

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF GEORGIA]

Some Allyl Nitrophenyl Thiosemicarbazides and their Analytical Properties

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Thiosemicarbazide and allyl groups have been present in a number of organic compounds which gave precipitates or color reactions with aqueous solutions of certain inorganic cations. While these groups together would appear to be the reactive part of the compound, both the selectivity and sensitivity of the reagent would seem to be affected by the constitution of the remainder of the molecule.

The purpose of this investigation was to study the effect on the selectivity and sensitivity of a related series of reagents which contained both the thiosemicarbazide and allyl groups. For this purpose 1-allyl-4-phenyl thiosemicarbazide^{2,3} was selected as the reference compound and a nitro group was successively introduced into the phenyl group in the ortho, meta and para positions. In addition to the selectivity and sensitivity possibilities mentioned above, the results of a study of this series of compounds might add to our information upon the effect of ortho, meta and para substitution in organic analytical reagents.

Distilled water solutions (0.1 *N*) of the metallic nitrates of most of the cations usually encountered in elementary qualitative analysis were tested. Each of the four reagents gave tests with silver, mercurous, mercuric and copper ions. Therefore, the nitro group had no effect upon the selectivity of the reactive group. The sensitivity of the four reagents, however, varied widely. The para nitro compound was by far the most sensitive in every instance, and the ortho nitro compound was next, while the meta nitro compound and the reagent without any nitro group present, were found to be the least sensitive and about equally poor.

1-Allyl-4-(*p*-nitrophenyl) thiosemicarbazide gave a red precipitate upon standing with mercuric mercury solutions of one part in a million and a slight color reaction with one part in ten million. Several attempts were made to use this reagent in a gravimetric quantitative determination of mercury, but the results obtained were unsatisfactory.

(1) Constructed from a thesis by J. T. Andrews, presented to the Graduate Faculty of the University of Georgia, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

(2) Dixon, *J. Chem. Soc.*, **57**, 263 (1890).

(3) Avernarius, *Ber.*, **24**, 268 (1891).

Experimental

1-Allyl-4-phenyl thiosemicarbazide was prepared according to Avernarius.^{2,3} It melted at 119° (uncor.) and agreed in all other respects to the compound described in the literature. An excess of the compound was added to water, heated to 90°, agitated for some time, and allowed to cool to 25°. Ten ml. of this saturated solution was pipetted into a tared dish, evaporated and dried in an oven at 90° and weighed. The result in grams times ten was taken as the water solubility of the compound in 100 ml. of water. Duplicate results gave the solubility as 0.118 g. at 25°. An alcoholic solution of the compound added to aqueous solutions of the cations gave a white precipitate with silver, a gray precipitate with mercurous mercury, a yellow precipitate with mercuric mercury, and a blue color with copper.

1-Allyl-4-(*o*-nitrophenyl) thiosemicarbazide was prepared according to Guha.⁴ The purified needles melted at 166° (uncor.). There was 0.029 g. found to be soluble in 100 ml. of water at 25°. An alcoholic solution of the compound added to aqueous solutions of the cations gave orange precipitates with both mercurous and mercuric mercury, a red precipitate with silver, and a green precipitate with copper.

1-Allyl-4-(*m*-nitrophenyl) Thiosemicarbazide.—To an alcohol solution of 10 g. of *m*-nitrophenylhydrazine was added 7 g. of allyl isothiocyanate. This solution was heated for five minutes and allowed to cool. The thick oil which separated was dissolved in hot 50% alcohol and allowed to cool. The yellow crystals obtained were soluble in acetone, bases (turning orange red), and very slightly soluble in water. Their m. p. was 120° (uncor.). The yield was 90% of the theoretical.

Anal. Calcd. for C₁₀H₁₂N₄O₂S: N, 22.21; S, 12.71. Found: N, 22.14; S, 12.63.

The solubility in 100 ml. of water at 25° was 0.033 g. An alcoholic solution of the compound added to aqueous solutions of the cations gave a cream colored precipitate with silver, a grayish-black precipitate with both mercurous and mercuric mercury, and a blue color with copper. It was not very sensitive with any of these.

1-Allyl-4-(*p*-nitrophenyl) Thiosemicarbazide.—To a solution of 8 g. of *p*-nitrophenylhydrazine dissolved in 95% alcohol was added 4.6 g. of allyl isothiocyanate. This mixture was heated for five minutes and allowed to cool. The yellow needles obtained were recrystallized from 95% alcohol until pure. They were very soluble in acetone, soluble in alcohol, slightly soluble in water and soluble in bases (turning a red color). At 25°, 3.273 g. of the compound was soluble in 100 ml. of 95% alcohol. At 25°, 0.031 g. of the compound was soluble in 100 ml. of water. The compound melted at 188° (uncor.), with some decomposition. The yield was 76% of the theoretical.

(4) P. C. Guha and S. K. Ray, *Quart. J. Indian Chem. Soc.*, **2**, 83-94 (1925); P. C. Guha and T. N. Ghosh, *ibid.*, **4**, 561-72 (1927).

| Concn., γ /l. (mcg.) | Reagent A | Reagent B | Reagent C |
|----------------------------------|-------------------|--------------------------|--|
| TABLE I | | | |
| Sensitivity for Cu^{++} | | | |
| 1×10^7 | Dark blue color | Black-green ppt. | Black ppt. |
| 1×10^6 | Blue color | Black-green some ppt. | Black-green ppt. |
| 1×10^5 | Blue color | Dark green colored soln. | Gray ppt. |
| 1×10^4 | Blue color | Light green color | Brown-red color, brown ppt. after standing |
| 1×10^3 | Slight blue color | No reaction | Very slight color |
| Sensitivity for Ag^+ | | | |
| 1×10^7 | | Brown ppt. | Orange ppt. |
| 1×10^6 | | Brown-purple ppt. | Orange-red ppt. |
| 1×10^5 | | Purple ppt. | Crimson ppt. |
| 1×10^4 | | No color or ppt. | Light red soln., ppt. after standing |
| 1×10^3 | | No reaction | Slight color |
| Sensitivity for Hg^{++} | | | |
| 1×10^7 | | Yellow ppt. | Orange ppt. |
| 1×10^6 | | Red ppt. | Red ppt. |
| 1×10^5 | | Purple red ppt. | Red ppt. |
| 1×10^4 | | Red color | Red ppt. |
| 1×10^3 | | Slight color | Some ppt. after standing |
| 2.5×10^2 | | No reaction | Red color that can be seen clearly |
| 1×10^2 | | No reaction | Slight change in color |

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2\text{S}$: N, 22.21; S, 12.71. Found: N, 22.26; S, 12.66.

An alcoholic solution of the compound when added to aqueous solutions of the cations gave an orange precipitate with both mercurous and mercuric mercury, a red precipitate with silver, and a dark green precipitate with copper.

Sensitivities.—The tests for the sensitivities of the compounds were made in the following way. A solution containing 1×10^7 mcg. per liter of the ion to be tested was prepared and diluted to other concentrations in volumetric flasks. A saturated alcohol solution of each reagent was used in the tests. When eight drops of this alcohol solution of the reagent were added to five ml. of water or to five ml. of dilute nitric acid, and allowed to stand overnight, no precipitation resulted. When eight drops of the reagent were added to 5 ml. of concentrated nitric acid and allowed to stand overnight, a slight precipitation occurred. The sensitivity of 1-allyl-4-(*m*-nitrophenyl) thio-

semicarbazide was not determined since it affected the mercurous, mercuric, silver and copper ions in fairly concentrated solutions only. For the same reason, the sensitivity of 1-allyl-4-phenyl thiosemicarbazide (Reagent A) was only tested for copper. The sensitivities of 1-allyl-4-(*o*-nitrophenyl) thiosemicarbazide (Reagent B) and 1-allyl-4-(*p*-nitrophenyl) thiosemicarbazide (Reagent C) are shown in the table.

Summary

1. Neither the presence of a nitro group, nor its position, affected the selectivity of the reactive group, but did materially affect the sensitivity of the compounds.

2. 1-Allyl-4-(*p*-nitrophenyl) thiosemicarbazide is a very sensitive reagent for mercuric mercury.

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