial basis, and the work of C. H. Penning² has extended the knowledge of the polychlorinated derivatives.

The present paper covers some new heterocyclic compounds derived from 4-amidodiphenyl, the derivatives chosen for study being such as might be expected to be of possible commercial application in the rubber industry, in froth flotation of ores, as inhibitors in steel pickling or in dyestuff manufacture.

Use has been made in this work of the method described by R. Herz³ for introducing sulfur into the ring by the action of sulfur chloride on the

¹ Jenkins, McCullough and Booth, *Ind. Eng. Chem.*, **22**, 31 (1930).

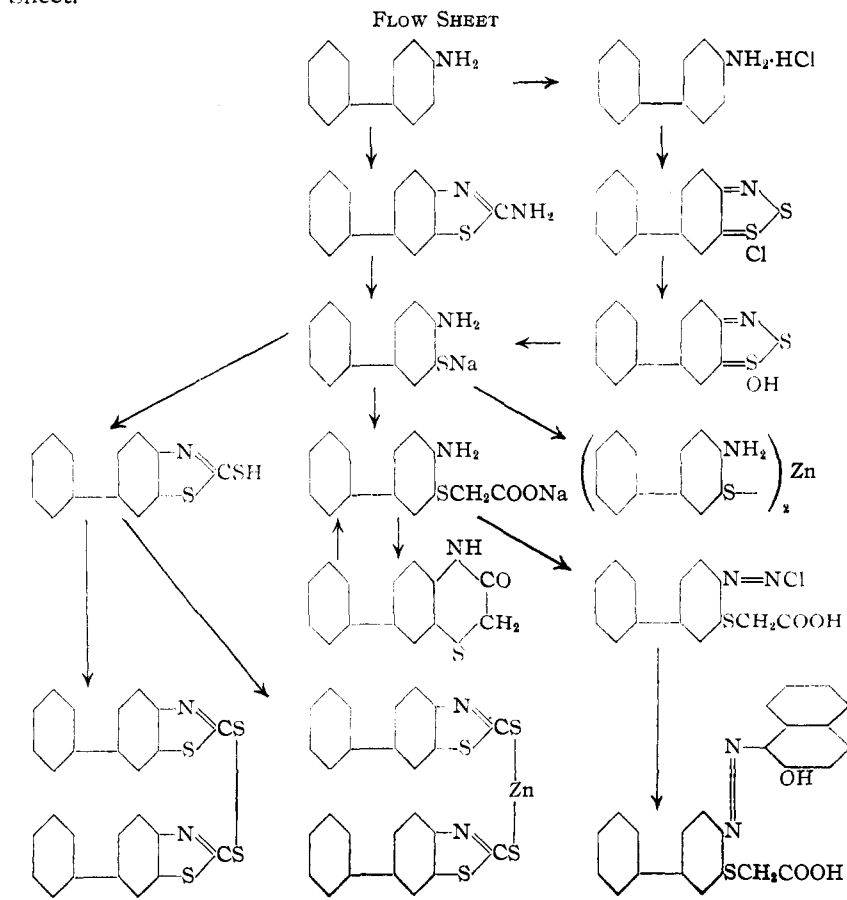
² Penning, *ibid.*, **22**, 1180 (1930).

³ Herz, German Patent 360,690.

hydrochlorides of amino compounds having a free ortho position. This reaction is the keystone of many important industrial syntheses, for example, in the Hydron Pink and Orange series of thioindigoids (Truttwin, "Enzyklopaedie der Kuepenfarbstoffe"), as also in the excellent method of A. H. Ney⁴ for the manufacture of substituted mercaptothiazoles.

Besides the characteristic ring grouping formed by the Herz reaction, chlorination of the amino compound also usually occurs if a free para position is present or if certain groups are in this position, and it appeared to the writer possible that in the case of diphenyl the tendency for chlorine substitution might extend through to the 4'-position. This, however, proved not to be the case since all derivatives obtained were unsubstituted in this part of the nucleus.

The course of the reactions described is graphically shown in the Flow Sheet.



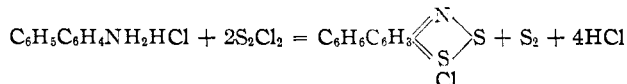
⁴ Ney, U. S. Patent 1,788,585.

Experimental Part

The diphenyl used for the work was the ordinary commercial product marketed by the Federal Phosphorus Company. Its setting point was 68° and it was considered unnecessary to subject it to recrystallization.

At the inception of this work the 4-aminodiphenyl used was prepared by the method of Bell, Kenyon and Robinson;⁵ later the methods of Jenkins, McCullough and Booth¹ became available and were found somewhat more convenient for preparing the finely divided hydrochlorides necessary for the Herz reaction. The 4-nitro compound used for the reduction was crystallized once from methanol, when it had a melting point of 113°. The 4-amino hydrochloride was obtained from the benzene solution of the base by first drying the latter over calcium chloride and then passing in dry hydrochloric acid gas with rapid agitation. The benzene was filtered on a Büchner funnel and air drawn through the hydrochloride until dry. The product was then ready for the Herz reaction.

Phenylphenylene Thiazthionium Chloride.—Seven hundred grams of sulfur monochloride was placed in a three-necked flask provided with an efficient agitator; 100 g. of thoroughly dry 4-aminodiphenyl hydrochloride was slowly added at 20° and agitation continued at this temperature overnight. The next morning 400 cc. of benzene was added and the temperature then raised to 75–80° and kept at this point with good agitation under a reflux condenser for four and one-half hours. Hydrogen chloride gas is evolved during this period and the color of the reaction mass changes from yellow to a reddish-brown. The reaction mixture was now allowed to cool to room temperature and filtered on a dry Büchner funnel. It was washed with enough benzene to remove yellow mother liquor and allowed to dry at room temperature; yield, 140 g. (calcd. 129 g.). The main impurity present is free sulfur formed in the reaction.



The excess sulfur chloride and benzene can be recovered readily from the filtrate by distillation. The product is a finely crystalline brownish-red powder, slightly soluble in ring hydrocarbons and in acetic acid. It may be purified by dissolving in cold acetic acid, filtering and adding to the filtrate sufficient dry ether to slowly precipitate the thiazonium chloride.

Anal. Calcd. for $\text{C}_{12}\text{H}_9\text{NS}_2\text{Cl}$: N, 5.28; S, 24.15; Cl, 13.37. Found: N, 5.20; S, 24.72; Cl, 13.13.

On attempting to obtain a melting point, the product charred at about 130°.

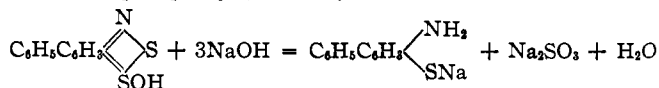
Phenylphenylene Thiazthionium Hydrate.—The chloride is stirred at room temperature with water overnight. The chloride appears to go partly into solution at first with a yellow color, quickly precipitating out again as a purplish powder, the solution meanwhile becoming strongly acid (HCl). On further stirring the precipitate becomes lighter colored until after about sixteen hours it is almost white when the reaction is complete. It is filtered off, washed with water until free from acid and dried. The weight obtained is the theoretical. A sample of the hydrate prepared from the purified chloride by the above method gave a negative test for chlorine, proving that the only chlorine in the chloride was that attached to the labile thiazonium sulfur.

Anal. Calcd. for $\text{C}_{12}\text{H}_9\text{ONS}_2$: N, 5.67; S, 25.91. Found: N, 5.59; S, 26.24.

The "hydrate" is soluble in alcohol, from which it may be precipitated in fine needles by careful addition of water and allowing to stand. It melts at about 135° with charring and decomposition.

⁵ Bell, Kenyon and Robinson, *J. Chem. Soc.*, 1239 (1926).

4-Amido-3-mercaptodiphenyl (Zinc Salt).—The reaction is as follows



the sodium salt being then precipitated as the zinc salt.

Forty grams of the hydrate, figured on the dry basis, preferably the still wet filtrate from the conversion of the chloride, are slurried with enough water to make about 400 cc. A little ice is added and 64 cc. of 35° Bé. sodium hydroxide with stirring. The hydrate goes into solution immediately with the exception of a small portion of insoluble impurity. The solution should now color Clayton yellow paper pink, indicating excess of sodium hydroxide over the sodium salt of the thiophenol. The solution is filtered and zinc chloride solution added until no further precipitate is obtained. The precipitate is redissolved in a mixture of dilute hydrochloric acid and alcohol. Excess of sodium acetate solution is added to precipitate zinc mercaptide.

Anal. Calcd. for $(\text{C}_{12}\text{H}_{10}\text{NS})_2\text{Zn}$: Zn, 14.05. Found: Zn, 13.55.

The pure zinc mercaptide may be used for any of the condensation reactions, but the crude solution of sodium mercaptide obtained by dissolving the hydrate in sodium hydroxide is quite suitable for all purposes and is much more convenient. The sodium salt may also be precipitated out with excess of sodium hydroxide if desired.

Air passed into the sodium hydroxide solution of the thiophenol precipitates the disulfide as a somewhat resinous mass, which is difficult to purify. No analysis was made of this.

2-Mercapto-6-phenylbenzothiazole.—Forty grams of crude phenylphenylene thiazonium chloride is converted to the hydrate as described above, the latter filtered off, washed well and re-slurried with enough water to make about 180 cc. and 40 cc. of 35° Bé. sodium hydroxide is added. The mixture is agitated for ten minutes and transferred to a flask; 10 cc. of carbon disulfide is added and the whole heated to refluxing temperature under a condenser. After about five minutes a crystalline magma appears in the reaction mass. With further heating the deep yellow color of trithiocarbonate changes to a light brownish color and at the end of about forty minutes the crystalline precipitate all goes into solution. The reaction of the solution is now alkaline to Brilliant yellow paper but not to Clayton yellow. The solution is diluted to 800 cc., cooled to room temperature and dilute hydrochloric acid added with agitation until neutral to Brilliant yellow. The thiazole comes out as an almost white precipitate. It is filtered, washed and dried; yield, 29.5 g. (87% of calcd. figured on the 4-aminodiphenyl), m. p. 220°. Recrystallized twice from benzene containing 10% "Cellosolve," the melting point remained constant at 230.5°.

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{NS}_2$: N, 5.76; S, 26.33. Found: N, 5.68; S, 26.16.

The product is soluble in sodium and potassium hydroxides but practically insoluble in ammonia (distinction from 2-mercaptobenzothiazole, which is soluble in ammonia), very slightly soluble in alcohol, somewhat more so in benzene and in glycol mono-ethyl ether ("Cellosolve").

Bis-6-phenyl-2-benzothiazole Disulfide.—Four and nine-tenths grams of phenylmercaptobenzothiazole is dissolved in 2.2 cc. of 35° Bé. sodium hydroxide and 100 cc. of water; 2.5 g. of iodine dissolved in 75 cc. of water containing potassium iodide are added to the thiazole solution. The creamy white precipitate of disulfide is filtered off, washed well and dried; yield, 4 g. The product is insoluble in alcohol, soluble in benzene, and very soluble in chloroform. Crystallized once from a mixture of alcohol and benzene and once from benzene, the product melts at 163°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_2\text{S}_4$: N, 5.78; S, 26.45. Found: N, 5.71; S, 26.72.

Zinc and Lead Salts of 2-Mercapto-6-phenylbenzothiazole.—The thiazole dissolved in alcohol is precipitated by the calculated amount of zinc sulfate in aqueous solution, the precipitated zinc salt washed and dried; it is a white powder.

Anal. Calcd. for $C_{28}H_{16}N_2S_4Zn$: Zn, 11.90. Found: Zn, 11.41.

The lead salt was made similarly using diethylene glycol monoethyl ether ("Carbitol") for dissolving the thiazole and an aqueous solution of lead acetate, and is a yellow crystalline powder.

Anal. Calcd. for $C_{28}H_{16}N_2S_4Pb$: Pb, 29.97. Found: Pb, 30.55.

It was thought desirable to prepare the 2-mercapto-6-phenylbenzothiazole by the method suggested by Herz and Schubert⁶ from 4-amidodiphenyl by treating with sodium thiocyanate and bromine in acetic acid solution giving 2-amido-6-phenylbenzothiazole, the latter then being heated with a considerable excess of potassium hydroxide, splitting the thiazole ring and giving the amidothiophenol. The alkaline solution of the latter is then treated with carbon disulfide as in the previous method.

2-Amido-6-phenylbenzothiazole.—8.3 g. of 4-amidodiphenyl and 3.2 g. of sodium thiocyanate are agitated with 120 cc. of glacial acetic acid at 50°; 2 cc. of bromine is added drop by drop and agitation continued for one hour. The mixture is then cooled, diluted and sodium hydroxide added until slightly alkaline. The amidothiazole precipitated as a creamy white powder. It was filtered, washed and dried; yield, 8.8 g. The product is soluble in hot dilute hydrochloric acid and is purified by filtering this hot solution and allowing the hydrochloride to crystallize out. This is washed a little and basified by treatment with sodium hydroxide, then washed, dried and recrystallized from hot benzene, separating in creamy white plates of m. p. 227–228°.

Anal. Calcd. for $C_{13}H_{10}N_2S$: N, 12.38; S, 14.16. Found: N, 12.46; S, 14.15.

This product was treated for four to five hours with strong potassium hydroxide in considerable excess, when ammonia was evolved and the heterocyclic ring split back to the amidothiophenol. The resulting solution was divided into two parts. One portion was treated with carbon disulfide as above, precipitated with hydrochloric acid and the separated yellow precipitate dried and recrystallized once from benzene. The product obtained melted at 229° and when mixed with 2-mercapto-6-phenylbenzothiazole previously obtained, there was no diminution in melting point. The second portion of the thiophenol solution was heated with sodium chloroacetate, the solution precipitated with hydrochloric acid and heated to form the thioglycolic anhydride. This was filtered off, dried and crystallized once from benzene. The product melted at 210° and when mixed with the anhydride obtained from the thiazthionium chloride described below, melted at 211°.

2-Amido-5-phenylthioglycolic Acid.—Forty grams of the thionium chloride was converted to the hydrate as above described, the latter filtered off, washed, mixed with water to make 400 cc., 65 cc. of 35° B \acute{e} . sodium hydroxide added, agitated for five minutes, filtered, 21 g. of chloroacetic acid previously neutralized with dilute sodium hydroxide added and the mixture heated for a half hour to 60° with agitation. The condensation is now complete and hydrochloric acid is added, precipitating the crude amidophenylthioglycolic acid. On heating the acidified mixture the precipitate, which is at first somewhat resinous, becomes crystalline, indicating a change to the inner anhydride. This is filtered off, washed and dried; yield, 31 g. (about 94% figured on amidodiphenyl). Recrystallized twice from hot benzene it gives white leaflets of m. p. 212–212.5°.

Anal. Calcd. for $C_{14}H_{11}ONS_2$: N, 5.81; S, 13.28. Found: N, 5.73; S, 13.41.

⁶ Herz and Schubert, U. S. Patent, 1,788,297.

On heating with concd. sodium hydroxide the anhydride is converted back to the sodium salt of amidothioglycolic acid.

Diazotization of Amidothioglycolic Acid.—A solution of the crude sodium salt obtained by addition of sodium hydroxide to the hydrate as described above was mixed with an equimolecular amount of sodium nitrite solution, and the mixture added slowly at 10° with good agitation to dilute hydrochloric acid, keeping the solution acid to Congo paper. Agitation is continued for one hour. The diazo solution was filtered and added to an alkaline β -naphthol solution as usual. The dye precipitates at once. Some acetic acid was added and the dye filtered off, washed, dried and crystallized from acetic acid, giving reddish needles with a metallic appearance.

Anal. Calcd. for $C_{24}H_{18}O_5N_2S$: N, 6.76; S, 7.73. Found: N, 6.73; S, 7.79.

A similar coupling was made also using *o*-phenylphenol (Dow) instead of β -naphthol. This gave a dyestuff having an orange color in acetic acid solution, the β -naphthol dye giving a bluish-red solution.

Preliminary Experiments Made on the Preparation of the Substituted Thioindigoid Dyestuff According to the Methods of Herz.⁷—Starting from the diazotized *o*-amidothioglycolic acid, it was converted to the nitrite by the Sandmeyer reaction and then to the substituted thionaphthene by saponification, the latter then being oxidized to the thioindigo, gave a dyestuff which dyed cotton bluish-red shades from a hydrosulfite vat. Further investigation of this dyestuff is reserved for later publication.

In connection with the sodium salt of the amidothioglycolic acid, an interesting fact was noted. It was at first intended to salt out this sodium salt from the crude solution obtained by heating the amidothiophenol with excess of sodium chloroacetate in order to obtain a purer product for diazotization, etc. It was found, however, that the sodium amidothioglycolate thus obtained was almost insoluble in cold water after salting out, whereas in the presence of the usual impurities, *i. e.*, sodium sulfide, sodium sulfite, sodium chloroacetate, etc., a quite concentrated cold solution could be obtained, which was more convenient for diazotization.

Summary

1. The course of the Herz reaction as applied to 4-amidodiphenyl was established.
2. Some new heterocyclic derivatives related to 3-mercapto-4-amino-diphenyl have been prepared and described.
3. 6-Phenyl-2-mercaptobenzothiazole was made by two methods.
4. A new azo dye was prepared.

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⁷ Herz, U. S. Patents 1,243,170 and 1,243,171.