

The disulfo derivative of methyl-*isopropyl*-quinoline yellow dyes wool and silk a greenish-yellow. It is equal in fastness to the corresponding quinoline yellow derivative (Quinoline Yellow S).

The absorption of the disulfo derivative as compared with that of Quinoline Yellow S failed to indicate any appreciable difference in the absorption maximum through the methyl-*isopropyl* substitution.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]

## REACTIONS OF CARBON DISULFIDE. I.<sup>1</sup>

### With Ammonium Hydroxide

BY E. WERTHEIM

RECEIVED JANUARY 2, 1926

PUBLISHED MARCH 5, 1926

Experiments in this Laboratory for the production of keto dithio acids<sup>1a</sup> have frequently called for the use of solutions of carbon disulfide in ammonium hydroxide. These were made up from concd. "ammonia water" and an excess of carbon disulfide, and allowed to stand in glass-stoppered bottles. Such solutions on standing a short time acquire a deep red color. While on mixing there is always considerable pressure of ammonia gas, the solutions show negative pressure after five or six days' standing.

In the literature the reaction of carbon disulfide and ammonia is reported as follows:<sup>2</sup>  $CS_2 + 2NH_3 \rightarrow NH_2-C \begin{array}{l} \diagup S \\ \diagdown S \end{array} -NH_4$ ;  $NH_2-C \begin{array}{l} \diagup S \\ \diagdown S \end{array} -NH_4 \rightarrow NH_4CNS + H_2S$ ;  $H_2S + 2NH_3 \rightarrow (NH_4)_2S$ . These equations are given for "alcoholic ammonia." Meyer and Jacobson's textbook<sup>3</sup> reports, "Alkoholisches Ammoniak wirkt leicht auf Schwefelkohlenstoff unter Bildung von dithiocarbamidsaurem Ammonium bzw. Rhodan-ammonium. Wässriges Ammoniak wirkt in gleicher Weise, aber langsamer." Another reference states that aqueous ammonia and carbon disulfide yield a mixture of ammonium trithiocarbonate and ammonium thiocyanate.<sup>4</sup>

The red color of the solution in hand would seem to give evidence of the presence of a trithiocarbonate, since it is known that soluble salts of trithiocarbonic acid yield red solutions.<sup>5</sup> Moreover, ammonium dithiocarbamate gives a practically colorless solution and ammonium poly-

<sup>1</sup> Paper No. 30, Journal Series, University of Arkansas.

<sup>1a</sup> *Science*, **58**, 494 (1923).

<sup>2</sup> Hofmann, *Jahresber.*, **1858**, 334.

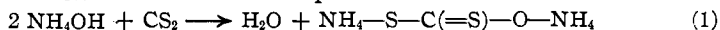
<sup>3</sup> "Lehrbuch der Organischen Chemie," Veit and Co., Leipzig, **1913**, vol. 1, part 2, p. 1360.

<sup>4</sup> Zeise, from (a) Gmelin-Kraut, "Handbuch der anorganischen Chemie," Carl Winter, Heidelberg, **1911**, vol. 1, part 3, p. 789.

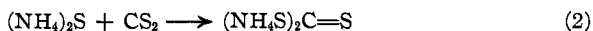
<sup>5</sup> *J. Chem. Soc.*, **89**, 1813 (1906); **119**, 41, 51 (1921).

sulfide solutions are quite different in color from those obtained in this work. It seemed advisable to find approximately the concentration of ammonium trithiocarbonate in these solutions in order to check the loss of carbon disulfide.<sup>6</sup>

In a solution of carbon disulfide in ammonium hydroxide there is the possibility of the formation of the ammonium salt of thionthiol-carbonic acid by direct interaction of the components.



Likewise, in the presence of an *excess of carbon disulfide* the ammonium salt of trithiocarbonic acid may be formed by *reaction with ammonium sulfide*.



It is well known that the analogous reaction occurs between the alkali sulfides and carbon disulfide.<sup>7</sup> Experiment has failed to show that Reaction 1 occurs under the conditions observed. Attempts to obtain thionthiol-carbonic acid or its derivatives gave only thiocyanic acid. However, Reaction 2 takes place to a considerable extent when an excess of carbon disulfide is present.

Thus, such a solution becomes a convenient source of materials for the preparation of normal esters of trithiocarbonic acid (by reaction with alkyl halides). The extreme simplicity of this operation makes it more desirable than previously reported methods; however, the yields are only moderately good.

Solutions that have stood for a few days show evidence of containing ammonium hydrosulfide in small amount, that is, reaction with alkyl halides yields mercaptans. An experiment with a solution that had stood for a month gave a yield of 33% of ethyl mercaptan plus 42% of ethyl trithiocarbonate (calculated from the alkyl halide used).

Appropriate tests show that a freshly prepared solution does not evolve hydrogen sulfide; this is noted in very small amount in three to four days and after a week's standing is present in considerable proportions.

Carbon disulfide in reaction with ammonia in absolute alcohol yields a precipitate of ammonium trithiocarbonate or ammonium dithiocarbamate according to the conditions of concentration and temperature.<sup>8</sup> Apparently the trithiocarbonate is formed first and then breaks down to give dithiocarbamate.<sup>9</sup>

Solutions of ammonia, alcohol and carbon disulfide were made up with

<sup>6</sup> One hundred cc. of  $\text{NH}_4\text{OH}$  absorbs 30–35 cc. of  $\text{CS}_2$  in two weeks, and 35–40 cc. in four weeks. No more is taken up.

<sup>7</sup> In absolute alcohol an excess of carbon disulfide increases the yield of ammonium dithiocarbamate. Ref. 4 a, p. 792.

<sup>8</sup> Ref. 4 a, pp. 792, 793.

<sup>9</sup> Dammer, "Handbuch der anorganischen Chemie," Ferdinand Enke, Stuttgart, 1894, vol. 2, part 1, p. 409.

various amounts of alcohol, the most concentrated solution containing 100 cc. of ethyl alcohol, 100 cc. of concd. ammonia water, and 40 cc. of carbon disulfide. These solutions had the same appearance as the aqueous solution and gave approximately equal yields of trithiocarbonic esters when similarly used. Thus it becomes evident that the reaction between ammonia and carbon disulfide assumes entirely different equilibria in absolute alcohol and in solutions containing water.

### Experimental Part

The solution for the two experiments given below was made as follows. Two hundred cc. of ammonium hydroxide (d., 0.90) was shaken with 40 cc. of carbon disulfide for two hours on a Camp machine. At this time 10 cc. of carbon disulfide had been used up and the solution was a deep cherry-red color.<sup>10</sup>

**Methyl Trithiocarbonate.**—One hundred cc. of the prepared solution was shaken in a glass-stoppered bottle for five minutes with 20 g. of methyl iodide. At this time the water layer was practically colorless, and clear. No odor of mercaptan was noted. The solution was extracted with ether, and the extract dried by the use of calcium chloride, followed by phosphorus pentoxide. The extract was filtered and the ether evaporated under reduced pressure. The last traces of ether were removed by holding the preparation for about five minutes at a pressure of 22 mm. and a temperature of 70°. The resulting oil weighed 5 g. (a 51.5% yield); b. p., 110–111° (18 mm.); b. p., 219–220° (760 mm.) Contrary to information in Beilstein it was found impossible to distil the compound. A sample which was distilled at 29 mm. upon analysis for sulfur content was found to contain 77.43, 77.40% as compared with 69.57% calculated. The identity of the compound was confirmed by a molecular-weight determination and by reaction with aniline.

*Mol. wt.* (Cryoscopic method using naphthalene as solvent.) Calcd.: 138. Found: 139.3, 129.3.

**THIOCARBANILIDE.**—Two g. of the compound was warmed with 5 g. of aniline in alcohol for 24 hours under a reflux condenser. The odor of mercaptan was noted during the reaction. The resulting crystals melted at 153–154° and the identity of the substance was confirmed by comparison with a known sample of thiocarbaniide.

**Ethyl Trithiocarbonate.**—One hundred cc. of the prepared solution was gently warmed and shaken for 20 minutes with 15 g. of ethyl bromide. The mixture was then cooled and extracted with ether. Further treatment was identical with that described above. The 5 g. of yellow oil obtained represents a yield of 44%; b. p., 102–104° (7 mm.); 145–147° (25 mm.); 241–244° (717 mm.). The liquid may not be distilled without decomposition. Two lots distilled at 25 mm. and 7 mm., respectively, gave analysis as follows.

*Anal.* Calcd. for  $C_6H_{10}S_3$ : S, 57.82. Found: (7 mm.) 65.55; (25 mm.) 65.34; (undistilled) 57.43.

Reaction of the compound with aniline gave thiocarbaniide whose identity was checked by comparison with a known sample.<sup>11</sup>

**Benzyl Trithiocarbonate.**—Three hundred cc. of ammonium hydroxide and 40 cc.

<sup>10</sup> A solution which has stood for 10–15 hours with frequent shaking gives equivalent results.

<sup>11</sup> Methyl and ethyl trithiocarbonates could not be successfully oxidized by the Carius method, by use of alkaline permanganate or by fusion with sodium peroxide and potassium hydroxide. The analyses were carried out with the Parr bomb.

of carbon disulfide were shaken together by machine for two hours; 250 cc. of the aqueous layer was then added to 20 g. of benzyl chloride. The mixture was warmed to 45° and shaken for ten minutes in a glass-stoppered bottle, after which it was allowed to stand for three hours. After cooling, the mixture was extracted with ether and the extract treated with a mixture of acetone and aqueous silver nitrate. The resulting yellow precipitate was removed and the filtrate again treated with acetone and silver nitrate. The resulting filtrate was dried with calcium chloride and phosphorus pentoxide. The ether was evaporated under diminished pressure, etc.; 11 g. of a thick, maroon oil was obtained; yield, 48%; b. p., 240-260° (55-60 mm.) with heavy decomposition. Its odor was peculiar but not unpleasant.

*Anal.* Calcd. for  $C_{15}H_{14}S_2$ : S, 33.11. Found: 33.00.

*Mol. wt.* (Ebullioscopic method, using acetone as solvent.) Calcd.: 290. Found: 316.3, 290.7.

**BENZYL MERCAPTAN.**—Fifty cc. of the aqueous layer from a mixture of ammonium hydroxide and carbon disulfide which had stood for longer than one month was treated with 10 g. of benzyl chloride. The mixture was gently warmed and after 30 minutes' shaking was cooled, made alkaline with 8 *N* sodium hydroxide solution and extracted with ether. The extract was rejected and the water layer again extracted with ether. The water layer was then acidified, extracted with ether, etc.; 4 g. of oil was obtained; b. p., 190-193°; yield, 40%.

**SILVER SALT.**—This was made by adding a mixture of acetone and silver nitrate solution to the oil obtained as described above. The salt was washed with acetone and dried, and was then amorphous and white.

*Anal.* Calcd. for  $C_7H_7SAg$ : Ag, 46.75. Found: 47.41, 47.01.

### Reaction with Benzaldehyde in Ammonium Hydroxide Solution. Formation of Thiobenzaldin

During experiments in which benzaldehyde was treated with carbon disulfide and ammonium hydroxide in the effort to prepare benzoyl-dithioformic acid<sup>1</sup> a copious white precipitate was obtained which after purification and analysis proved to be thiobenzaldin. This interesting compound was first made by Laurent<sup>12</sup> by treating benzaldehyde with ammonium sulfide solution. Attempts to follow Laurent's technique did not yield thiobenzaldin but instead a compound, m. p. 147°, was obtained. This was not further investigated. The following technique was found satisfactory for the preparation of thiobenzaldin and is accordingly presented.

Twenty g. of benzaldehyde, 20 g. of carbon disulfide and 150 cc. of ammonium hydroxide solution (d., 0.90) are well mixed and allowed to stand for 24 hours in a closed container. The resulting precipitate is removed and washed with water. It is dissolved in a mixture of one part of alcohol and 15 parts of acetone, and precipitated by addition of water. The precipitate is warmed to 80° for three minutes with 2 *N* sodium hydroxide solution and a little alcohol, then cooled, removed by filtration and washed on the filter with water. The crystals are then left for 30-40 minutes in warm methyl alcohol, after which they are filtered off and washed with ether. The dry compound is composed of odorless, white flakes; m. p., 131-133° (Laurent gives a melting point of 125°, and Baumann and Fromm, 126°; by fairly rapid heating of the bath a melting

<sup>12</sup> Laurent, *Ann.*, **38**, 323 (1841). Baumann and Fromm, *Ber.*, **24**, 1438 (1891).

point of 136–137° is obtained); yield, 11 g., or 50%. Warmed alone or with sodium hydroxide solution the compound evolves ammonia. When it is boiled in alcohol, hydrogen sulfide is liberated. When it is warmed with dil. nitric acid benzaldehyde is regenerated. Concd. sulfuric acid gives a vivid red solution which evolves sulfur dioxide (?) and which on addition of water slowly turns a brilliant green and deposits a green precipitate. Those of the above tests which Laurent tried with his compound gave the same results.

*Anal.*<sup>13</sup> Calcd. for C<sub>21</sub>H<sub>19</sub>NS<sub>2</sub>: C, 72.21; H, 5.44; N, 4.01; S, 18.34. Found: C, 71.90, 71.59; H, 6.19, 5.85; N, 3.90, 3.90; S, 17.10, 18.85.

*Mol. wt.* (Cryoscopic method, employing naphthalene as solvent.) Calcd. for C<sub>21</sub>H<sub>19</sub>NS<sub>2</sub>: 349. Found: 331, 338, 335.

### Summary

Additional data are presented bearing on the reaction of carbon disulfide with aqueous ammonia, and on the preparation and properties of several esters of trithiocarbonic acid made from carbon disulfide-ammonia solutions. Two new compounds are described in part.

The preparation of thiobenzaldin is described.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE COUPLING ACTION OF THE GRIGNARD REAGENT

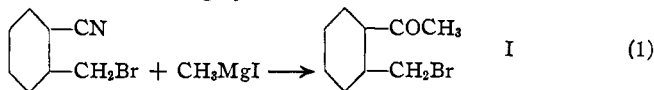
### I. THE ORTHO- AND PARA-CYANOBENZYL HALIDES

BY REYNOLD C. FUSON<sup>1</sup>

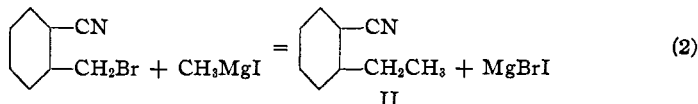
RECEIVED JANUARY 4, 1926

PUBLISHED MARCH 5, 1926

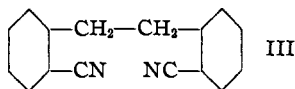
This research arose from an attempt to prepare *o*-acetylbenzyl bromide (I) by treating *o*-cyanobenzyl bromide with methylmagnesium iodide. It was expected that the following synthesis would be effected.



It might have been predicted also that alkylation would result according to the equation,



The reaction, however, took an unexpected course. Neither I nor II could be isolated but *s*-bis(*o*-cyanophenyl)ethane (III) was obtained instead:



<sup>13</sup> Analyses for carbon, hydrogen and nitrogen were performed by Mr. John Olin.

<sup>1</sup> National Research Fellow in Chemistry.