the experimental techniques are described in previous publications in this series.

Isopropylamine (Eastman Kodak Company) was dried over anhydrous barium oxide for several days. It was then distilled over sodium and a middle fraction which boiled at 31.4° at 750 mm. was collected. This sample was introduced into the high vacuum apparatus and retreated with sodium. The purified amine exhibited a constant vapor pressure of 194 mm. at 0°.

Diisopropylamine and **di-*n*-propylamine** were commercial samples obtained from Sharples Chemicals, Inc. The amines were treated with lead–sodium alloy for several days and then were distilled through a small column (15 plates) over sodium. Middle fractions which distilled at 82.6° at 750 mm. for diisopropylamine ($n^{20}\text{D}$ 1.3922) and 108.6° at 747 mm. for di-*n*-propylamine ($n^{20}\text{D}$ 1.4041) were collected and used. Diisopropylamine exhibited a vapor pressure of 23.5 mm. at 0°; di-*n*-propylamine, a pressure of 6.5 mm. at the same temperature.

***t*-Butylamine** was prepared by a Hofmann rearrangement of trimethylacetamide, prepared by standard procedures. The hydrochloride of the amine was recrystallized several times from absolute alcohol and the free amine then generated from the hydrochloride with potassium hydroxide and collected directly in the high vacuum apparatus. The amine was then treated with sodium to remove traces of water and fractionated in the high vacuum apparatus, discarding the first and last fractions. The product thus obtained exhibited a constant vapor pressure of 117 mm. at 0°.

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Summary

1. With trimethylboron as the reference acid, the sequence of base strength of the isopropylamines is $[(i\text{-C}_3\text{H}_7)_3\text{N}] < (i\text{-C}_3\text{H}_7)_2\text{NH} < \text{NH}_3 < i\text{-C}_3\text{H}_7\text{NH}_2$.

2. With the same reference acid, the sequence of base strength of the *t*-butylamines is $[(t\text{-C}_4\text{H}_9)_3\text{N}] < [(t\text{-C}_4\text{H}_9)_2\text{NH}] < t\text{-C}_4\text{H}_9\text{NH}_2 < \text{NH}_3$.

3. Diisopropylamine forms a highly unstable addition compound with trimethylboron; di-*n*-propylamine, a much stabler derivative.

4. The sequences observed and the relative stabilities of the addition compounds of the two isomeric dipropylamines are in excellent agreement with the predicted effect of F-strain on the behavior of the bases.

5. In the course of the investigation, the new addition compounds isopropylamine-trimethylboron, diisopropylamine-trimethylboron, di-*n*-propylamine-trimethylboron, and *t*-butylamine-trimethylboron were prepared and characterized.

DETROIT, MICHIGAN RECEIVED AUGUST 11, 1945

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

4-Allylthiosemicarbazide Derivatives and Some of their Analytical Properties[1]

BY ALFRED W. SCOTT AND MARVIN A. MCCALL

Several compounds containing the 4-allylthiosemicarbazide grouping have been reported useful as organic precipitating agents.[2,3] Compounds containing similar structures, such as allylthiourea,[4] thiosemicarbazide,[5] and diphenylthiocarbazone,[4] have been recommended as organic precipitating agents for certain metallic ions.

We have now prepared the allylthiosemicarbazones of some six hydroxy and methoxy benzaldehydes and have tested their usefulness as precipitants for the metallic ions of qualitative analysis. The properties of these new substances and their analytical behavior are listed in the table.

The carbazones were prepared by refluxing for about thirty minutes in ethanol a solution of equivalent molecular quantities of 4-allylthiosemicarbazide and the aldehyde. Upon cooling, minute white crystals were obtained (yellow crystals with isatin) which were recrystallized from ethanol.

The carbazones were tested by adding 2–4 drops of an aqueous alcoholic solution to 3 ml. of a 0.1 *N* solution of the ions. Those ions which showed promise of giving a precipitate were then tested more fully, following the same procedure, in solutions of progressively increasing dilution.

4-Allylthiosemicarbazone of *p*-hydroxybenzaldehyde as a precipitating agent for Bi^{+++} was the most promising. A comparison with sodium stannite gave the following results, respectively, at different concentrations of Bi^{+++}; at 10 to 0.1 g./liter a bright red *versus* a black precipitate; at 0.01 g./liter a slightly red *versus* a very slightly black precipitate, while at a ten times greater dilution neither reagent gave any precipitate. It would appear, therefore, that this carbazone can be used advantageously as a qualitative precipitant for bismuth. Its brilliant red color is very distinctive and it is sensitive enough for use in most qualitative procedures of analysis, being equal to the sensitivity of the test using sodium stannite. The use of the organic reagent eliminates the necessity of preparing fresh sodium stannite as usually required.

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[1] Abstracted from a thesis submitted by Marvin A. McCall to the Graduate School of The University of Georgia in partial fulfillment of the requirements for the degree of Master of Science.

[2] Scott and Adams, THIS JOURNAL, **57**, 541 (1935).

[3] Scott and Andrews, *ibid.*, **64**, 2873–2874 (1942).

[4] C. J. van Nieuwenburg, "Tables of Reagents for Inorganic Analysis," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1938.

[5] Ibert Mellan, "Organic Reagents in Inorganic Analysis," The Blakiston Co., Philadelphia, Pa., 1941.

TABLE I

4-ALLYLTHIOSEMICARBAZONES OF SOME AROMATIC ALDEHYDES

Benzaldehyde derivative	Yield, %	M. p., °C.	Formula	Percentage composition Nitrogen Calcd.	Nitrogen Found	Sulfur Calcd.	Sulfur Found	Sensitivity[a] (g./liter) and color of precipitates Ag^+	Bi^{+++}[b]	Cu^{++}	Fe^{+++}	Hg^+	Hg^{++}	Pb^{++}
m-Hydroxy-	75	143–144	$C_{11}H_{13}ON_3S$	17.86	17.62	13.62	13.35	0.01 wh.	0.01 or.	Gr.			0.1 wh.	Wh.
3-Methoxy-4-hydroxy-	66	134	$C_{12}H_{15}O_2N_3S$	15.84	15.90	12.08	12.05	Wh.	0.1 yellow	0.1 gr.		Gr.	Wh.	Wh.
p-Hydroxy-	63	181–182	$C_{11}H_{13}ON_3S$	17.86	17.85	13.62	13.61	Wh.	0.01 red++	Gr.		Yl.	Yl.	
2,4-Dihydroxy-	65	201–202	$C_{11}H_{13}O_2N_3S$	16.72	16.42	12.75	12.72	Wh.	Yl. sol.	Gr.	Amb. sol.	Gr.	Yl.	
3,4-Dihydroxy-	63	199–200	$C_{11}H_{13}O_2N_3S$	16.72	16.72	12.75	12.69	Wh.	0.01 or.	0.01 br.	0.02 gr.	Gr.	Wh.	1.0 yl.
Isatin	70	210–211	$C_{11}H_{12}ON_4S$	21.53	21.46	12.30	11.97	No test—too insoluble						

[a] Where no figures are given for the sensitivity it was very poor and was not recorded. [b] The test for the Bi^{+++} ion is best carried out in a nitric acid solution. Sometimes the precipitate formed had a yellow-orange color, but upon addition of more concentrated nitric acid it changed to the characteristic brilliant red. It was found by experiment that 5 drops of concentrated nitric acid per 3 ml. of solution gave the best results; if an additional 25 drops of concentrated nitric acid were added, the precipitate dissolved.

A series of tests was made using a mixture of Cu^{++} and Bi^{+++} at equal concentrations. Since Cu^{++} gave a green precipitate which completely obscured the red bismuth precipitate, the Bi^{+++} ion was first precipitated as the hydroxide with NH_4OH and washed. The bismuth hydroxide left on the filter paper was dissolved in 1 or 2 ml. of 6 *N* nitric acid and then the organic reagent was added drop by drop, producing the characteristic red precipitate. This confirms the above conclusion.

It was found that 4-allylthiosemicarbazone of 3,4-dihydroxybenzaldehyde gave some very interesting color reactions with two of the anions. The most interesting reaction was the one with the NO_2^- ion, which gave in concentrated acetic acid solutions a red-colored solution or brown precipitate, depending upon the amount of acid and the concentration of the anion. A series of tests was carried out to determine the sensitivity of this reagent for the NO_2^- ion. The test may be carried out either in the presence or absence of the NO_3^- ion, since this ion has no effect under the conditions of the experiment. The lowest detectable concentration of NO_2^- was 0.1 g./liter.

The $CrO_4^=$ ion gave the solution a red color which soon turned brown and gave off a mustard oil odor. None of the other anions usually found in the schemes of analysis reacted under the conditions of the test.

Tests of 4-allylthiosemicarbazide itself and of 1-thiocarbamido-3-allylthiocarbamide, 4-allylthiosemicarbazone of benzaldehyde and 4-allylthiosemicarbazone of salicylaldehyde previously described in the literature showed them to be of no particular value as precipitating agents, since their sensitivity and selectivity for these ions were very poor.

Summary

Six new compounds containing the 4-allylthiosemicarbazide structure were prepared and their analytical properties investigated. Of the 4-allylthiosemicarbazones tested, that of *p*-hydroxybenzaldehyde has been found to be an advantageous test for the bismuth ion, rivaling the familiar sodium stannite test. Also, the 4-allylthiosemicarbazone of 3,4-dihydroxybenzaldehyde may be used advantageously as an organic reagent for the detection of nitrites in the presence of nitrates and many other anions. The $CrO_4^=$ ion was the only anion found to interfere since it gives a similar red-colored solution. This test using the organic reagent is sensitive enough to detect 0.1 g. of NO_2^- per liter of solution.

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