[CONTRIBUTION FROM GEORGE WASHINGTON UNIVERSITY]

THE CONDENSATION OF RHODANIC ACIDS WITH 5-NITRO-ISATIN. RHODANAL-Δ-$^{5,3'}$-5'-NITRO-OXINDOLES[1]

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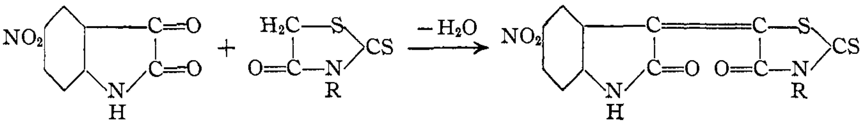
The susceptibility to reaction of various heterocyclic rings containing as an integral portion of their structure the CO-CH_2-S linkage has resulted in considerable study of these compounds. Among the more interesting of such heterocycles may be mentioned the rhodanic acids, the anhydrides of substituted dithiocarbamoglycolic acids. The methylene hydrogen of these 2-thio-4-thiazolidones reacts readily in the presence of a condensing agent with ketonic and quinoid oxygen. Advantage has been taken of this fact to prepare derivatives with aldehydes,[4] alloxan,[5] isatin[6] and phenanthraquinone.[7]

Hill and Henze[8] have condensed isatin and isatin-α-chloride with hydantoin and substituted hydantoins to obtain the corresponding oxindoles and pseudo indoxyls. Gränacher and Mahal[9] have demonstrated conclusively that isatin and rhodanic acid condense with elimination of the ketonic oxygen in the 3-position with formation of rhodanal oxindole. The generality of the reaction has been further examined in this Laboratory by the preparation of a series of substituted rhodanal-Δ$^{5,3'}$-oxindoles.[10]

In continuing a study of the effect of constitutional variation upon absorption of light, we have had occasion to prepare certain rhodanal-Δ$^{5,3'}$-5'-nitro-oxindoles, and the present paper reports the preparation and properties of these new derivatives. The condensation of rhodanic acids with 5-nitroisatin proceeds normally in an acetic acid medium in the presence of sodium acetate, the indigoid derivatives being separated by addition of water. The reaction is as follows



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[4] Andreasch and Zipser, *Monatsh.*, **26**, 1191 (1905).

[5] Butscher, *ibid.*, **32**, 9 (1911).

[6] Gendelman, *ibid.*, **43**, 537 (1922).

[7] Hann, *Thesis*, George Washington University, June, 1926.

[8] Hill and Henze, THIS JOURNAL, **46**, 2806 (1924).

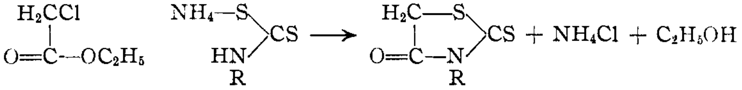
[9] Gränacher and Mahal, *Helv. Chim. Acta*, **6**, 467 (1923).

[10] Hann, THIS JOURNAL, **47**, 1189 (1925).

Experimental

Preparation of rhodanic acids. The rhodanic acids used in this investigation were prepared by the Miolati–von Braun synthesis. The general steps in this synthesis are (1) the preparation of the substituted ammonium dithiocarbamate from the primary amines and (2) the interaction of these intermediate products with esters of α-halogen fatty acids, resulting in loss of alcohol and ammonium halide and subsequent ring closure to yield rhodanic acids. The reactions are

$$RNH_2 + CS_2 + NH_4OH = HNRCSSNH_4 + H_2O \qquad (1)$$



(2)

The synthesis for phenyl, *o*- and *p*-anisyl, ψ-cumyl and β-naphthyl homologs was carried out along the general procedures of Andreasch and Zipser,[11] Antulich,[12] Kaluza[13] and Wagner[14] with the substitution of bromo-acetic ester in place of the corresponding chloro compound. The yield was increased by this procedure, due to a more complete reaction in ring closure.

Preparation of 5-Nitro-isatin.—The substituted isatin was prepared by nitration of isatin according to the directions of Calvery, Noller and Adams.[15] The yield was excellent and the substance was used without further purification.

Preparation of Aryl Rhodanal-$\Delta^{5,3'}$-5′-nitro-oxindoles.—Two grams of 5-nitro-isatin was dissolved in 25 cc. of glacial acetic acid and to this solution a molecular quantity of rhodanic acid and 5 g. of fused sodium acetate were added. The solution was then refluxed under a condenser for about three hours, unless bumping due to separation of reaction product became too violent to allow such treatment. In the latter case, the solution was cooled, the solid filtered off and the filtrate again refluxed until the time of total heating was three hours. After cooling, the solution was treated with water to precipitate the condensation product and dissolve any separated sodium acetate. The combined solid products of reaction were recrystallized or reprecipitated from glacial acetic acid.

The rhodanal-$\Delta^{5,3'}$-5′-nitro-oxindoles are red, crystalline derivatives, somewhat soluble in acetic acid and insoluble in water. They dissolve in sulfuric acid with the production of brilliant red colors. The melting points of the derivatives were obtained by Mr. J. F. Clevenger[16] in the micro melting point apparatus recently designed and described by him.

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[11] Andreasch and Zipser, *Monatsh.*, **24**, 499 (1903).

[12] Antulich, *ibid.*, **31**, 891 (1910).

[13] Kaluza, *ibid.*, **30**, 701 (1909).

[14] Wagner, *ibid.*, **27**, 1233 (1906).

[15] Calvery, Noller and Adams, This Journal, **47**, 3059 (1925).

[16] Clevenger, *Ind. Eng. Chem.*, **16**, 854 (1924).

TABLE I

TABLE OF ARYL RHODANAL-$\Delta^{5,3'}$-5'-NITRO-OXINDOLES ANALYSIS (SALICYL-SULFONIC ACID METHOD)

Aryl group	M. p., °C.	Weight	0.1 *N* acid, cc.	N found, %	N calcd., %
Phenyl	260–267	0.1731	13.6	11.01	10.97
o-Anisyl	247	.1289	9.1	9.89	10.17
p-Anisyl	370	.1277	9.2	10.09	10.17
ψ-Cumyl	245	.1293	9.0	9.75	9.88
β-Naphthyl	330	.1053	7.3	9.71	9.70

Summary

Phenyl, *o*- and *p*-anisyl, *ψ*-cumyl and *β*-naphthyl rhodanic acids have been condensed with 5-nitro-isatin to form the corresponding aryl rhodanal-$\Delta^{5,3'}$-5'-nitro-oxindoles.

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CHLOROFORM SOLUBLE METAL PYRIDINE CYANATES

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Many compounds of pyridine with inorganic salts have been prepared and described.[1] The first mention that any of these substances is soluble in chloroform appears to be in the paper of Spacu,[2] in which the author described a delicate qualitative test in which cupric pyridine thiocyanate was precipitated from a water solution of cupric thiocyanate by the addition of pyridine. Chloroform dissolved the substance more readily than water and yielded an emerald green solution which served for the detection of one part of copper in 300,000–800,000, one of pyridine in 2000 and one of thiocyanate in 50,000. Spacu, on the basis of copper and nitrogen determinations, assigned to his substance the composition, $Cu(NCS)_2 \cdot 2C_5H_5N$. E. A. Werner[3] later developed a similar test for cyanate. The

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[1] Pyridine compounds with the cadmium halides, zinc iodide and cyanide and nickel bromide, Varet, *Compt. rend.*, **115**, 464 (1892), **124**, 1155 (1897); with the permanganates of silver, copper, cadmium, zinc and nickel, Klobb, *Compt. rend.*, **118**, 1271 (1894); with the sulfates and halides of iron, cobalt, nickel, cadmium, lead, copper, and manganese, Reitzenstein, *Ann.*, **282**, 267 (1894); *Z. anorg. Chem.*, **18**, 253 (1898); with copper sulfate, nitrate and acetate, Tombeck, *Ann. chim. phys.*, **21**, 433 (1900), **22**, 113 (1901); with cupric and cuprous thiocyanate, Litterscheid, *Arch. Pharm.*, **239**, 336 (1901), **240**, 74 (1902); with the thiocyanates of silver, lead, copper, manganese, nickel, cadmium, zinc, mercury, cobalt and iron, Grossmann, *Ber.*, **37**, 559 (1904); with copper nitrate, Pfeiffer and Pimmer, *Z. anorg. Chem.*, **48**, 98 (1905); and with the halides of cobalt and chromium, Werner, Feenstra and Osann, *Ber.*, **39**, 1538 (1906), etc.

[2] Spacu, *Bull. soc. Stiinte Cluj.*, **1**, 284 (1922).

[3] Werner, *J. Chem. Soc.*, **123**, 2577 (1925).