[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF INDIANA UNIVERSITY]

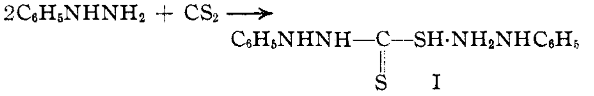
An Improved Method for the Preparation of Dithizone (Diphenylthiocarbazone)

BY JOHN H. BILLMAN AND ELIZABETH S. CLELAND

Although dithizone is a very important reagent for the quantitative determination of lead, there is no completely satisfactory method for its preparation in the literature. The method now in use is that described by Fischer[1] except for some recent improvements described by Grummitt and Stickle.[2]

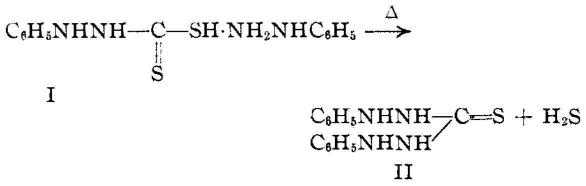
An extensive study has been undertaken to develop a good method for the synthesis of dithizone. We now have an improved process involving three steps, which is a modification of Fischer's, that gives higher yields.

Step one consists in the preparation of the phenylhydrazine salt of β-phenyldithiocarbazic acid (I). No essential changes have been made but experimental conditions have been worked out which give a 97% yield.



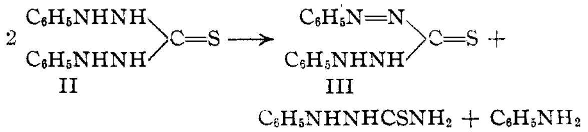
$$2C_6H_5NHNH_2 + CS_2 \longrightarrow C_6H_5NHNH{-}\underset{\underset{S}{\|}}{C}{-}SH\cdot NH_2NHC_6H_5 \quad \text{I}$$

The second step, involving driving off hydrogen sulfide from the phenylhydrazine salt, according to the following equation, must be carried out with careful control of the temperature. When we used temperatures as high as those recommended by Fischer, decomposition of the compound took place ten to twenty minutes after the heat was removed. A series of experiments was run in which only the temperature was allowed to vary, and it was found that 96–98° was the optimum temperature range. As described in the experimental part, this reaction is carried out without a solvent to give a 60–75% yield of diphenylthiocarbazide (II) based on the phenylhydrazine.



$$\underset{\text{I}}{C_6H_5NHNH{-}\underset{\underset{S}{\|}}{C}{-}SH\cdot NH_2NHC_6H_5} \xrightarrow{\Delta} \underset{\text{II}}{\begin{matrix}C_6H_5NHNH\\C_6H_5NHNH\end{matrix}}\!\!>\!C{=}S + H_2S$$

In the third step a series of experiments was carried out studying the effect of time and solvent on the reaction



$$2\underset{\text{II}}{\begin{matrix}C_6H_5NHNH\\C_6H_5NHNH\end{matrix}}\!\!>\!C{=}S \longrightarrow \underset{\text{III}}{\begin{matrix}C_6H_5N{=}N\\C_6H_5NHNH\end{matrix}}\!\!>\!C{=}S + C_6H_5NHNHCSNH_2 + C_6H_5NH_2$$

Both methyl and ethyl alcohols were tried as solvents and it was finally determined that a methanolic potash solution heated for five minutes gave the optimum yield, 75–102% based on the phenylhydrazine. It was found that dithizone could be heated in an oven at 40° without any noticeable decomposition, thereby shortening the time necessary for drying.

A new process for the purification of dithizone has been developed. By the use of ether we were able to obtain higher yields and a purer product than with chloroform. An over-all yield of 52–66% of dithizone was obtained.

Experimental

Phenylhydrazine Salt of β-Phenyldithiocarbazic Acid (I).—In a 1-liter three-necked flask, fitted with a motor stirrer, a condenser and a dropping funnel, is placed 128 cc. (sp. gr. 1.097) of pure redistilled phenylhydrazine, dissolved in 600 cc. of ordinary ether. The mixture is stirred vigorously during the addition of 52 cc. of carbon disulfide (sp. gr. 1.26), which is added at the rate of two drops per second, taking about one-half hour in all. The flask should be cooled with ice water whenever the mixture tends to boil. The stirring is continued for another half hour after addition of all the carbon disulfide. The precipitate is filtered by suction, and washed with 50 cc. of ether. It is then spread out on filter paper for fifteen to twenty minutes to allow evaporation of the ether. The yield is 183 g. (97%, based on phenylhydrazine).

Diphenylthiocarbazide (II).—The above salt is transferred to a 1-liter beaker and heated under a hood in a water-bath that is kept between 96–98°. *Caution*—do not heat above 98°. A heavy glass rod, bent or flattened at the end, acts as an efficient stirrer. The powder is stirred continuously by hand. After about ten to fifteen minutes the compound melts, becomes yellow and foamy, and liberates hydrogen sulfide. After about twenty to thirty minutes ammonia is given off. When a distinct odor of ammonia is *first detected*, the beaker is removed from the hot bath and placed in a pan of cold water for a minute and then cooled with cracked ice immediately. If the compound is heated as high as 100°, and allowed to stand without immediate cooling after removal from the water-bath, the compound decomposes violently. The mass may be olive green or brown when the heating is stopped, but it turns light brown on cooling. About 150 cc. of absolute alcohol is added, the mixture is warmed

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(1) Fischer, *Ann.*, **190**, 114 (1878); **212**, 316 (1882).

(2) Grummitt and Stickle, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 953 (1942).

slightly to loosen the mass, and then stirred until the taffy-like material has changed to a granular white precipitate. The mixture is allowed to stand at room temperature for one hour. The precipitate is collected on a Büchner funnel and washed with 50 cc. of absolute alcohol. If the red alcoholic filtrate is allowed to evaporate slowly, more of the carbazide will precipitate out. The yield of crude diphenylthiocarbazide is 100–125 g. (60–75%, based on the phenylhydrazine).

Diphenylthiocarbazone (III).—The crude carbazide is added to a solution of 60 g. of potassium hydroxide in 600 cc. of methanol in a 1-liter round-bottomed flask. The flask is heated in a water-bath until refluxing takes place. The mixture is refluxed for exactly five minutes, after boiling begins. (If it is boiled for a longer time, the yield is decreased.) The red solution is cooled with ice water and filtered by gravity. The carbazone is precipitated by adding ice-cold 1 *N* sulfuric acid with stirring, until the solution just tests acid to congo red paper. About 900–1100 cc. is necessary. When the end-point is reached, the liquid is no longer red but colorless. The blue-black precipitate is filtered by suction and washed with 50 cc. of cold water. The crude carbazone is recrystallized by dissolving it in 500 cc. of 5% sodium hydroxide solution, filtering by suction and acidifying immediately with 1 *N* sulfuric acid (about 650 cc.) until just acid to congo red paper. The precipitate is filtered by suction and then washed thoroughly with water by transferring it to a 2-liter beaker, adding 1600–1800 cc. of cold water, stirring thoroughly and refiltering. This process is repeated until there is no trace of sulfate in the washings. Four or five washings are usually necessary. Air is drawn through the precipitate on the Büchner funnel for twenty to thirty minutes. It is then dried in an oven at 40°. The yield of this crude diphenylthiocarbazone is 63–85 g. (75–102% based on phenylhydrazine). The decomposition range is anywhere from 120–140°. The carbazone is purified by putting a 5–10 g. portion of it in a Soxhlet extractor, covering with ether, allowing it to stand one hour, and then extracting one and one-half hours. The product is transferred immediately to a beaker, washed again with 50 cc. of ether, filtered by suction just long enough to remove most of the liquid, and then further dried by pressing between filter paper. The recovery is 60–87%. The purer the crude dithizone, the higher the percentage recovery. The pure compound is completely soluble in chloroform and decomposes sharply at a temperature between 165–169°.

The over-all yield of pure diphenylthiocarbazone based on the phenylhydrazine is 43–54.8 g. (52–66%).

Summary

An improved method for the preparation of dithizone has been developed.

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Complex Ions. V. The Magnetic Moments of Some Complex Ions of Nickel and Copper[1]

BY CHARLES D. RUSSELL,[2] GERALD R. COOPER AND W. C. VOSBURGH

Shaffer and Taylor[3] have shown that the paramagnetic susceptibilities of nickel and copper (II) ions in solution decrease on addition of substances that form complex ions with them. They concluded, in agreement with Pascal,[4] that the formation of a chemical bond lowers the susceptibility of a paramagnetic ion and that this lowering is proportional to the firmness of the bond.

The magnetic moments of the iron group ions are not much larger than the calculated spin moments of the unpaired 3*d* electrons and the relatively small differences between calculated and observed values are considered to be contributions of the orbital moments. These contributions are small because the orbital moments are largely "quenched" by the perturbing action of the electrostatic fields of neighboring atomic groups.[5] Nickel is typical of the latter half of the iron group, the ion having a calculated spin moment of 2.83 Bohr magnetons and an observed moment of about 3.2 or 3.3 Bohr magnetons.

The theory of Pauling[5b] and Van Vleck[5a] suggests that when the formation of a bond with a paramagnetic ion is accompanied by a small reduction of the magnetic moment, it is the orbital contribution to the moment that is reduced. Some additional measurements of the changes in the moments of nickel and copper (II) ions on formation of paramagnetic complex ions have given results in agreement with this.[6]

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(1) Thesis submitted by Charles D. Russell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, June, 1941.

(2) Now at The Texas Company, Research Laboratories, Beacon, N. Y.

(3) Shaffer and Taylor, THIS JOURNAL, **48**, 843 (1926). A number of references to older work are given by Shaffer and Taylor.

(4) Pascal, *Ann. chim. phys.*, [8] **16**, 571 (1909).

(5) (a) Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," The Clarendon Press, Oxford, 1932, pp. 283–301. (b) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 106.

(6) The magnetic moments of ferric and manganous ions are purely spin moments according to Van Vleck (ref. 5a, p. 301) and have no orbital contribution. If the formation of a bond affects only the orbital moment of an ion, the moments of iron (III) and manganese