dish, evaporated to dryness and heated to constant weight at 100°. With the acid salts, the amount of solute was determined by titration. The sampling of the solutions saturated at 60° and 100° was done entirely under the surface of the water in the thermostat with an apparatus described by Pawlewski.[22]

The solubility results are given in Table I.

Summary

The data in the literature regarding the salts of maleic, fumaric and *i*-malic acids have been reviewed and the water of crystallization of a number of these salts determined. In some cases the work agrees with that of past observers, but in others new numbers are apparently justified. Some 11 salts, not previously described, were prepared and the water of crystallization determined in certain cases definitely.

The solubilities in water of 22 salts were determined and tabulated. In general, fumarates are less soluble than the corresponding maleates.

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THE REACTION OF CARBON DISULFIDE ON PARA-PHENYLENEDIAMINE

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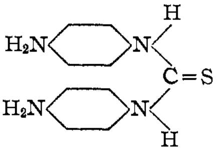
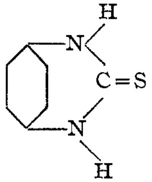
In the description of a patented process[1] for making symmetrical *p*-diamino-diphenyl-thio-urea, the statement is made that when carbon disulfide reacts on *p*-phenylenediamine in alcoholic solution two compounds are formed, symmetrical *p*-diamino-diphenyl-thio-urea, I, and phenylene-thio-urea, a compound insoluble in cold, dil. acids and all ordinary solvents. This compound was originally described by Lellmann[2] and given Formula II.



I



II

The description of the patented reaction is meager, and the formation by primary reaction of two substances to one of which is assigned Formula

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[22] Pawlewski, *Ber.*, **32**, 1040 (1899).

[1] Wm. Noetzel and Co., *Ber.*, **24**, 849 (1891).

[2] Lellmann, *Ann.*, **221**, 29 (1883). Gucci, *J. Chem. Soc. Abs.*, **64**, 588 (1893).

II is illogical. Formula II, also, is not in accord with the probable structure of most *para* ring compounds. This paper, then, is a contribution to the study of *para* ring compounds which have been the subject of several investigations including those of von Braun,[3] Perkin and Titley,[4] and Adams and Wilson.[5]

In carrying out the patented reaction it was found that when the usual procedure of prolonged boiling in alcoholic solution was followed, a very small percentage of the reaction product consisted of the diamino-thio-urea, I. To avoid the formation of the insoluble compound, *p*-amino-acetanilide was substituted for *p*-phenylenediamine, the intention being to mask one of the amino groups during the reaction with carbon disulfide, and to restore this group later by hydrolysis of the reaction product. The acetyl derivative of the diamino-diphenyl-thio-urea, $(CH_3CO.NH.C_6H_4NH)_2CS$, formed readily, but all attempts to hydrolyze this compound resulted in its decomposition with the formation of phenylenediamine.

After several unsuccessful attempts to overcome the difficulty by the preparation of diazobenzene-*p*-thio-urea, and some of its derivatives, and their subsequent reduction, a more complete study of the patented reaction was made. This revealed that the yield of diamino-diphenyl-thio-urea could be increased by causing the reaction to proceed at a lower temperature with a reduced concentration of carbon disulfide, and the frequent removal of the reaction product by filtration. These experimental conditions indicated that success depended upon the removal by filtration of the diamino-diphenyl-thio-urea, which, due to its relatively slight solubility in alcohol at the lower temperature, crystallized from the solution when the proper concentration was attained. This in turn suggested that the insoluble product was not the result of primary reaction of carbon disulfide on phenylenediamine, but was due rather to secondary reaction, and that its formation would be prevented in proportion to the completeness of the removal of the primary product, I.

To accomplish this result, water in which diamino-diphenyl-thio-urea is much less soluble was substituted for alcohol as a solvent, and a special apparatus was devised to keep the temperature as near the boiling point of carbon disulfide as possible, and the concentration of the latter low. This procedure resulted in suppressing the formation of the insoluble material almost entirely. The next step was obviously to bring diamino-diphenyl-thio-urea into reaction with carbon disulfide in alcoholic solution. As expected, an insoluble compound was formed in approximately the amount demanded by the only logical formulation of the reaction, namely, $(H_2NC_6H_4NH)_2CS + CS_2 = SC(HNC_6H_4NH)_2CS + H_2S$.

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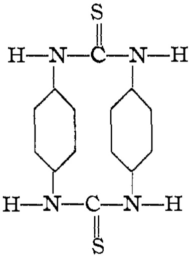
[3] von Braun, *Ber.*, **45**, 1274, 2512 (1912), and later articles.

[4] Perkin and Titley, *J. Chem. Soc.*, **122**, 1562 (1922).

[5] Adams and Wilson, THIS JOURNAL, **45**, 528 (1923).

Final proof that the reaction of carbon disulfide on phenylenediamine proceeds in two stages would, of course, demand that the identity of the insoluble compound formed directly from phenylenediamine with that formed from diamino-diphenyl-thio-urea be established. By neither reaction was it possible to obtain a pure product. This is apparently due to occlusion of impurities from which the product, on account of its insolubility, cannot be freed by crystallization. Both products decompose above 285°. When heated with strong acids, they dissolve with the formation of phenylenediamine. Fortunately, they are decomposed, although extremely slowly, by boiling acetic anhydride with the formation of *p*-phenylene-diisothiocyanate, $SCNC_6H_4NCS$. This substance was obtained in small quantity, and was identified by its crystal form, its melting point (130°) and by the fact that a dithio-urethane of the proper melting point (197°) and crystal form was obtained from it. Not only does this reaction prove that the compounds in question are identical, but it furnishes further proof of their constitution. The formula of the substance must be



III

and the reaction formulated as follows: $SC(HNC_6H_4NH)_2CS + (CH_3CO)_2O = SCNC_6H_4NCS + (CH_3CONH)_2C_6H_4 + 2CH_3COOH$; for with Formula II the dimustard oil could not be formed, but should give the acetyl derivative of *p*-aminophenyl-isothiocyanate. Since this acetyl derivative is unknown, we prepared it. It crystallizes in needles melting at 195°. We were unable to discover any of it in the reaction product.

Complex thio-ureas of a higher molecular weight than that of *p*-diphenylene-dithio-urea were formed only by the reaction of carbon disulfide on diamino-thio-ureas having a higher molecular weight than *p*-diamino-diphenyl-thio-urea, I. Theoretically, such compounds might form. The homogeneity of the diamino-thio-urea formed, as shown by its crystal form, constant melting point after repeated crystallizations, and the analysis of its sulfate, seems to preclude this possibility.

In the various attempts to hydrolyze acetyl-aminophenyl-isothiocyanate referred to above, small amounts of a substance insoluble in hydrochloric acid had been obtained which, in the light of facts already discussed, led us to believe that *p*-aminophenyl-isothiocyanate had been formed, and that two molecules of this had then reacted to form *p*-diphenylene-dithio-urea, III, whose constitution has just been established. However, it would seem logical that if the simple thio-urea, II, had any tendency to form under any conditions it would do so here where an intramolecular change alone is involved. It seemed highly desirable, therefore, to find some reaction by which *p*-aminophenyl-mustard oil would be formed and not further decomposed, in order that its behavior might be studied. Now, when diamino-diphenyl-thio-urea is boiled with glacial acetic acid a white insoluble powder results which yields phenylene-dimustard oil on treatment with acetic anhydride and is, therefore, *p*-diphenylene-dithio-urea. The amount formed is approximately that demanded by the equation: $2(H_2NC_6H_4NH)_2CS + 4CH_3COOH = SC(HNC_6H_4NH)_2CS + 2C_6H_4(NH_2)_2.2CH_3COOH$. When the reaction mixture is diluted with water and filtered, the mother liquor deposits slowly an additional quantity of the same substance. When this mother liquor is rendered alkaline an immediate precipitate of the same substance results. These facts show clearly that the *p*-aminophenyl-mustard oil is first formed but that even in acetic acid solution the major portion condenses to form diphenylene-dithio-urea. They show further that the free base cannot exist, in solution at least, but that it immediately forms the complex thio-urea.

To bring out this point still more conclusively we prepared azobenzene-*p*-isothiocyanate by the reaction of thiophosgene on *p*-amino-azobenzene and reduced this compound in acetic acid solution with stannous chloride and hydrochloric acid. Under these experimental conditions, lower temperature and presence of hydrochloric acid, the mustard oil formed does not immediately form the thio-urea, as was the case at the boiling point of acetic acid, but as soon as the clear acid solution was made sufficiently alkaline to dissolve the tin hydroxides and free the base, the insoluble high-melting diphenylene-dithio-urea appeared. Here again, as under the other conditions cited, the more complex rather than the simpler compound forms.

The simpler compound is supposed to have been obtained[2] by heating phenylene-diphenyl-dithio-urea, the addition product of two molecules of aniline and one of phenylene-diisothiocyanate, to high temperature. It is well known that under these conditions intermolecular changes readily take place. In the light of these facts, the demonstrated stability of the dimolecular compound and its tendency to form, where the formation of the simpler substance might be expected, throws a reasonable doubt on the existence of the latter compound.

We are now extending this method of investigation to other diamines, especially to *o*- and *m*-phenylenediamine and to benzidine.

Experimental Part

Reaction of Carbon Disulfide on *p*-Phenylenediamine in Alcoholic Solution.— Ten g. of phenylenediamine was dissolved in 250 cc. of alcohol and boiled on a steam-bath with an excess of carbon disulfide for 10 hours. The reaction mixture was filtered and the residue extracted with cold, dil. hydrochloric acid. By making the extract alkaline, 0.45 g. of diamino-diphenyl-thio-urea was obtained. The insoluble residue was boiled with alcohol, then with water, and finally dried; yield, about 10 g. In a melting-point tube the substance commences to darken at about 200° and rapid decomposition takes place above 280°.

Reaction of Carbon Disulfide with *p*-Phenylenediamine in Aqueous Solution.—A solution of 10 g. of phenylenediamine in 250 cc. of water was placed in a round-bottomed flask to which was fitted the apparatus shown in Fig. 1. The tube A, connected with a reflux condenser at D, contained about 5 cc. of carbon disulfide and when the flask was heated on the steam-bath to the proper temperature, the vapor of carbon disulfide escaped through Tube B into the reaction mixture. The excess of vapor entered the condenser through the opening C and the condensed liquid was returned to Tube A. During the reaction, which was allowed to continue for 10 hours, a precipitate gradually formed. This was filtered out, washed with alcohol, and extracted with dil. hydrochloric acid at room temperature. All but a small amount (about 0.8 g.) dissolved immediately and the residue was allowed to stand in the acid overnight. The solution was then filtered from the insoluble residue and made alkaline. A voluminous crystalline, nearly white precipitate was obtained, which was crystallized from boiling water—about 2 liters were required—filtered and dried. The compound separates in plates melting at 194–195°; yield, 8.95 g.; calculated yield, 11.94 g. The normal sulfate was prepared by precipitation.

Analysis. Subs., 0.3025: $BaSO_4$, 0.1958. Calc. for $C_{13}H_{14}N_4S.H_2SO_4$: SO_3, 22.47. Found: 22.20.

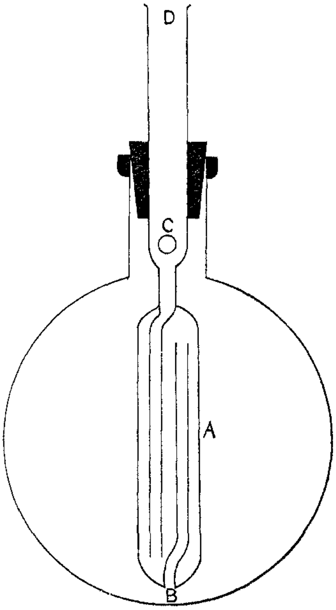


Fig. 1

Reaction of Carbon Disulfide with Diamino-diphenyl-thio-urea.—Five g. of diamino-diphenyl-thio-urea was dissolved in 200 cc. of alcohol and the solution boiled with a large excess of carbon disulfide under a reflux condenser for 12 hours. The clear solution soon became clouded with a precipitate which gradually increased in amount. The separated reaction product was treated successively with cold, dil. hydrochloric acid, boiling alcohol, and boiling water, and finally dried; yield, 5.55 g.; calculated yield, 5.81 g. This compound behaved in a melting-point tube exactly like the insoluble substance described above.

Proof of the Composition of the Insoluble Substances thus Obtained.—Lots of 7 g. of each of the insoluble compounds obtained by the reactions described above were boiled in separate flasks with 15 cc. of acetic anhydride for half an hour.[6] Apparently, very little of the substance had gone into solution, but for fear of decomposition of the reaction product, the operation was interrupted and the reaction mixture filtered into water. This was then repeated several times with each residue. The combined filtrates in each case were warmed to decompose excess of acetic anhydride and a crystalline solid

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[6] Werner, *J. Chem. Soc.*, 59, 396 (1891).

remained. By repeated recrystallization of this solid from glacial acetic acid there was obtained from each of the insoluble substances in question approximately 0.1 g. of a white compound crystallizing in long, shiny needles; m. p., 130°. Heated on the steam-bath with ethyl alcohol for 8 hours, this compound yielded a white crystalline powder melting at 197°. These crystal forms and melting points identify these compounds as phenylene-diisothiocyanate and the corresponding *p*-thio-urethane.[7] These substances are then identical and are diphenylene-dithio-urea, III.

Reaction of Glacial Acetic Acid on Diamino-diphenyl-thio-urea.—Three g. of diamino-diphenyl-thio-urea was heated to boiling with 15 cc. of glacial acetic acid. Complete solution took place as the mixture was warmed. At the boiling point a finely divided substance began to separate, and in two or three minutes it was so abundant that the reaction mixture was nearly white. The boiling was continued for 10 minutes, when the product was poured into water. From the finely divided white powder obtained by filtration no unchanged diamino-diphenyl-thio-urea could be obtained by extraction with dil. hydrochloric acid. This powder was boiled with alcohol, then with water, and dried; yield, 1.60 g.; calculated yield, 1.92 g. In a melting-point tube it behaved like the diphenylene-dithio-urea identified as described above.

Analysis. Subs., 0.1516: N, 25.8 cc. (22°, 754.4 mm.). Calc. for $C_{14}H_{12}N_4S_2$: N, 18.66. Found: 19.06.

By treatment with acetic anhydride, phenylene-*p*-diisothiocyanate was obtained from this substance, and its identity with diphenylene-dithio-urea thus further established.

***p*-Diacetylamino-diphenyl-thio-urea,** $(CH_3COHNC_6H_4NH)_2CS$.—Ten g. of *p*-amino-acetanilide was dissolved in 400 cc. of alcohol and the solution was heated in a water-bath under a reflux condenser with an excess of carbon disulfide for about 10 hours. A white, insoluble precipitate was formed, which in the agitated mother liquor somewhat resembled long-fibered asbestos. After it was filtered, washed and dried, 10.2 g. of pure, white solid was obtained that was insoluble in all ordinary solvents; m. p., 235–237°.

This compound could not be hydrolyzed except by boiling with strong acids. Under these conditions the expected diamino-diphenyl-thio-urea decomposed with formation of phenylenediamine which was identified by Lauth's violet test.

Analysis.[8] Subs., 0.1896: N, 27.90 cc. (18.8°, 736 mm.). Calc. for $C_{17}H_{18}N_4O_2S$: N, 16.3. Found: 16.4.

***p*-Acetylamino-phenyl-isothiocyanate,** $CH_3CONHC_6H_4NCS$.—Ten g. of the thio-urea described above was boiled in an oil-bath with 30 g. of acetic anhydride. Solution took place in about 10 minutes, whereupon 200 cc. of water was immediately added. After the mixture had cooled, the precipitated solid was crystallized from alcohol as white needles; m. p., 195–196°; yield, 4.1 g. Care had to be taken not to heat it long enough with the alcohol to cause the formation of the thio-urethane.

Analysis.[9] Subs., 0.2285: N, 29.4 cc. over 30% KOH (21.5°, 756 mm.). Subs., 0.1916: $BaSO_4$, 0.2304. Calc. for $C_9H_8ON_2S$: N, 15.58; S, 16.66. Found: N, 14.53; S, 16.51.

Hydrolysis of *p*-Acetyl-amino-phenyl-isothiocyanate.—Two g. of this compound was suspended in 30 cc. of concd. hydrochloric acid and the mixture was heated on the water-bath. Solution took place with foaming and white plates of phenylenediamine hydrochloride separated. Upon the addition of concd. hydrochloric acid a further sepa-

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[7] Billeter and Steiner, *Ber.*, **20**, 230 (1887).

[8] This analysis was made by Mr. G. W. Anderson.

[9] This analysis was made by Mr. F. W. Vogel.

ration took place. This precipitate (0.9 g.) was then filtered, washed, dried over potassium hydroxide and analyzed.

Analysis. Subs., 0.3012: AgCl, 0.4736. Calc. for $C_6H_{10}N_2Cl_2$: Cl, 39.18. Found: 38.90.

Azobenzene-*p*-isothiocyanate, $C_6H_5NNC_6H_4NCS$.—Fifteen g. of *p*-amino-azobenzene and the same weight of thiophosgene were heated in 400 cc. of carbon tetrachloride for 4 hours on a boiling water-bath. The solution was filtered from amino-azobenzene hydrochloride and the filtrate allowed to evaporate spontaneously. The residue was crystallized from 80% acetic acid, forming salmon-colored needles; m. p., 94–95°; yield, 8.4 g.

Analyses. Subs., 0.2003: CO_2, 0.4778; H_2O, 0.0713. Subs., 0.1556: $BaSO_4$, (Carius) 0.1526. Calc. for $C_{13}H_9N_3S$: C, 65.22; H, 3.79; S, 13.41. Found: C, 65.06; H, 3.98; S, 13.47.

Reduction of Azobenzene-*p*-isothiocyanate.—When 2 g. of this substance was dissolved in 300 cc. of glacial acetic acid and 12 g. of stannous chloride in a small quantity of hot concd. hydrochloric acid was added, the orange color of the solution almost entirely disappeared. Upon dilution and the addition of enough concd. sodium hydroxide solution to redissolve the precipitated tin hydroxides, a finely divided powder separated. This powder was insoluble in dil. hydrochloric acid and in boiling 80% acetic acid and resembled completely the diphenylene-dithio-urea obtained by other reactions described above, except for a slight greenish tinge.

Summary

1. The reaction of carbon disulfide on *p*-phenylenediamine proceeds in two stages. In the first *p,p′*-diamino-diphenyl-thio-urea is formed, and in the second this is changed into diphenylene-dithio-urea. There is no evidence of the formation of phenylene-thio-urea, which was thought to be a product of the primary reaction of carbon disulfide on *p*-phenylenediamine.

2. *p*-Aminophenyl-isothiocyanate cannot exist in the free state in solution. It changes immediately into the complex dithio-urea. This reaction also takes place in boiling acetic acid, and slowly in dil. acetic acid at room temperature. There is no evidence of the formation of phenylene-thio-urea under these conditions.

3. Reasonable doubt has been thrown on the existence of phenylene-thio-urea.

4. These results are in agreement with the probable constitution of most *para* ring compounds.

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