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Preparation of *N*-Substituted Thiourea

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Results on the preparation of *N*-substituted thioureas by the reaction of organic isothiocyanates with compounds containing an amino-group, by the action of alkali-metal thiocyanates on amine hydrochlorides, and by the treatment of primary and secondary amines with thiocarbonyl chloride or carbon disulphide, published in the Soviet and foreign literature including 1972, are systematically discussed. The reactions of hydrogen sulphide with substituted cyanamides and of thiourea with compounds containing various functional groups are also examined. Certain views are presented on the mechanism of the formation of *N*-substituted thioureas, and the advantages and disadvantages of various methods for their preparation are compared. Practical applications of *N*-substituted thioureas are considered. A list of 247 references is included.

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I. INTRODUCTION

Thiourea is able to give both *S*-substituted and *N*-substituted derivatives. It was therefore thought possible that tautomeric transition into the thiol forms

$$-NH-\underset{|}{C}=S \rightleftarrows -N=\underset{|}{C}-SH$$

occurred in solutions of thiourea and its derivatives. However, the ultraviolet absorption spectra and Raman spectra of thiourea and its mono- and di-phenyl derivatives showed that the thione form was stable both in the crystalline state and in solutions, and no tautomerism was observed[1].

Since the time of the first syntheses of thiourea and its derivatives in the 1860s a vast literature has accumulated. The present Review is therefore restricted to methods of preparation and aspects of the practical application of *N*-substituted thioureas, and ignores metal-substituted derivatives and sulphothioureas. The literature up to 1954 is covered by specialised reviews on the chemistry of thiourea[2] and sulphonylthiourea[3], which emphasise specific aspects of individual methods of preparation and application of thiourea derivatives. The present Review has been guided by these surveys, and includes only a few of the literature sources cited. In every case, however, re-examination of these references has been dictated by a novel approach and the desire to preserve the integrity of the material reported.

The interest taken in thiourea and its derivatives can be explained by their wide applications: they have valuable pharmacological properties, exhibit insecticidal, fungicidal, and nematocidal activity, and are also widely employed as brighteners in the electrodeposition of metals.

II. METHODS OF PREPARATION OF *N*-SUBSTITUTED THIOUREAS

Methods of preparing *N*-substituted thioureas can be divided into six main groups.

1. Interaction of Organic Isothiocyanates with Compounds containing an Amino-group

The method consists in the direct interaction of organic isothiocyanates with compounds containing an amino-group, and can conveniently be used to obtain unsymmetrical thioureas. It can yield 1-monosubstituted derivatives[4-19]

$$RNCS + NH_3 \rightarrow RNHC(S)NH_2$$

1,3-disubstituted derivatives[4-9,11-13,17,18,20-167]

$$RNCS + R_1NH_2 \rightarrow RNHC(S)NHR_1$$

and 1,3,3-trisubstituted derivatives[7,10,17,18,34,35,37,42,49,58,68,77,79,89,105,145,160,168-178]

$$RNCS + R_1R_2NH \rightarrow RNHC(S)N\begin{matrix}R_1\\ \diagdown\\ R_2\end{matrix}.$$

Various compounds containing an amino-group can be used for the preparation of thioureas by this method (Table 1), and various organic isothiocyanates can undergo this reaction (Table 2).

The condensation of organic isothiocyanates with amino-compounds is usually conducted in methanol or ethanol, but other solvents may also be used (Table 3). Papers have recently appeared on the possibility of carrying out the reaction in the absence of a solvent[49,71,83,106,116,140,141,153,164,170,171,176]. The process is

Table 1.

Amino-compounds	Ref.
Ammonia	4—6, 9, 11—19, 105, 154, 164
Chloral-ammonia	116
primary amines	
Saturated aliphatic	4—7, 11—13, 22, 34, 44, 47, 49, 54, 58, 59, 89, 105, 128, 135, 136, 140, 141, 144, 151, 154
Unsaturated aliphatic	16, 151
Aromatic	5, 6, 9—12, 17, 19—21, 23—28, 30—36, 38, 40, 41, 43, 50—57, 69—71, 89, 105, 108, 109, 134, 138—148, 150, 151, 154, 157, 159, 165—167
Heterocyclic	6, 8, 11, 12, 17, 18, 20, 21, 23, 25, 28, 32, 36, 50, 58, 74—80, 82—84, 86, 87, 90, 91, 94—107, 109—112, 115, 117—120, 123, 124, 138, 139, 144, 149—152, 155—158, 167, 171, 172, 177
Carbocyclic	6, 9, 46, 49, 59, 105, 109, 123, 124, 154
secondary amines	
Aliphatic	7, 10, 18, 34, 37, 49, 58, 89, 105, 145, 168, 169, 176
Aromatic	7, 17, 58, 105, 168, 176
Heterocyclic	9, 18, 37, 49, 72, 73, 77, 81, 85 86, 89, 92, 93, 104, 145, 168, 170, 178
Phenetidines	57, 62, 63, 88, 137
Hydroxylamines	161, 173, 174
Diamines	42, 45, 113, 114, 157
Amidines	162
Amides of carboxylic acids	74, 175
Amino-acids	39, 50, 54, 59, 121, 125, 126, 128—130, 158, 160, 165, 178
Esters of amino-acids	121, 122, 127, 131
Hydrazides of amino-acids	125
Lactones of hydroxy-carboxylic acids	132
Peptides	126
Amino-nitriles	133, 164, 175

Table 2.

Organic isothiocyanates	Ref.
Saturated aliphatic	4, 5, 8, 14, 20—22, 34, 35, 51, 53, 74, 75, 91, 92, 97, 98, 100, 106, 110, 112—114, 125, 131, 133, 136, 140, 152, 153, 157, 161, 162, 164, 168, 175, 176
Unsaturated aliphatic	8, 14, 23—28, 31, 32, 35, 62, 63, 70, 74, 75, 78, 79, 91, 97, 98, 110, 113, 114, 123, 124, 152, 153, 164, 171
Aromatic with saturated side-chain	5, 7, 8, 10, 14, 17, 27, 28, 34, 38—56, 60, 69—87, 90, 91, 93—103, 106—108, 110—113, 115—124, 127—130, 132—135, 137—144, 147—152, 155, 157—165, 167, 169—174, 176, 178
Aromatic with unsaturated substituents	6, 15, 16
Heterocyclic	10, 18, 76, 78, 79, 88, 89, 104, 105, 108, 120, 124, 139, 146, 156, 171
Saturated carbocyclic	75, 110, 113, 154, 161, 176
Unsaturated carbocyclic	11, 12
Acyl	13, 30, 32, 33, 36, 37, 39, 51, 56, 57, 60—66, 105, 157, 166
Aroyl	13, 57—59, 109, 123, 124, 126, 175
Carbamoyl	145
Cyanoalkyl	128

generally accomplished with cooling or at room temperature, sometimes with heating[4,6,8,9,12,15-17,20,21,23-26,28,30,34,36,38-41,43,44,51,52,55-57,60-63,65,66,70,71,72,74-80,82,83,85,86,88,90-108,111-113,115-117,120-122,125,127,129,134,135,137,140,141,143,144,147,149,151-153,157,158,160,163-165,167,169-171,173,175]. There are also exceptions to the usual equimolecular quantities of the reactants, when excess of the organic isothiocyanate[20,21,23-25,93,98,99,113,117,131] or excess of the amino-compound[5,7,29,48-50,96,104,105,117,170] is taken.

The usual products of the reaction of primary amines with isothiocyanates are unsymmetrical 1,3-disubstituted thioureas. However, there are indications[87,147,171] that the condensation of heterocyclic amines with aryl isothiocyanates gives ambiguous results on more prolonged heating: symmetrical 1,3-disubstituted thioureas are formed together with the unsymmetrical derivatives. Symmetrically substituted thioureas are probably products of secondary reactions of the initially formed unsymmetrical thioureas, cleavage of which leads to the accumulation

Table 3.

Solvent	Ref.	Solvent	Ref.
Acetone	9, 13, 17, 18, 30, 33, 43, 55, 56, 58, 61, 64—68, 109, 111, 117, 129, 130, 134, 135, 140, 157, 159, 164—166, 175	Toluene	32, 80, 92, 93, 131
		Dioxan	22, 31, 39, 117, 178
		Chloroform	80, 114, 140, 141
		Ethyl acetate	83, 148
Diethyl ether	5, 31, 39, 51, 52, 89, 110, 128, 156, 161, 162, 175	Acetonitrile	59, 99, 119, 120, 145
		Pyridine	34, 95, 98, 106
Petroleum ether	29, 140, 168, 176	Methylene dichloride	4
Benzene	6, 9, 13, 30, 33, 44, 45, 47, 57, 58, 62, 63, 75—79, 82—88, 91, 94, 96, 99, 101—103, 105, 107, 109, 117, 118, 126—128, 133, 141, 148, 149, 155, 157, 161, 163, 167, 168, 171, 174	Hexane	6
		Cyclohexane	48
		Acetic acid	54, 163
		Pentanol	106
		Water	4, 11, 37, 59, 140

of two different amines and two different isothiocyanates in the mixture, which then yield two symmetrical thioureas:

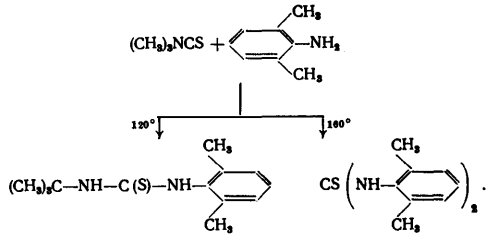
$$RNCS + R_1NH_2 \rightleftarrows \underset{(I)}{RNHC(S)NHR_1} \rightleftarrows RNH_2 + R_1NCS,$$

$$R_1NH_2 + R_1NCS \rightarrow I,$$

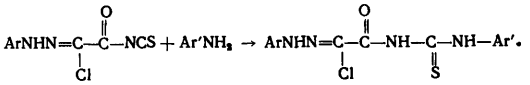
$$RNH_2 + RNCS \rightarrow RNHC(S)NHR,$$

The driving force of such changes is provided by differences between the basic strengths of the amines RNH_2 and R_1NH_2 and between the reactivities of amines and aryl isothiocyanates. The proportions of the products depend on the stability of the thiourea derivative formed initially.

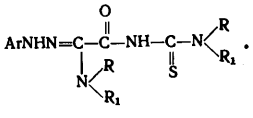
Aliphatic isothiocyanates react very slowly with aromatic amines, to form symmetrical or unsymmetrical 1,3-disubstituted thioureas depending on the temperature[140]:



Isothiocyanates of arylazochloroacetic acids react very peculiarly with amines. The isothiocyanate group interacts with the formation of 1-aryl-3-arylazochloroacetylthioureas[67,68]:



Also the chlorine atom is replaced by the amine residue[68] to yield thioureas of the type



2. Reaction of Alkali-metal Thiocyanates with Amine Hydrochlorides

Heating mono- and di-substituted ammonium thiocyanates at 160°C for a few hours brings about rearrangement into thioureas:

$$\underset{(II)}{RR_1NH_2SCN} \rightarrow RR_1NHC(S)NH_2.$$

Such rearrangement is impossible with tri- and tetra-substituted ammonium cations.

This rearrangement is used for the preparation of 1-monosubstituted thioureas[91,179-190]:

$$RNH_2 + HCl + NH_4SCN \rightarrow RNHC(S)NH_2 + NH_4Cl$$

and also 1,1-disubstituted derivatives[191,192]

$$RR_1NH + HCl + NH_4SCN \rightarrow II + NH_4Cl.$$

The method is straightforward, and can be used for aliphatic, aromatic[179-183,185,186,191,192], and heterocyclic[91,186-188] amines, esters of amino-acids[184], and diamines[189,190]. An example of the reaction with a diamine is the preparation of *N*-2′-aminoethylthiourea:[190]

$$KSCN \xrightarrow{5} H_2NCH_2CH_2NH_2 + HCl \rightarrow H_2NCH_2CH_2NH_2{}^+SCN^- \rightarrow$$
$$\rightarrow H_2NCH_2CH_2NHC(S)NH_2.$$

The reaction of alkali-metal thiocyanates with amines is usually conducted in an inert organic solvent, most frequently chlorobenzene[179,180,182,184] or in aqueous medium[181,183,185,186,189,190]. Other solvents—glacial acetic acid[187,188], methanol[191], and ethanol[191,192]—may also be used. Chlorobenzene is saturated with hydrogen chloride, the appropriate amine and the alkali-metal thiocyanate are added, and the mixture is heated at 110–120°C for a time depending on the nature of the components. When the reaction is conducted in water, hydrochloric acid, the appropriate amine, and a small excess of the alkali-metal thiocyanate are added, and the solution is boiled and evaporated to dryness. The residue is dissolved in an appropriate solvent, and then precipitated with hydrochloric acid. The saturation of chlorobenzene with hydrogen

chloride or the addition of hydrochloric acid to water can be avoided by using the amine hydrochlorides[179,180,182,183,185-189,191,192] or sulphates[180].

The yield of thiourea increases slightly with increase in the concentration of the reactants, but it remains low, since side-reactions occur with the formation of an isothiocyanate

$$RNH_2 + 2HCl + NH_4SCN \rightarrow RNCS + 2NH_4Cl$$

and a symmetrical 1,3-disubstituted thiourea

$$RNCS + RNH_2 \rightarrow RNHC(S)NHR.$$

In the reaction of 1 mole of ammonium thiocyanate with 2 moles of tryptamine hydrochloride, for example, 1,3-di-[2-(5-methoxyindol-3-yl)ethyl]thiourea is obtained[107].

This method can be used to prepare arylthioureas having either electropositive or electronegative substituents, and is considerably more convenient and rapid than the preparation of arylthioureas from aryl isothiocyanates and amines.

3. Reaction of Thiocarbonyl Chloride with Primary and Secondary Amines

Primary amines react with thiocarbonyl chloride to form, depending on their quantity, either isothiocyanates[19,193]

$$RNH_2 + CSCl_2 \rightarrow RNCS + 2HCl$$

or symmetrical 1,3-disubstituted thioureas[193-195]

$$2RNH_2 + CSCl_2 \rightarrow RNHC(S)NHR + 2HCl.$$

Secondary amines form only symmetrical 1,1,3,3-tetrasubstituted thioureas[196]:

$$2RR_1NH + CSCl_2 \rightarrow RR_1NC(S)NRR_1 + 2HCl.$$

In order to prepare thioureas by this method, 1 mole of thiocarbonyl chloride is heated with 2 moles of the amine in an aqueous[193,194] or in an aqueous acetone[195] medium.

The course of the reaction may be

$$RR_1NH + CSCl_2 \rightarrow \underset{(III)}{(RR_1NHClCSCl)} \rightarrow RR_1NCSCl + HCl.$$

If the compound (III) is stable, the reaction

$$III + RR_1NH \rightarrow RR_1NC(S)NRR_1 + HCl \qquad (a)$$

takes place independently of the nature of the radical R_1. If, however, (III) is unstable ($R_1 = H$), a different reaction takes place:

$$III \rightarrow RNCS + HCl,$$
$$RNCS + H_2NR \rightarrow RNHC(S)NHR. \qquad (b)$$

Primary amines are able to react with thiocarbonyl chloride in conformity both with (*a*) and (*b*), but secondary amines can undergo only reaction (*a*). The correctness of this mechanism is supported by the fact that in some cases compound (III) has been isolated from the reaction mixture and identified[196].

Owing to the toxic properties of thiocarbonyl chloride this method is very rarely used—only when other methods do not give the results to be expected, e.g. for the preparation of symmetrically 1,3-disubstituted thioureas containing strongly electronegative substituents.

4. Reaction of Carbon Disulphide with Primary and Secondary Amines

This method is most simply and generally applied to the preparation of symmetrical 1,3-disubstituted thioureas[38,40,52,71,90,97,142,167,182,188,196-208].

$$2RNH_2 + CS_2 \rightarrow RNHC(S)NHR + H_2S$$

Because of the great volatility of carbon disulphide, excess is used over the 1 mole per 2 moles of the amine indicated by the equation. The reaction is complete when the evolution of hydrogen sulphide ceases.

This method can be employed for the preparation of 1-monosubstituted derivatives[182]

$$RNH_2 + CS_2 \rightarrow \underset{(IV)}{RNHC(S)SH},$$
$$RNHC(S)SH + NH_3 \rightarrow [RNHC(S)S]^-[NH_4]^+ \rightarrow RNHC(S)NH_2 + H_2S,$$

unsymmetrical 1,3-disubstituted derivatives[208-210]

$$IV + R_1NH_2 \rightarrow [RNHC(S)S]^-[NR_1H_2]^+ \rightarrow RNHC(S)NHR_1 + H_2S,$$

and 1,3,3-trisubstituted thioureas[142,169,211]

$$IV + (R_1)_2NH \rightarrow [RNHC(S)S]^-[N(R_1)_2H_2]^+ \rightarrow RNHC(S)N(R_1)_2 + H_2S.$$

Carbon disulphide reacts with primary amines—aliphatic[199,202,207], aromatic[38,40,52,71,167,169,182,196-198,200,207,208,211], heterocyclic[39,90,97,167,188,199,201,209,210], and hydroxylamines[208]—to form symmetrical and unsymmetrical 1,3-disubstituted thioureas and with secondary amines—aliphatic[142,169,211] and cyclic[142]—to form 1,3,3-trisubstituted thioureas.

This method is not advisable with arylamines having strongly electronegative substituents, since the latter greatly lower the yields of thioureas, nor with heterocyclic amines, which react with carbon disulphide with very great difficulty.

Carbon disulphide reacts not only with primary and secondary amines but also with amino-acids[142,203-205] esters of amino-acids[204], dicyclohexylcarbodi-imide[199,200], and *N*-benzylbis-*p*-methoxyphenylmethanimine[212]

The solvent used is normally ethanol[38-40,52,71,97,142,167,169,182,188,196,197,201,202,210,211] or benzene[167,182,197], but sometimes methanol[205], water[203,206], diethyl ether[90,199,200], oxolan[199], pyridine[197,200,204], or dimethylformamide[208].

A substantial disadvantage of this method is its duration. Catalysts for the reaction are sulphur[38,97,142,167,197,201], hydrogen peroxide[197,207], caustic potash[40,52,167,188,196], caustic soda[198,203,205,206,209,211], pyridine[197,200,204], pyridine together with iodine[197,204], and potassium ethyl xanthate[39]. Sulphur accelerates the reaction, but difficulties arise in separating it from the reaction products. Hydrogen peroxide is an efficient catalyst, but in this case free sulphur is formed (from the carbon disulphide), which is difficult to remove.

The most practicable catalysts are caustic potash and caustic soda, which involve the intermediate formation of thiuram disulphides and isothiocyanates:

$$RNH_2 + CS_2 + NaOH \rightarrow RNHC(S)SNa + H_2O \rightarrow$$
$$\rightarrow RNHC(S)S{-}SC(S)NHR \rightarrow 2RNCS + H_2S + S. \qquad (a)$$

Thioureas are formed in subsequent stages of the reaction:

$$RNCS + NH_2R \rightarrow RNHC(S)NHR,$$
$$RNHC(S)S{-}SC(S)NHR \rightarrow RNHC(S)NHR + S.$$

If R = Alk, thioureas can be formed only in conformity with Eqn. (*c*), for an aliphatic isothiocyanate rearranges

rapidly into the corresponding amine, without having time to react with the primary amine.

Pyridine can also be used to accelerate the reaction. It forms unstable products with hydrogen sulphide. Still better results are obtained by adding to the solution of pyridine the calculated quantity of iodine, which is easily removed as pyridinium iodide:

$$2RNHI_2 + CS_2 + I_2 + 2C_5H_5N \rightarrow RNHC(S)NHR + 2C_5H_5N \cdot HI + S.$$

During the reaction the solution becomes decolorised, and pyridinium iodide is precipitated. The quantity of iodine is measured out very carefully, for excess will lead to formation of the corresponding isothiocyanate:

$$RNH_2 + CS_2 + I_2 + 2C_5H_5N \rightarrow RNCS + 2C_5H_5N \cdot HI + S.$$

Small quantities of potassium ethyl xanthate catalyse this reaction. Although the acceleration is less than with sulphur, purer products are obtained.

5. Reaction of Hydrogen Sulphide with Substituted Cyanamides

Thioureas are formed by the reaction of cyanamides with hydrogen sulphide. Monosubstituted cyanamides yield 1-monosubstituted thioureas[213,214]:

$$RNHCN + H_2S \rightarrow RNHC(S)NH_2.$$

Disubstituted cyanamides yield 1,1-disubstituted thioureas[14]:

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!NCN + H_2S \rightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!NC(S)NH_2.$$

The reaction is best accomplished by saturating an ethanolic solution with the corresponding cyanamide, ammonia, and hydrogen sulphide, used either as a saturated solution[214] or in the gaseous state[14,213]. Ammonia acts as catalyst in this reaction. The reaction mixture is then boiled[213] or heated in a sealed tube at 100°C.[214]

At high pressures hydrogen sulphide can add also to dicyanodiamide to form amidinothiourea[215]:

$$\begin{matrix} H_2NCNHCN \\ \| \\ NH \end{matrix} + H_2S \rightarrow \begin{matrix} H_2NCNHC(S)NH_2 \\ \| \\ NH \end{matrix}.$$

6. Reaction of Thiourea with Compounds containing Various Functional Groups

Since thiourea contains mobile hydrogen atoms, it will react with compounds having various functional groups to form mono-, di-, tri-, and tetra-substituted derivatives.

Quite a few papers have been published on the condensation of thiourea with aldehydes[216-226]. Thiourea can condense with formaldehyde both in equimolecular proportions to form hydroxymethylthiourea[216-218,221,225] and at a molar ratio of 1 : 2 to form bishydroxymethylthiourea[216-225]. This reaction has been conducted with 36.4%[219] and 40%[216,218] solutions of formaldehyde made alkaline with caustic soda[219] or baryta[216,218].

Mono-, bis-, and tetrakis-hydroxyalkylthioureas have been obtained by the condensation of thiourea with other aliphatic, alicyclic, aromatic, and heterocyclic aldehydes in molar proportions of 1 : 1, 1 : 2, and 1 : 4 in ethanol at pH 9:[226]

$$RC\!\!<\!\!\begin{matrix} O \\ H \end{matrix} + NH_2C(S)NH_2 \rightarrow RCHOHNHC(S)NH_2,$$

$$2RC\!\!<\!\!\begin{matrix} O \\ H \end{matrix} + NH_2C(S)NH_2 \rightarrow RCHOHNHC(S)NHCHOHR,$$

$$4RC\!\!<\!\!\begin{matrix} O \\ H \end{matrix} + NH_2C(S)NH_2 \rightarrow \begin{matrix} RCHOH \\ RCHOH \end{matrix}\!\!>\!NC(S)N\!<\!\begin{matrix} CHOHR \\ CHOHR \end{matrix}.$$

1-Monosubstituted thioureas can also undergo condensation with formaldehyde at pH 7, to form unsymmetrical 1,3-disubstituted thioureas[227]. The condensation of unsymmetrical substituted thioureas with aldehydes in acid media yields the thioureas RR'C:CH.NH.CS.NR'R'''.[228]

Thiourea and 1-monosubstituted thioureas will condense not only with aldehydes but also with ketones, forming 1-monosubstituted[229,230] or unsymmetrical 1,3-disubstituted[230] thioureas.

Thiourea reacts with alkylphenols in the presence of concentrated hydrochloric acid in 37% aqueous formaldehyde solution to form bishydroxyalkylbenzylthioureas[231,232].

Thiourea will react with amines to form 1-aminothioureas[57,234] and symmetrical 1,3-diaminothioureas[57,233,234] respectively below and above 150°C. At high temperatures equilibrium is established between thiourea and ammonium thiocyanate:

$$NH_2C(S)NH_2 \rightleftarrows NH_4SCN.$$

The latter reacts with amines to form aminothioureas. 1-Monosubstituted thioureas yield unsymmetrical 1,3-disubstituted thioureas with amines[235]. Thiourea reacts with organic acids[236-238] or esters[239,240] to yield symmetrical 1,3-disubstituted[236,237] and unsymmetrical 1,3-disubstituted[238-240] derivatives.

Thiourea will react with mono- and di-arylated cyanamides[241], chlorides of carboxylic acids[242], and substituted propiolactones[243] to give 1-monosubstituted[241,243], symmetrical[241], and unsymmetrical[242] 1,3-disubstituted thioureas.

III. SOME ASPECTS OF THEIR PRACTICAL APPLICATION

N-Substituted thioureas have great preparative value for the identification of organic compounds, e.g. amines and organic isothiocyanates[2,144]. They are also able to form complex compounds with several metal ions. In this connection *N*-substituted thioureas are used in analytical chemistry as complexing agents[6,17,65,172,244,245].

Certain unsymmetrically 1,3-disubstituted thioureas exhibit biological[20,21,23,131], physiological[20,27,77-79,227,243], bacteriostatic[63,178], and bactericidal[35,50,110,166] activity, and find application in medicine.

Most *N*-substituted thioureas possess pharmacological properties[15,25,41,138,155], and therefore find widespread application as tuberculostatic[28,38,39,47,50,52-54,60,62,64-68,70,72-76,80,82,85,86,93,96-98,104,108,111,112,117,118,123-125,129,137,143,149-152,157,160,185,194,195,209,235], antineoplastic[51], antispasmodic[69], antitrichomonad[95], antiviral[112,154], and other[84,92,166,214] therapeutically active substances.

Descriptions have recently appeared of 1,1-dimethyl-3-[2,3(2,4)-dimethylphenyl]-2-thiourea[110] and a 3-substituted 1-(1,2,3,4-tetrahydroisoquinol-2-yl)alkyl-2-thiourea[169], both possessing hypotensive activity and used for the treatment of high blood pressure, and of 1,3-bis-*p*-aminophenylimidazolylthiourea[195], which exhibits chemotherapeutic activity and is employed in the treatment of cancerous conditions, chiefly leukaemia.

Several derivatives of allylthiourea[23-27] and phenylthiourea[41,127,159] find application as plant-growth regulators; and 3-substituted 1-hydroxythioureas[161] exert an inhibiting effect on certain microbiological systems.

Several *N*-substituted thioureas possess herbicidal[44,116,196,211,238], fungicidal[52,63,139,166,170], nematocidal[10], and rodenticidal[42,186-188] activity, and are used in agriculture against soil nematodes[10], insects[174], rodents[42,186-188], and other pests.

Derivatives of *N*-substituted thioureas are employed as protective agents against radiation[246] and are capable of enhancing the resistance of the organism to X-rays[69].

N-Substituted thioureas are widely used in industry as starting materials for the production of polymers[16,31], stabilisers of copolymers in polyalkenes[222], vulcanisation accelerators in the manufacture of porous rubbers[136,166], agents for whitening wool[223] and for impregnation of acrylonitrile[224], corrosion inhibitors[166,232], antioxidants[166,231], and brighteners in sulphate copper-plating electrolytes[225,247].

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