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HYDRAZINE DERIVATIVES OF THE CARBONIC AND THIOCARBONIC ACIDS. I. THE PREPARATION AND PROPERTIES OF THIOCARBOHYDRAZIDE

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INTRODUCTION

Although an extensive amount of information is already at hand concerning the hydrazine derivatives of the carbonic and the thiocarbonic acids, no real effort has been made to correlate the physical and chemical properties of these substances, nor has any attempt been made to elucidate the relationships which make possible the systematic classification of these potentially important and useful compounds. The present paper dealing specifically with thiocarbohydrazide, as well as those publications which are to follow, are designed to present information regarding the type reactions which are generally applicable to the synthesis of such hydrazine derivatives.

Practically all of the hydrazine compounds which have been subjected to experimental study in this laboratory may be regarded as carbonic acid derivatives related to water, ammonia, and hydrogen sulfide as parent substances. Certain groups derivable from each of these parent solvents are structurally analogous and in many cases chemically similar (see Table I). It therefore becomes obvious that appropriate replacement of the oxo and hydroxo groups in carbonic acid by such analogous groups will lead to a wide variety of so-called solvo and mixed solvo compounds, as illustrated in Table II. It should be pointed out that these examples represent only a few of the more familiar and simpler carbonic acid derivatives. This same formal method of classification could be extended to include the O-, S-, and N-substituted derivatives of each of the parent substances listed in Table I and of the compounds given in Table II. These analogies are more than formal in character since the solvent system concept emphasizes not only the structural relationships which exist between the various compounds, but definitely suggests possible methods of preparation which may be employed for the various members of each series of compounds.

The following type reactions, implicit in the solvent system theory, have been employed in the present investigation.

1. **Solvation** or **hydrazination** reactions in which hydrazine or a substituted hydrazine is added to a carbonic acid ansolvide, *i.e.* CO_2, CS_2, COS, HNCO,

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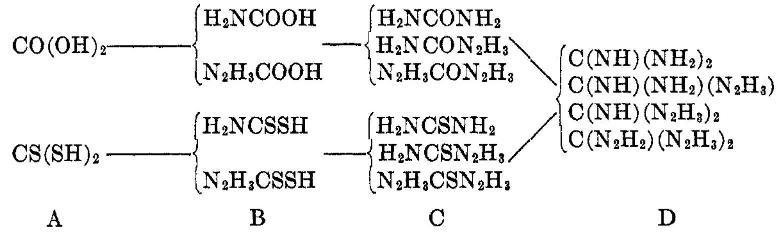
TABLE I

ANALOGOUS GROUPS DERIVED FROM PARENT SOLVENTS

HXH	XH	X
HOH	OH	O
HSH	SH	S
HNH_2	NH_2	(NH or N)
HN_2H_3	N_2H_3	N_2H_2

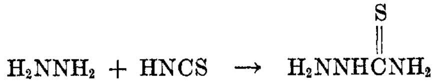
TABLE II

HYDRAZINE DERIVATIVES OF THE AQUO, AMMONO, AND THIO CARBONIC ACIDS*

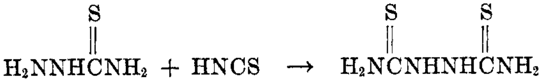


* Parent substances are represented by carbonic and trithiocarbonic acids, respectively (A). The "amic" acids and their hydrazine analogs are listed over (B). The compounds in which substitution of hydrazide functions for amide groups in both urea and thiourea has been accomplished are given in column (C). Guanidine and the aminoguanidines represent ammonia and hydrazine analogs of the carbonic acids in which complete replacement of the analogous groups of the parent aquo and thio acids has been achieved. In many of the above instances interconversion, both horizontally as well as vertically, has been accomplished by appropriate solvolytic reactions.

HNCS, or H_2NCN. The classical reaction of thiocyanic acid with hydrazine may be cited to serve as an illustration of such a type process.

1.


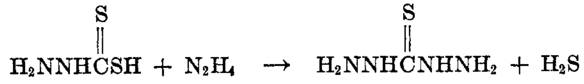
$$H_2NNH_2 + HNCS \rightarrow H_2NNH\overset{\displaystyle S}{\overset{\|}{C}}NH_2$$

2.


$$H_2NNH\overset{\displaystyle S}{\overset{\|}{C}}NH_2 + HNCS \rightarrow H_2N\overset{\displaystyle S}{\overset{\|}{C}}NHNH\overset{\displaystyle S}{\overset{\|}{C}}NH_2$$

Despite the fact that the conditions required to carry out the hydrazination of the various carbonic acid ansolvides vary widely, the reactions may be considered to be the same schematically.

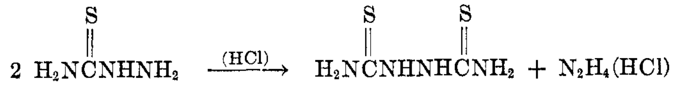
2. **Solvolysis** or **hydrazinolysis** reactions where hydrazine reacts with a carbonic acid derivative to displace a solvent molecule for the purpose of introducing a hydrazine function. The molecule evolved in this reaction may be H_2O, ROH, H_2S, RSH or NH_3 in the cases to be considered in the present series of papers.

3.


$$H_2NNH\overset{\displaystyle S}{\overset{\|}{C}}SH + N_2H_4 \rightarrow H_2NNH\overset{\displaystyle S}{\overset{\|}{C}}NHNH_2 + H_2S$$

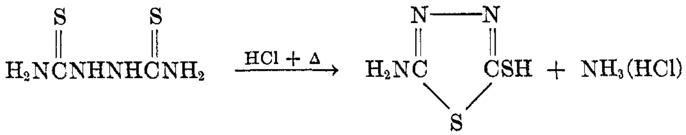
3. **Desolvation** reactions in which a solvent molecule is removed either from two molecules of a linear structure to form a more complex chain or from one molecule of a sufficiently long chain compound in the formation of a cyclic derivative.

4.



$$2\ H_2N\overset{\overset{S}{\|}}{C}NHNH_2 \xrightarrow{(HCl)} H_2N\overset{\overset{S}{\|}}{C}NHNH\overset{\overset{S}{\|}}{C}NH_2 + N_2H_4(HCl)$$

5.



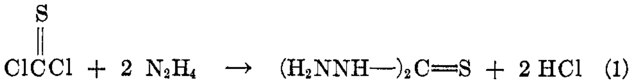
The experimental conditions employed to bring about such desolvation cyclization processes vary widely depending upon the structure and composition of the starting material and the type of ring closure desired.

PREPARATION AND PROPERTIES OF THIOCARBOHYDRAZIDE

The preparation of thiocarbohydrazide, one of the simplest of the hydrazine derivatives of thiocarbonic acid, in relatively large quantities was essential to the investigation of the more complex derivatives. Since attempts to prepare this compound using the experimental conditions described in the literature failed to produce efficiently the amounts of material desired, a study of the various possible syntheses was undertaken in order to develop a more convenient method of preparing this compound in quantity.

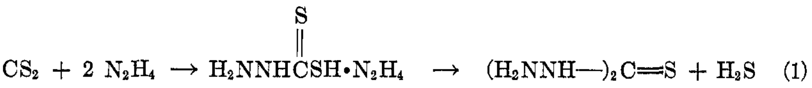
Four methods of preparing thiocarbohydrazide represented by Equations 6 through 9 have been reported previously.

6.



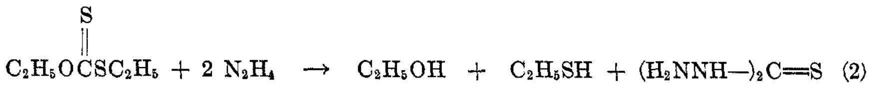
$$Cl\overset{\overset{S}{\|}}{C}Cl + 2\ N_2H_4 \rightarrow (H_2NNH—)_2C{=}S + 2\ HCl \quad (1)$$

7.



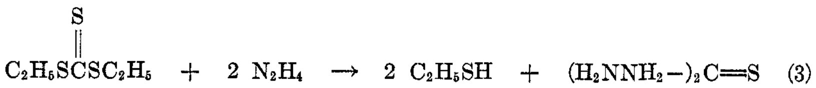
$$CS_2 + 2\ N_2H_4 \rightarrow H_2NNH\overset{\overset{S}{\|}}{C}SH{\cdot}N_2H_4 \rightarrow (H_2NNH—)_2C{=}S + H_2S \quad (1)$$

8.



$$C_2H_5O\overset{\overset{S}{\|}}{C}SC_2H_5 + 2\ N_2H_4 \rightarrow C_2H_5OH + C_2H_5SH + (H_2NNH—)_2C{=}S \quad (2)$$

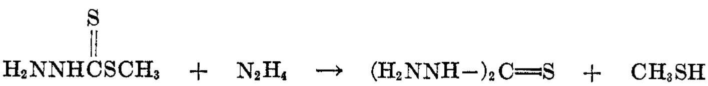
9.



$$C_2H_5S\overset{\overset{S}{\|}}{C}SC_2H_5 + 2\ N_2H_4 \rightarrow 2\ C_2H_5SH + (H_2NNH_2-)_2C{=}S \quad (3)$$

In addition to these, a fifth synthetic method, represented by Equation 10, was investigated.

10.



$$H_2NNH\overset{\overset{S}{\|}}{C}SCH_3 + N_2H_4 \rightarrow (H_2NNH-)_2C{=}S + CH_3SH$$

Each of these procedures involves the hydrazinolysis of a simpler thiocarbonic acid derivative. The choice of the most convenient synthetic method will, therefore, depend upon the reactivity toward hydrazine of the various functional groups involved and upon the ease of preparing and handling the starting materials.

From the standpoint of the availability of starting materials, the reaction of hydrazine with carbon disulfide is by far the most attractive method of preparing thiocarbohydrazide in quantity. As indicated in Equation 6, these two reagents react immediately to form hydrazinium dithiocarbazinate. However, attempts to effect the elimination of hydrogen sulfide by mild heating of dilute, aqueous solutions of hydrazinium dithiocarbazinate, even in the presence of lead oxide (1), gave only very small yields of the desired product. Moderate yields of thiocarbohydrazide were obtained by actively refluxing more concentrated solutions of hydrazinium dithiocarbazinate. Addition of hydrazine to the reaction mixture was found to increase the yield of thiocarbohydrazide. This reaction was, therefore, investigated further to determine the effects on the yield of such variables as (a) the mole ratio of hydrazine to hydrazinium dithiocarbazinate; (b) the reaction time; (c) the total concentration of reactants; (d) the *p*H of the reaction mixture.

The yield of thiocarbohydrazide increased as the ratio of hydrazine to hydrazinium dithiocarbazinate increased until a 3-mole excess of hydrazine was used. (See Table III.) The increase in yield obtained by using a 4-mole excess of hydrazine was insignificant. The yield was shown to depend somewhat upon the time the reaction mixture was refluxed. When reaction mixtures containing hydrazine and hydrazinium dithiocarbazinate (ratio 3:1) were refluxed for 1, 1.5, and 2 hours, yields of 44.7%, 49.0%, and 43.5%, respectively, were obtained. The decreased yield at the longer reflux time is undoubtedly due to the decomposition of thiocarbohydrazide known to take place in basic solution. Dilution of the reaction mixture with water causes a decrease in the yield of thiocarbohydrazide (Table IV). This is in agreement with the previous observation that thiocarbohydrazide was not formed efficiently in very dilute solutions. Decreasing the *p*H of the reaction mixture by the use of hydrazine monohydrochloride and hydrazine dihydrochloride instead of hydrazine decreased the yield of thiocarbohydrazide to 11.5% and 0%, respectively. The formation of carbon disulfide during these experiments suggests that dissociation of hydrazinium dithiocarbazinate occurs in more acidic solutions.

TABLE III

EFFECT OF MOLE RATIO OF HYDRAZINE TO HYDRAZINIUM DITHIOCARBAZINATE ON THE YIELD OF THIOCARBOHYDRAZIDE

MOLE RATIO OF HYDRAZINE TO HYDRAZINIUM DITHIOCARBAZINATE	YIELD CRUDE PRODUCT, %	YIELD PURE PRODUCT, %
1:1	40.6	30.7
2:1	51.0	44.3
3:1	57.2	49.0
4:1	57.3	49.5
5:1	54.0	39.4

TABLE IV

EFFECT OF CONCENTRATION OF REAGENTS[a] ON YIELD OF THIOCARBOHYDRAZIDE

TOTAL VOLUME, ML.	CRUDE YIELD, %	PURE PRODUCT, %
100	60.7	46.4
200	57.2	49.0
300	42.5	34.8

[a] Hydrazine (0.6 mole) and hydrazinium dithiocarbazinate (0.2 mole).

It is unnecessary, however, to isolate hydrazinium dithiocarbazinate in order to effect its conversion into thiocarbohydrazide. The direct addition of carbon disulfide to an aqueous solution of hydrazine, followed by refluxing of the resulting mixture, represents a distinct improvement, provided that an excess of hydrazine is employed, corresponding essentially to mole ratios specified above for the hydrazinolysis of hydrazinium dithiocarbazinate. Yields were essentially the same as those obtained using hydrazinium dithiocarbazinate as the starting material except that the optimum time of refluxing was decreased to 1 hour. It was also found that periodic removal of thiocarbohydrazide from the reaction mixture increased the over-all yield (to 61.7% and 63.3% in two separate preparations). This same modification would undoubtedly also improve the yields obtained when hydrazinium dithiocarbazinate is used as a starting material. Since the effect of using a solvent other than water could not be predicted, reactions were carried out in ethanol and in 1:1 water-ethanol mixture. The yields obtained were essentially the same as those reported above.

Attempts to prepare thiocarbohydrazide by refluxing alcoholic solutions of diethyl xanthate and hydrazine as described by Guha (2) were only moderately successful. It was discovered that the hydrazinolysis of diethyl xanthate could be carried out more effectively and more rapidly using water as the solvent, rather than ethyl alcohol. The insolubility of diethy xanthate in water caused no difficulty since it reacts rapidly with the hydrazine at about 50° to produce ethyl mercaptan and a homogeneous solution presumably containing O-ethyl monothiocarbazinate, from which thiocarbohydrazide is isolated after a short period of heating. Acidification of the reaction mixture to litmus at the end of the reaction period prevented excessive oxidation of the product during the isolation procedure.

Even with water as a solvent up to 25% of the diethyl xanthate was found to have been converted (at 50–60°) into the by-product 3-hydrazino-4-amino-5-mercapto-1,-2,4-triazole, m.p. 228–230° (4). It is doubtful if the formation of this substance can be suppressed completely since it is obtained when aqueous solutions containing hydrazine and thiocarbohydrazide are heated. The reaction temperature does, however, have an effect on the yield of the two main products since a good yield of thiocarbohydrazide (65%) and only an insignificant amount of the cyclization product were obtained when the reactants were allowed to stand at room temperature for a period of two days.

It was anticipated that the hydrazinolysis of methyl dithiocarbazinate would proceed more readily than the hydrazinolysis of dithiocarbazinic acid since it involves attack of an ester as opposed to an acid functional group. Experimental results support this assumption since a 65% yield of thiocarbohydrazide was obtained when hydrazine and the ester were allowed to react in refluxing alcoholic solution.

An evaluation of the three synthetic methods described above leads to the conclusion that the direct reaction between hydrazine and carbon disulfide is the best method yet developed for the preparation of thiocarbohydrazide. It is a very convenient, single stage operation making use of easily available starting materials. It suffers from the disadvantage that good yields are obtained only when large excesses of hydrazine are employed. It is probable, however, that a large part of the unused hydrazine can be recovered from the mother liquors in any large scale operation. The hydrazinolysis of methyl dithiocarbazinate is more convenient and gives better yields than does the hydrazinolysis of diethyl xanthate and may have some application in special circumstances.

PHYSICAL PROPERTIES OF THIOCARBOHYDRAZIDE

Although the general physical properties of thiocarbohydrazide have been reported, no quantitative data are available concerning the solubilities of this compound, its thermal stability, hygroscopicity, or its acid or basic character in water.

The solubility of thiocarbohydrazide in a number of solvents was determined and the results are summarized in Table V. The low solubility of thiocarbohydrazide in organic solvents is characteristic of this group of compounds. The high solubility in 100% hydrazine hydrate may be ascribed to salt formation. Hydrazine hydrate is a basic solvent and therefore accentuates the acidic character of a weakly acidic solute.

Thiocarbohydrazide is soluble in both acidic and basic aqueous solution. However, no definitive data have been published concerning the exact nature of its acidic and basic properties. A saturated solution of thiocarbohydrazide in pure, carbon dioxide-free water has a *p*H of 6.95, very close to the neutral point. It may be assumed that the acid character of this compound is due to the hydrogen atom on the nitrogen atom in the position α to the thiocarbonyl function and that thiocarbohydrazide is a monobasic acid, like other molecules of this type. It has also been shown that thiocarbohydrazide is a diacidic base by isolation of the dihydrochloride and the sulfate. Since these salts are very soluble in water, their isolation from that solvent is difficult. They may, however, be prepared easily by the addition of the mineral acid to an acetic acid (100%) solution of thiocarbohydrazide. The desired salts precipitate in good yield on cooling. The acidic nature of that solvent enhances the basic character of thiocarbohydrazide. Titration of solutions of the hydrochloride and sulfate so obtained (m.p. 182–183° and 200–201°, respectively) established their compositions as the dihydrochloride and a mono-sulfate, respectively.

Thiocarbohydrazide was found to undergo considerable decomposition in air at 110°. The decomposition was slow initially, but increased to a constant, fairly rapid rate at about the sixth day. A 26.54% loss in weight over a period of two weeks was observed.

Thiocarbohydrazide is an essentially non-hygroscopic solid and suffers only slight increase in weight when exposed to atmospheres with relative humidities up to 90% at room temperature (see Table VI).

EXPERIMENTAL

Hydrazinium dithiocarbazinate. This intermediate was prepared by the method of Stolle (1). Carbon disulfide (76 g., 1 mole) was added dropwise to a solution of 119 g. of 85% hydrazine hydrate (2 moles of N_2H_4) in 300 ml. of ethanol which was stirred continuously and cooled with an ice-bath. The resulting mixture was allowed to stand in the ice-bath for 1 hour; the precipitate of hydrazinium dithiocarbazinate was collected, washed well with alcohol and with ether, and finally air-dried. Yield, 131.5 g. (94%) melting at 124° (lit. 124°). The product was used directly in the synthesis of thiocarbohydrazide.

Preparation of thiocarbohydrazide from hydrazinium dithiocarbazinate. (a). Effect of excess hydrazine (Table III). Hydrazinium dithiocarbazinate (28 g., 0.2 mole) was dissolved in 200 ml. of an aqueous solution containing sufficient hydrazine to establish the desired mole ratio of hydrazine to hydrazinium dithiocarbazinate. The resulting solution was refluxed on a steam-bath for 1.5 hours (Reflux temperature, 90–95°). The reaction mixture was cooled in an ice-bath for 0.5 hour to crystallize the product which was then collected, washed with 95% ethanol, then ether, air-dried, and weighed. The crude product was purified by recrystallization from water containing a few drops of concentrated hydrochloric acid.

(*b*) *Effect of reflux time* (See discussion). Hydrazinium dithiocarbazinate (28 g., 0.2 mole) was dissolved in an aqueous solution containing 35.55 g. of 85% hydrazine hydrate (0.6 mole of N_2H_4) and refluxed for the desired length of time. The product was isolated and purified as described above.

(*c*) *Effect of concentration* (Table IV). Hydrazinium dithiocarbazinate (28 g., 0.2 mole) was dissolved in a solution containing 35.55 g. of 85% hydrazine hydrate (0.6 mole of N_2H_4) and sufficient water to give the desired total volume. The resulting solution was refluxed for 1.5 hours and the product was isolated and purified as described above.

Preparation of thiocarbohydrazide from carbon disulfide and aqueous hydrazine. The investigation of the reaction of hydrazine with carbon disulfide was carried out by adding carbon disulfide to the specified quantity of hydrazine in aqueous solution and then refluxing the resulting solution for the desired time. The product was isolated and purified as described above. Details of the best method of preparing thiocarbohydrazide, as determined by this study, follow.

To a vigorously stirred solution of 250 g. of 100% hydrazine hydrate (5 moles) in 150 ml. of water, 76 g. (1 mole) of carbon disulfide was added dropwise. The temperature of the solution rose to 62°. The reaction mixture was then heated at reflux for 30 min., cooled in an ice-bath for 30 min. and the precipitated thiocarbohydrazide was filtered off, washed with ethanol and ether, and air-dried. The mother liquor was returned to the reaction flask and the process repeated twice, after which no more thiocarbohydrazide was obtained. Yields of 62.0 g., 13.28 g. and 4.0 g. were obtained. The three samples were combined and recrystallized from the minimum amount of water acidified with a few drops of concentrated hydrochloric acid; 67.1 g. thiocarbohydrazide (63.3%) was obtained (m.p. 171°).

Preparation of thiocarbohydrazide from diethyl xanthate and hydrazine. Potassium ethyl xanthate was prepared by the method of Bulmer and Mann (5), sufficient ethanol being employed to keep the potassium ethyl xanthate in solution at room temperature. The resulting solution was used directly in the preparation of diethyl xanthate using the method described by Debus (6). The product was dried over sodium sulfate and used without distillation in the preparation of thiocarbohydrazide. Yields of 80% to 87% were obtained.

The preparation which is described below is representative of those experiments which gave the most consistent and best yields of thiocarbohydrazide. Sixty ml. of 95% hydrazine (1.8 moles of N_2H_4) and 90 ml. of 85% hydrazine hydrate (1.5 moles of N_2H_4) were combined in a 500-ml. round-bottom, 3-neck flask equipped with a stirrer, a reflux condenser, and an inlet tube for the introduction of diethyl xanthate and a continuous stream of nitrogen. The system was then swept out with a stream of nitrogen which was permitted to run until the product was isolated. The reaction vessel was placed in a water-bath maintained at 60° and 150 g. of diethyl xanthate (1 mole) was added to the well-stirred solution over a period of 30 min. Ethyl mercaptan was evolved rapidly. The reaction mixture was stirred for another 30 min. at 60° to complete the hydrazinolysis reaction.

The reaction mixture was then acidified by the addition of 200 ml. of 1:25 hydrochloric acid, diluted to a total volume of 550 ml. with slightly acidified water, and heated to boiling to dissolve the thiocarbohydrazide. The water insoluble by-product was filtered off and the filtrate was cooled to crystallize the desired product which was collected, washed with alcohol and ether, and air-dried. Thus 62 g. (59%) of thiocarbohydrazide (m.p. 169–170°) was obtained. Crude 3-hydrazino-4-amino-5-mercapto-1,2,4-triazole (20 g.) was obtained as a by-product. The yield of by-product accounts for 28% of the diethyl xanthate employed.

Preparation of thiocarbohydrazide from methyl dithiocarbazinate. (a) Preparation of methyl dithiocarbazinate. A solution of 66 g. (1.18 moles) of potassium hydroxide and 65 ml. of 85% hydrazine hydrate (1.1 moles of N_2H_4) in 200 ml. of ethanol was stirred and cooled in an ice-bath while 80 g. (1.04 moles) of carbon disulfide was added dropwise. A heavy yellow oil containing potassium dithiocarbazinate separated during the course of this addition. The resulting mixture was stirred and chilled and two volumes of ether were added to cause the separation of more of the desired product. The oily layer was separated from the ether-alcohol layer and filtered to remove a small amount of unidentified solid which had formed in the reaction. The clear yellow solution was then dissolved in 300 ml. of water. The resulting solution was cooled in an ice-bath and 150 g. (1.05 moles) of methyl iodide was added in approximately 10-g. batches. The reaction vessel was shaken and cooled alternately after each such addition until the methyl iodide was consumed. Methyl dithiocarbazinate

TABLE V

SOLUBILITY OF THIOCARBOHYDRAZIDE

SOLVENT	TEMP., °C.	SOLUBILITY IN G. OF THIOCARBOHYDRAZIDE PER 100 G. OF SOLVENT
H_2O	0	0.18
H_2O	24.7	.55
C_2H_5OH	24.7	.26
$HCCl_3$	24.7	.05
CCl_4	24.7	.03
100% $N_2H_4 \cdot H_2O$	24.7	13.60

TABLE VI

HYGROSCOPICITY OF THIOCARBOHYDRAZIDE

SATURATED SOLUTION	RELATIVE HUMIDITY AT 20°	INCREASE IN WEIGHT, %
$CaCl_2$	32.3	<0.1
KSCN	47.0	< .1
NH_4Cl	79.2	< .1
$ZnSO_4$	90.0	< .1
H_2O	100.0	.38

precipitated during the course of the reaction. The reaction mixture was allowed to stand for several hours, being shaken occasionally, to permit complete reaction. The methyl dithiocarbazinate was collected and recrystallized from ethanol. A yield of 95 g. (66% based on CS_2) was obtained; m.p. 82° (lit. 82°).

(*b*). *Preparation of thiocarbohydrazide.* Methyl dithiocarbazinate (24.4 g., 0.2 mole) was dissolved in 200 ml. of absolute ethanol and 18 ml. (0.3 mole of hydrazine) of 85% hydrazine hydrate was added. The resulting solution was refluxed until no more solid thiocarbohydrazide precipitated (about 45 min.). The reaction mixture was chilled, and the solid product was collected and recrystallized from water acidified with a few drops of hydrochloric acid to remove a small amount of 3-hydrazino-4-amino-5-mercapto-1,2,4-triazole which had formed. Yield, 13.8 g. (65%). (m.p. 171°).

Solubility of thiocarbohydrazide. The solubility of thiocarbohydrazide was determined by equilibrating the solvent with an excess of thiocarbohydrazide in a stoppered test tube immersed in a constant temperature water bath for 24 hours. The test tube was shaken continuously to insure intimate contact between the two phases. A sample of the liquid was then removed through a filter, weighed, and evaporated to dryness carefully. The solubilities, expressed in grams thiocarbohydrazide per 100 g. of solvent, are recorded in Table V.

Thermal stability of thiocarbohydrazide at 110°. A tared sample bottle containing a known weight of thiocarbohydrazide was heated in air in an oven at 110° and the weight was recorded at various time intervals. Only hydrogen sulfide was identified among the gaseous products. The nature of the solid decomposition products was not determined.

Hygroscopicity of thiocarbohydrazide. Tared weighing bottles containing known amounts of thiocarbohydrazide were placed in desiccators containing saturated solutions of various salts to produce known relative humidities. The samples were weighed after 7 days and the weight increases recorded. The data are recorded in Table VI. Up to a relative humidity of 90% thiocarbohydrazide is essentially non-hygroscopic but shows a slight weight increase in air saturated with water vapor.

SUMMARY

Methods for preparation of thiocarbohydrazide involve hydrazinolysis of various thiocarbonic acid derivatives such as hydrazinium dithiocarbazinate, diethyl xanthate, and methyl dithiocarbazinate. Direct reaction of carbon disulfide with excess aqueous hydrazine solutions is recommended as the most convenient method for preparing this substance. Thiocarbohydrazide possesses only limited solubility in water and the common organic solvents. It is soluble both in acid and base. A dihydrochloride and a monosulfate can be isolated from acetic acid solution. It is a non-hygroscopic substance and undergoes thermal decomposition when heated for extended periods of time at 110°.

URBANA, ILLINOIS

REFERENCES

(1) STOLLE AND BOWLES, *Ber.*, **41**, 1099 (1908).
(2) GUHA AND DE, *J. Chem. Soc.*, **126**, 1215 (1924).
(3) SANDSTROM, *Arkiv Kemi*, **4**, 297 (1952).
(4) HOGGARTH, *J. Chem. Soc.*, 4817 (1952).
(5) BULMER AND MANN, *J. Chem. Soc.*, 666 (1945).
(6) DEBUS, *Ann.*, **75**, 127 (1850).