Anal. Calcd. for $C_6H_5SO_4K$: S, 15.1. Found: S (from quinoline), 15.1, 15.05; (from dimethylaniline), 15.0, 15.0.

CHEMICAL DEPARTMENT OF THE CANCER RESEARCH INSTITUTE OF THE UNIVERSITY OF JERUSALEM, AND THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY
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The Change in Magnetic Susceptibility of Nickel Disalicylaldehyde on Hydrogenation

BY M. A. FOBES AND GEORGE N. TYSON, JR.

A mechanism that accounts for the uptake of hydrogen in copper disalicylaldehyde has been reported previously.[1] In the course of further magnetic susceptibility measurements of hydrogenated disalicylaldehydes it appears reasonable to extend the concept to the hydrogenated nickel compound. Green nickel disalicylaldehyde becomes yellow when hydrogenated, and both forms of the compound exhibit two unpaired electrons as shown in the experimental data.

Solutions and Hydrogenations.—The divalent nickel disalicylaldehyde used in this investigation has been described previously.[2] 1.9332 g. was diluted to 100 ml. using J. T. Baker and Co. C. P. grade pyridine. The solution so obtained was measured magnetically within a few minutes of mixing. The solution was then hydrogenated by placing approximately 50 ml. in a 250-ml. Florence flask, cooling to about 5° and evacuating to 15 mm. pressure, with subsequent introduction of hydrogen into the evacuated flask, to a pressure slightly greater than atmospheric. When the flask containing the hydrogen and the solution was heated to 90° for approximately 200 hours, hydrogenation occurred. The original solution was a light green, while the hydrogenated compound formed a yellow liquid with a brownish cast, which readily reverted to the green color when exposed to oxygen.

Magnetic Measurements.—The magnetic susceptibility measurements were made by the Gouy method. The susceptibilities due to the nickel disalicylaldehyde in the freshly prepared green solution (I) (measured at 24°) and the yellow brown hydrogenated nickel disalicylaldehyde (II) (measured at 26°) are shown in Table I. In the column listing the Bohr magnetons, the calculations have been made assuming complete quenching of the orbital contribution to the magnetic moment. In the conversion of the experimental data into Bohr magnetons, a correction has been made for the diamagnetism of the nonmetal portion of the molecule.

TABLE I

Soln.	$\chi_s \times 10^6$	$\chi_m \times 10^6$	Bohr magnetons Exptl.	Bohr magnetons Calcd.	Unpaired electrons
I	12.32	3706	3.0	2.83	2
II	12.08	3625	3.0	2.83	2

CHEMISTRY DEPARTMENT
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RECEIVED JUNE 30, 1941

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(1) Tyson and Vivian, THIS JOURNAL, **63**, 1403 (1941).

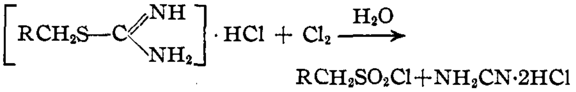
(2) Tyson and Adams, *ibid.*, **62**, 1228 (1940).

[CONTRIBUTION FROM MERCK AND CO., AND UNIVERSITY OF NORTH CAROLINA]

Explosion Hazard in the Chlorination of Alkyl Isothioureas to Prepare Alkyl Sulfonyl Chlorides

BY KARL FOLKERS, ALFRED RUSSELL AND R. W. BOST

In a series of papers, Sprague and Johnson[1] recently described a new and excellent method for the preparation of a considerable number of alkyl sulfonyl chlorides. The method consisted in the reaction of chlorine upon S-alkyl-isothiourea salts in aqueous solution according to the scheme



$$\left[RCH_2S{-}C{\overset{\textstyle NH}{\underset{\textstyle NH_2}{\lessgtr}}}\right]\cdot HCl + Cl_2 \xrightarrow{H_2O} RCH_2SO_2Cl + NH_2CN\cdot 2HCl$$

It was stated that when R was the carboxyl group, the reaction did not produce the sulfonyl chloride derivative. In connection with one of the problems in the Merck Research Laboratory, one of the research chemists investigated the reaction of chlorine upon formamidine thiolacetic acid hydrochloride ($R{=}CO_2H$) since the corresponding sulfonyl chloride was desired. The first experiment gave a very hygroscopic product melting at 78–81° which was apparently sulfoacetic acid.[2] This result suggested that the reaction actually did go, but that the sulfonyl chloride was hydrolyzed to the sulfonic acid. In the next experiment, greater care was taken to have all the materials and apparatus more carefully cooled throughout, but the solution was refrigerated over the week-end. After further brief passage of chlorine, the oily globules were collected in a vial from a separatory funnel; they exploded violently. The chemist suffered severe

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(1) Sprague and Johnson, THIS JOURNAL, **58**, 1348 (1936); **59**, 1837 (1937); **59**, 2439 (1937); **61**, 176 (1939); "Sulfonic Halides," U. S. Patent 2,147,346 by T. B. Johnson, assignor to Röhm and Haas Company, Philadelphia, Pa.; "Process of Preparing Sulfonyl Halides and Sulfonic Acid from Pseudothioureas," U. S. Patent 2,146,744 by T. B. Johnson, assignor to Röhm and Haas Company, Philadelphia, Pa.

(2) Sulfoacetic acid monohydrate was hygroscopic and melted at 84–86° according to O. Stillich, *J. prakt. Chem.*, **73**, 538 (1906).

and permanent injuries to a hand. Particles of glass were driven through his laboratory coat and clothing into his skin. His wrist watch was remarkably shattered, and the lenses of his glasses were cracked.

A similar explosion occurred at the University of North Carolina during the preparation of ethyl sulfonyl chloride by a graduate student. Chlorine was passed through a cooled suspension of S-ethyl isothiourea sulfate for about ten hours. The explosion occurred as the material was about to be removed from the reaction vessel. The explosion was very violent. Pieces of glass penetrated the operator's abdomen, and he suffered severe cuts on his arms. His condition involved extended dangerous surgical work, and was critical for several weeks. The general effect of the explosion was obvious in the laboratory. Much glass was entirely reduced to powder, but large pieces were driven through a nearby door and even, for example, through a standard acid bottle from one side to the other.

In personal communications, nitrogen trichloride was suggested by Dr. J. M. Sprague as the probable cause of the explosions. Nitrogen trichloride can be formed by the action of chlorine upon ammonia in acid solution. Guinchant[3] found[4] that nitrogen trichloride was formed by the action of hypochlorites upon urea. In these chlorinations, cyanamide, which is the second primary product, could hydrolyze through urea to give considerable amounts of ammonia as the chlorination time is prolonged. Thus, an ammonia concentration would be slowly formed for the production of nitrogen trichloride. The refrigeration period over the week-end of the solution in the Merck Laboratory and the ten-hour chlorination period in the North Carolina Laboratory were probably the steps which resulted in nitrogen trichloride formation.

Dr. Sprague carried out his chlorination research over a period of two years without an explosion, but on a few occasions he did observe that the droplets, extracted with ether, did react very vigorously with sodium bisulfite. After hearing of the explosions, Professor Treat B. Johnson reinvestigated the reaction and wrote in a personal communication that he observed no explosions. He has recently reported by correspondence that no explosion has ever resulted in his laboratory during such chlorination experiments, since the inception of the research in 1935. Their experience without explosions suggests that no appreciable nitrogen trichloride forms during the separation of the sulfonyl chlorides, and that the chlorination should be stopped after the first signs of excess chlorine in the solution.

This note is to suggest that until clear differentiation can be made between the completion of the formation of the sulfonyl chlorides and the beginning of the formation of nitrogen trichloride, the chlorinations should be performed with the realization that they may possess a serious explosion hazard. Safety precautions should be employed particularly when investigating new chlorination reactions or when making long and involved chlorinations. Because of the excellence of this method for the preparation of sulfonyl chlorides, further study is merited to carefully define the safety limits.

Formamidine Thiolacetic Acid Hydrochloride.[5]—The thiocarbamide (10.0 g.) was dissolved in 250 ml. of hot acetone, and 12.4 g. of monochloroacetic acid dissolved in 50 ml. of cold acetone was added. After standing for two days at 20–25°, 19.8 g. of formamidine thiolacetic acid hydrochloride was obtained by filtration. It had an indistinct melting point of 185–200°. Ray and Fernandez did not mention the melting point of their product.

Reaction of Chlorine upon Formamidine Thiolacetic Acid Hydrochloride. Sulfoacetic Acid.—Pulverized formamidine thiolacetic acid hydrochloride (10 g.) was suspended in 800 ml. of water and the mixture vigorously stirred mechanically. After cooling to 0°, chlorine was passed in for twenty minutes. After fifteen minutes, the solution was clear. No oil droplets became apparent after twenty minutes and the solution was not colored green. Five extractions with 100-ml. portions of diethyl ether yielded 209 mg. of gum.

Chlorine was passed into the solution at 0° for thirty minutes longer. Heavy yellow oil globules were now apparent, and the solution was green colored. The solution was extracted five times with 100-ml. portions of diethyl ether, and the extracts were washed three times with 50-ml. portions of 5% sodium bisulfite solution followed by washing with three portions of 50 ml. of water at 5°. The extract was dried with calcium chloride, and after distilling the ether at 20–25° *in vacuo* (10 mm.), there was 4.3 g. of a colorless oil containing a small amount of white solid. The oil solidified. The material was very hygroscopic and melted at 78–81°. It appeared to be sulfoacetic acid. Since any sulfonyl chloride must have hydrolyzed, a second experiment was tried.

Pulverized formamidine thiolacetic acid hydrochloride (10 g.) was suspended in 800 ml. of water, cooled to 0° and stirred mechanically. Chlorine was passed in so that there was no rise in temperature. After thirty to forty-five

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(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans Green and Co., 1931, pp. 599.

(4) Guinchant, *Compt. rend.*, **140**, 1170 (1905).

(5) Ray and Fernandez, *J. Chem. Soc.*, **105**, 2159 (1914).

minutes, the suspended material had dissolved and the solution began turning yellow. The chlorination was stopped after one hour. A small amount of a yellow crystalline material was filtered. (The entire apparatus was kept at 0–5°.) It was apparently chlorine hydrate, m. p. 10°. The filtrate was refrigerated (10–15°) over the week-end. No oil was present, so the solution was chlorinated for fifteen minutes. Separation of a heavy yellow oil took place. Approximately 4 or 5 ml. of the oil were drained from a separatory funnel into a vial. The substance exploded immediately.

S-Ethyl Isothiourea Sulfate.—This was prepared by the method of Sprague and Johnson,[1] using 76 g. of thiourea and 85 g. of diethyl sulfate. The yield of S-ethyl isothiourea sulfate was 102 g.

Reaction of Chlorine on S-Ethyl Isothiourea Sulfate.—The S-ethyl isothiourea sulfate (102 g.) was suspended in 350 g. of ice and water and stirred mechanically. After cooling to 5°, chlorine was passed in until the mixture had become yellow-green and a heavy oil had separated, while the mixture was kept below 10°. This required about ten hours. Stirring was continued for half an hour after the chlorination was stopped. The flask was then removed from the cooling bath, approximately ten minutes previous to the explosion. The explosion occurred as the flask was grasped preparatory to removal from the clamp holding it.

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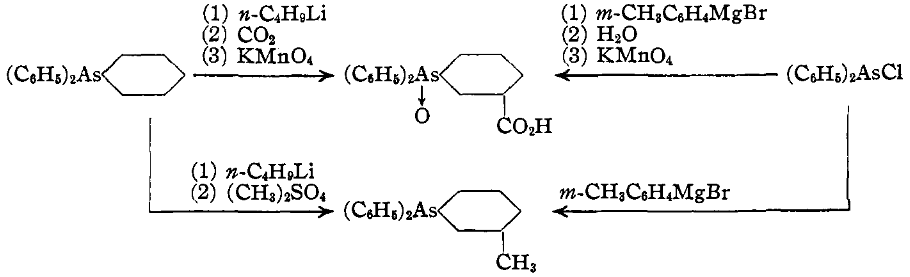
Metalation of Triphenylarsine

BY HENRY GILMAN AND CLARENCE G. STUCKWISCH

The metalation of triphenylamine by *n*-butyllithium takes place in a meta position,[1a] and not ortho as might have been predicted on the basis of earlier general observations.[1b,c] This anomalous orientation suggested an examination of the metalation of the related triphenylarsine. Here, also, metalation occurred in a meta position, and the structures of the products were established by the reactions



By analogy with N-phenylcarbazole,[1c] it is to be expected that metalation of As-phenyldibenzarsenole will take place in an ortho position of the As-phenyl group.

Experimental

Triphenylarsine and *n*-Butyllithium.—A solution of 20 g. (0.10 mole) of triphenylarsine and 0.25 mole of *n*-butyllithium in 500 ml. of ether was stirred and refluxed for forty-eight hours. The resulting solution was poured jetwise on solid, crushed carbon dioxide and the carbon dioxide allowed to evaporate. The ether solution was extracted with 10% potassium hydroxide. Acidification of the alkaline extract yielded 0.5 g. of a gummy, acidic material which could not be crystallized.

***m*-Carboxyphenyldiphenylarsine Oxide.**—The gummy material obtained from the metalation of triphenylarsine was dissolved in 10 ml. of acetone and refluxed for thirty minutes with 1 g. of potassium permanganate, in accordance with the directions of Blicke[2] for the conversion of arsines to arsine oxides. After cooling, the solution was diluted with water and acidified with hydrochloric acid. The solid which separated was filtered off and crystallized from dilute ethanol; m. p. 215°.

Anal. Calcd. for $C_{19}H_{15}O_3As$: neut. equiv., 266; As, 20.5. Found: neut. equiv., 262; As, 20.3.

***m*-Tolyldiphenylarsine.**—To the Grignard reagent from 17.7 g. (0.1 mole) of *m*-bromotoluene and 2.5 g. of magnesium in 60 ml. of ether was added dropwise 12 g. (0.05 mole) of diphenylchloroarsine in 50 ml. of ether. After addition was completed the solution was refluxed for one hour, cooled in an ice-bath, and hydrolyzed with dilute hydrochloric acid. The ether layer was dried and the ether was evaporated. The residue was distilled at 3 mm. The yield of *m*-tolyldiphenylarsine distilling at 170–173° (3 mm.) was 11.5 g. or 72%.

Anal. Calcd. for $C_{19}H_{17}As$: As, 20.8. Found: As, 20.6.

The mercuric chloride derivative crystallized in colorless plates from glacial acetic acid and melted at 201–202°.

Oxidation of *m*-Tolyldiphenylarsine.—A mixture of 6.4 g. (0.02 mole) of *m*-tolyldiphenylarsine and 250 ml. of water saturated with potassium permanganate was heated on an oil-bath at 60° for four weeks. The excess permanganate was removed with ethanol. The solution was then filtered and the filtrate acidified with hydrochloric acid. The solid which separated melted at 213–214° after crystallization from dilute ethanol. A mixed melting point with the product of the oxidation of the acidic material obtained from the metalation and subsequent carbonation of triphenylarsine gave no depression.

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[1] (a) Gilman and Brown, THIS JOURNAL, **62**, 3208 (1940); (b) Gilman and Bebb, *ibid.*, **61**, 109 (1939); (c) Gilman, Stuckwisch and Kendall, *ibid.*, **63**, 1758 (1941).

[2] Blicke and Safir, *ibid.*, **63**, 575 (1941).