GENERAL INTRODUCTION

Heteroacyclic compounds and heterocyclic compounds have their own importance and values in organic chemistry. These compounds contain N, S, O and S, N and O, O and S etc. in the open chain or in the ring. Heterocyclic compounds may be present in benzenoids, non-benzenoids and in fused forms in ring structure. Due to the medicinal, pharmaceutical, agricultural values\textsuperscript{1-10} of heteroacyclic and heterocyclic compounds, tremendous work on these compounds is carried out to investigates their pharmaceutical, medicinal, agricultural, physiochemical and biochemical impotance in all directions.\textsuperscript{11-21}

Heteroacyclic and heterocyclic compounds occurs widely in nature. The purine and pyrimidine bases that are the structural units of RNA and DNA heterocyclic compounds. The chemistry of heterocyclic compounds is a vast subject and it is not possible to discuss whole of them. Heterocyclic compounds having 3 to 6 atoms in the ring are numerous but only those having a total 5 or 6 atoms in the ring are the most important.

The chemistry of the heterocyclic compounds is such an extensive field that this thesis is by necessity at a highly selective look at some of them. The thesis emphasizes reactions that will expand and reinforce our understanding.

The present study was undertaken as a part of wider programme of research on S and N containing heteroacycles and heterocycles under programme in this laboratory.

It is difficult to consider the reactions of any one set of these compounds without referring to other.
Alkyl/Aryl isothiocyanate, semicarbazides, guanidinethio-
carbamides, alkyl/aryl isothiocyanate oxides, dicyandiamide, biurets, bis-
formamidine sulphide cyanamides, carbamides etc. and their salts and derivatives
were used for the synthesis of several varieties of Nitrogen, Nitrogen and Sulpher
containing 5 and 6 membered heterocyclic compounds.

As we are interested in diformidinothiocarbamides and their
reactions. So, present brief review mainly deals with the applications of
dicyandiamides (1) and alkyl/aryl isocyanodichlorides (2b).

A| Dicyandiamide (1):

Dicyandiamide is an important organic compound having
antimalarial, dye stuff, optical bleaches, pesticide properties. It is used in rubber
and resins industries. It is also used as surface active agents and in explosive.

Dicyandimide is an important organic compound and also used in
the synthesis of various nitrogen and sulphur containing heterocyclic compounds
like thiadiazines, triazines, triazoles, pyroguanazoles and their derivatives.

Dicyandiamide was first prepared by Bielsten\(^2\), by the interaction
of water on cyanamidine.

\[
2 \text{H}_2\text{N}-\text{C}≡\text{N} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N}-\text{C} \equiv \text{NH}-\text{C}≡\text{N} \quad \text{NH}
\]

\[
\text{Cyanamide} \quad \text{Water} \quad \text{Dicyandiamide}
\]

Hagg\(^3\) named it as dicyandiamide. Several structures such as (1),
(2) and (3) have been suggested for this compound by different workers, but
the most accepted structure is \(1\)\(^7\).
Dicyandiamide molecule is a bifunctional molecule. It has a basic formamidino group at position 3 and a cyano/nitrilo group at position 1. This molecule therefore, expected to produce varieties of certain interesting heteroacyclic and heterocyclic nitrogen, nitrogen and sulphur containing organic compounds, through its reactive basic amino group at position 3 and nitrilo group at position 1.

The present review deals with chemistry of dicyandiamide and its applications to synthesis of nitrogen and nitrogen and sulphur containing heteroacyclic and heterocyclic compounds.

a) Applications in the synthesis of heteroacyclic compounds:

Dicyandiamide is used in synthesis of several heteroacyclic compounds. Many of them get cyclized into related heterocyclic compounds. some of heteroacyclic compounds prepared from dicyandiamide have been depicted below.
The most important reaction of dicyandiamide was its controlled thiohydrolyses with sodium hydrogen sulphide. In this thiohydrolysis, the parent 2,4-dithiobiuret (6) was formed. This is formed through an important intermediate the amidinothiocarbamide (5).

\[
\begin{align*}
\text{H}_2\text{N} & \text{C} & \text{NH} & \text{C} = \text{N} & \text{NH} \\
\text{Dicyandiamide} & \rightarrow & \text{H}_2\text{S} \\
\rightarrow & \text{H}_2\text{N} & \text{C} & \text{NH} & \text{C} & \text{NH}_2 \\
\rightarrow & \text{S} & \text{S} & \text{S} & \text{S} & \text{S} \\
\text{Amidinothiocarbamide} & \rightarrow & \text{2,4-Dithiobiuret}
\end{align*}
\]

Kaiser in 1903 prepared, 2,4-dithio-6-amino-1,3,5-triazine also called as dithioammelide (8) by the interaction of dicyandiamide and carbondisulphide in the presence of potassium hydroxide. Here the intermediate, potassium salt of \(\omega\)-cyanoguanidinothiocarbonic acid (7) has been isolated which was readily cyclized into 2,4-dithio-6-amino-1,3,5-triazine (8).
Ostrogovich in 1912 prepared 2-thio-4-amino-6-methyl-1,3,5-triazine also called as mercaptoamino-1,3,5-triazine (13) through the reaction of thioacids with dicyandiamide. Initially he obtained mercaptoamino-1,3,5-triazine directly as an intermediate (11). It was then cyclized into the desired product (13).

\[
\begin{align*}
\text{Dicyandiamide} & \quad \text{Thioacetic acid} \\
\text{H}_2\text{N} & \quad \text{C} \quad \text{NH} \quad \text{C} \equiv \text{N} + \text{CH}_3 \quad \text{C} \quad \text{SH} \quad \text{\rightarrow} \quad \text{NONH} & \quad \text{C} \quad \text{NHC} & \quad \text{CH}_3 \quad + \quad \text{H}_2\text{S} \\
\text{(1)} & \quad \text{(10)} & \quad \text{(11)} & \quad \text{(12)}
\end{align*}
\]

LinDholm in 1913 prepared guanidine sulphite (14) by the interaction of dicyandiamide and conc. sulphuric acid.

\[
\begin{align*}
\text{Dicyandiamide} & \quad \text{Guanidine sulphate} \\
\text{H}_2\text{N} & \quad \text{C} \quad \text{NH} \quad \text{C} \equiv \text{N} + \text{H}_2\text{SO}_4 \quad \xrightarrow{\text{i) Alcohol}} \quad \left[ \text{H}_2\text{N} \quad \text{C} \quad \text{NH}_2 \right] \quad \xrightarrow{\text{ii) BaCO}_3} \quad \text{H}_2\text{SO}_4 + \text{CO}_2 \\
\text{(1)} & \quad \text{(14)}
\end{align*}
\]

Bamberger prepared 2-hydroxy-4,6-diamino-1,3,5-triazine also called as ammeline (16), which he obtained by heating dicyandiamide with urethane at 180-190°C. Here an intermediate cyanoamidinourea (15) was isolated first, which was cyclized to (16).
Smolka Friedreich in 1935 prepared cyanoamidinourea (17) by the interaction of dicyandiamide and urea. In this reaction, vigorous evolution of ammonia was noticed. This reaction involved the conversion of urea to cyanic acid and ammonia. The latter reacted with dicyandiamide and produced cyanoamidinourea (17).
Nagy in 1943 prepared acetylated carbonylguanidine (18) by the interaction of dicyandiamide and carboxylic acids in presence of oleum, the acetylated carbonyl guanidine was then cyclized into 2-substituted-4-hydroxy-6-amino-1,3,5-triazine (19) on neutralization and warming (18) of the aqueous solution.

\[
\begin{align*}
\text{H}_2\text{N}-\text{C}-\text{NH}-\text{C}≡\text{N} & \quad \text{oleum} \quad \text{RCN}-\text{NH}-\text{C}-\text{NH}-\text{C}-\text{NH}_2 \\
\text{NH} & \quad \text{O} \quad \text{O} \quad \text{NH} \quad \text{H}_2\text{SO}_4 \\
\end{align*}
\]

(18)

Dicyandiamide

Acetylated carbonylguanidine

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{C} \quad \text{OH} \\
\text{C} & \quad \text{N} \quad \text{C} \quad \text{N} \\
\text{C} & \quad \text{N} \quad \text{NH}_2
\end{align*}
\]

(19)

2-Substituted-4-hydroxy-6-amino-1,3,5-triazine

Wystrach and Erickson in 1953 prepared 2-substituted-4,6-diamino-1,3,5-triazine (21) by the interaction of dicyandiamide and dialkoxy acetonitriles. The first step in the reaction involved the formation of dialkoxyacetimidodicyandiamide (20) which was cyclized into related 1,3,5-triazines (21).
b) **Application in the synthesis of heterocyclic compounds:**

Rathke\textsuperscript{56} in 1885, isolated 2,4-diamino-6-mercapto-1,3,5-triazine also called as thioammeline (22) by heating dicyandiamide with ammonium thiocyanate in presence of hydrochloric acid.

\[
\begin{align*}
H_2N-C-NH-C&=N \\
\text{NH} &\quad + \quad NH_4SCN \\
\text{NH} &\quad \xrightarrow{\text{HCl}} \quad HS-C=N-C\equiv N \\
\text{NH}_2 &\quad + \quad NH_4Cl
\end{align*}
\]

(1) Dicyandiamide

(22) 2,4-Diamino-6-mercapto-1,3,5-triazine

Keller\textsuperscript{37} in 1881 prepared 3-methyl-5,7-diamino-1,2,4-triazole (4, 3a) 1,3,5-triazine (24) by refluxing dicyandiamide and 3-amino-5-methyl-1,2,4-triazole hydrochloride (23) in acidic medium.
Pellizarri Gazz\textsuperscript{38} in 1894 prepared 3,5-diamino-1,2,4-triazole (25) from dicyandiamide and hydrazine.

Ostogrovich\textsuperscript{39} in 1912 prepared 2-thio-4-amino-6-substituted-1,3,5-triazine also called as mercaptoamino-1,3,5-triazine (26) by the interaction of dicyandiamide and substituted thioacid.

\begin{equation}
\begin{align*}
H_2N-C-NH-C=\equiv N & \quad + \quad H_2N-NH_2 \quad \rightarrow \quad H_2N-C-NH-\equiv N \quad + \quad H_2S + RCOOH
\end{align*}
\end{equation}

where R = methyl, ethyl, phenyl
Ostogrovich\textsuperscript{40} in 1912 prepared thioliminomethyl-1,3,5-triazine (27) by the interaction of dicyandiamide and thioacetic acid in ethereal medium.

\[
\begin{align*}
\text{H}_2\text{N} \cdot \text{C} \cdot \text{NH} \cdot \text{C} \equiv \text{N} + \text{CH}_3 \cdot \text{C} \cdot \text{SH} & \xrightarrow{\text{Eth}er, \Delta 2h} \text{Thioliminomethyl-1,3,5-triazine} \\
\text{(1)} & \\
\text{Dicyandiamide} & \text{Thioacetic acid}
\end{align*}
\]

Hofmann\textsuperscript{41} in 1912 prepared 3,7,11-triimino-5-triazole [4, 3a, 4, 3c, 4, 3-c]-1,3,5-triazine more commonly called as pyroguanazole (28) by the interaction of dicyandiamide and hydrazine hydrochloride.

\[
\begin{align*}
\text{H}_2\text{N} \cdot \text{C} \cdot \text{NH} \cdot \text{C} \equiv \text{N} + \text{NH}_2\text{NH}_2 \cdot 2\text{HCl} & \xrightarrow{\text{Hydrazine dichloride}} \text{Pyroguanazole} \\
\text{(1)} & \\
\text{Dicyandiamide}
\end{align*}
\]

Moore\textsuperscript{42} in 1918 found that o-aminoacetophenone reacted with dicyandiamide to isolate 2-guanidino-4-methyl-quianazoline (29).

\[
\begin{align*}
\text{H}_2\text{N} \cdot \text{C} \cdot \text{NH} \cdot \text{C} \equiv \text{N} + \text{COMe} \xrightarrow{\text{MeOC} \cdot \text{CH}_2} \text{2-Guanidino-4-methyl-quianazoline} \\
\text{(1)} & \\
\text{Dicyandiamide} & \text{Acetylacetone}
\end{align*}
\]
Zerweck\textsuperscript{43} in 1942 prepared 2-substituted-4,6-diamino-1,3,5-triazine (30) by the interaction of substituted nitriles and dicyandiamide.

\[ \text{H}_2\text{N}^-\text{C}^-\text{NH}^-\text{C}==\text{N} + \text{R}^-\text{C}==\text{N} \rightarrow \text{R}^-\text{C}==\text{N}^-\text{C}^-\text{N}^-\text{N}^-\text{C}==\text{N}^-\text{N}^-\text{C}^-\text{NH}^- \]

Dicyandiamide

Ansterwell\textsuperscript{44} in 1943 prepared 2,4-diamino-6-substituted-1,3,5-triazine (31) by heating guanidine salt with dicyandiamide. The guanidine salt was prepared by heating dicyandiamide with an ammonium salt of the acid, followed by addition of second mole of dicyandiamide.

\[ \text{H}_2\text{N}^-\text{C}^-\text{NH}^-\text{C}==\text{N} + \text{H}_2\text{N}^-\text{C}^-\text{NH}^-\text{H}_2\text{COOR} \rightarrow \text{R}^-\text{C}==\text{N}^-\text{C}^-\text{NH}^- + 2\text{NH}_3 + \text{CO}_2 \]

Dicyandiamide

where, \( R = \text{methyl, ethyl, phenyl} \)

2,4-Diamino-6-substituted-1,3,5-triazine

Vol'fkovich\textsuperscript{45} in 1946 isolated 2,4,6-triamino-1,3,5-triazine also called as melamine (32) by heating dicyandiamide and guanidine carbonate.

\[ \text{H}_2\text{N}^-\text{C}^-\text{NH}^-\text{C}==\text{N} + \text{H}_2\text{N}^-\text{C}^-\text{NH}^-\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{N}^-\text{C}^==\text{N}^-\text{C}^-\text{NH}^- \]

Dicyandiamide

\[ \text{H}_2\text{N}^-\text{C}^-\text{NH}^-\text{C}==\text{N}^-\text{NH}_2 \]

2,4,6-Triamino-1,3,5-triazine
Ostogrovich\textsuperscript{46} in 1949 prepared 2,4-diamino-6-substituted-1,3,5-triazine (33) by interaction of acetamidine hydrochloride and also benzamidine hydrochloride with dicyandiamide at 200-230°C.

\[
\begin{align*}
H_2N-C-NH-C\equiv N + R-C\equiv NH \xrightarrow{200-300^\circ C} & R-C\equiv N-C\equiv N - NH_2 + NH_4Cl \\
\text{(1)} & \text{Dicyandiamide} \quad \text{Substituted amidinohydrochloride} \\
\end{align*}
\]

where, \( R = \text{methyl, ethyl, phenyl} \)

MaClean\textsuperscript{47} in 1951 studied in some detail reactions of dicyandiamide with anhydrous inorganic acids and he obtained monoguanylmelamine (34). Mostly the condition used was dicyandiamide in pyridine nitrobenzene solvent mixture yields monoguanylmelamine (34).

\[
\begin{align*}
2H_2N-C-NH-C\equiv N & \xrightarrow{HX} H_2N-C\equiv N-C\equiv N-NH-C-NH_2 \\
\text{(1)} & \text{Dicyandiamide} \quad \text{Monoguanylmelamine} \\
\end{align*}
\]

Benneville\textsuperscript{48} in 1954 carried out the reaction of cyanoaminotrile with two molecules of dicyandiamide, and obtained bis [amino-1,3,5-triazine] (35) which may be regarded as both substituted melamine (i.e. 2,4,6-triamino-1,3,5-triazine) and substituted 2,4-diamino-1,3,5-triazine.
Kaiser, Peter, Wystrach in 1953 prepared 3,5,7-triamino-1,2,4-triazole [4, 3a] 1,3,5-triazine also called as guanazoguanazole (36) by heating hydrazine hydrochloride and dicyandiamide.

\[
\text{H}_2\text{N} - \text{C} - \text{NH} - \text{C} \equiv \text{N} + \text{H} - \text{N} = \text{NH}_2 \cdot \text{HCl} \rightarrow \text{H}_2\text{N} - \text{C} \equiv \text{N} - \text{C} - \text{NH}_2
\]

(36)

Kaiser in 1953 prepared 3,5,7-triamino-1,2,4-triazole [4, 3a] 1,3,5-triazine (38) by the interaction of dicyandiamide and guanazole (37).
B] N-Aryl/Alkylisocyanodichloride (2b):

Dyson and Haringston\(^51\) in 1940 prepared phenyl, \(p\)-tolyl and \(p\)-anisylisocyanodichlorides first time by the action of molecular chlorine on the related isothiocyanates in chloroform medium. Murphy\(^52\) in 1958 prepared these aryl/alkyl isocyanodichlorides in carbontetrachloride medium.

\[
\text{R-N=C=S} + \text{Cl}_2 \xrightarrow{\text{Chloroform or Carbontetrachloride}} \text{R-N=CCl}_2
\]

Literature survey reveals that, several varieties of heterocycles to each class have been reported. It will not be out of place here to review all those compounds. The present review deals mainly with respect to heterocycles of thiadiazines, dithiazines and triazines.

Pathe and Paranjape\(^53\) prepared 5-aryl-4,5-dihydro-2,6-dimercapto-4-phenylimino-s-triazine (40) by the isomerisation of 6-arylimino-2-phenylimino-4-imino-1,3,5-dithiazine (39) with the help of warm ethanol. The latter has been prepared by the interaction of phenylisocyanodichloride and 1-aryl-2,4-dithiobiurets.

Where, \(R = \text{aryl}\)
Pathe and co-workers have used this reagent in the synthesis of 1,3,5-dithiazines involving the interaction of N-phenylisocyanodichloride and 1,3,5-triaryl-2,4-dithiobiuret. 1,3,5-dithiazines did not isomerise into corresponding s-triazine.

\[
\begin{align*}
\text{Ph} - \text{N} &= \text{C} \quad \text{Cl} + \\
&\text{H} \quad \text{S} \quad \text{C} \\
\text{H} \quad \text{S} \quad \text{C} \\
&\text{Ar} - \text{N} = \text{C} \\
\text{N} \quad \text{Ph}
\end{align*}
\]

They have also reported the synthesis of series of s-triazines by the interaction of N-phenylisocyanodichloride with 1-aryl-4-S-benzyl-2,4-isodithiobiuret, 1,5-diaryl-2,4-dithiobiuret, 1,5-diaryl-2-S-benzyl-2,4-isodithiobiuret and 1,5-diaryl-2-thiobiuret.

\[
\begin{align*}
\text{Ph} - \text{N} &= \text{C} \quad \text{Cl} + \text{R} \quad \text{NH} - \\
&\text{C} \\
\text{S} \\
\text{S} \\
\text{Bz} \\
\text{Ph} - \text{N} = \text{C} \\
\text{C} = \text{N} - \text{R}
\end{align*}
\]

Where, R = phenyl, \( n \)-tolyl, \( p \)-tolyl, \( m \)-chlorophenyl and \( p \)-chlorophenyl

\[
\begin{align*}
\text{Bz} &= \text{benzyl}
\end{align*}
\]
General Introduction

N-phenyl isocyanodichloride (2b)

1,5-Diaryl-2,4-dithiobiuret

2-Phenylimino-4,6-diarylmino-1,3,5-dithiazine

Warm ethanol

Isomerization

1,5-Diaryl-2-S-benzyl-2,4-isodithiobiuret

3-Aryl-2-phenylimino-4-mercaptobenzyl-6-arylimino-1,3,5-thiadiazine

Where, R and R' = aryl

N-phenyl isocyanodichloride (2b)

1,5-Diaryl-2-thio-6-arylimino-1,3,5-thiadiazine

Where, R and R' = aryl

M. E. Sheike, Ph.D. Thesis... 16
Khandelwal\textsuperscript{56} reported the synthesis of s-triazine involving interaction of 1-aryl-2,4-dithiobiurets and N-\textit{t}-butylisocyanodichloride.

\begin{align*}
\text{TB} - \text{N} = \text{C} & \text{Cl} + \\
\text{N-}\text{t}-\text{butyl isocyanodichloride} & \text{1-Aryl-2,4-dithiobiuret} \\
\text{H-S-C} & \text{NH} \\
\text{S=C} & \text{NHR} \\
\end{align*}

Where, R : phenyl, \textit{p}-tolyl, \textit{m}-tolyl, TB = \text{t}-butyl

3-Aryl-4-t-butylimino-2,6-dithiohexahydro-s-triazine

Pachade\textsuperscript{57} synthesised 5-aryl-2,6-di-\textit{t}-butylimino-4-mercapto-benzyl-dihydro-1,3,5-thiadiazine hydrochloride and 1-aryl-2-S-benzyl-5-\textit{t}-butyl-2,4-isodithiobiurets.
Pachade has also reported the synthesis of 3-aryl-4-\(-t\)-butylimino-6-imino-2-mercaptobenzyltetrahydro-s-triazine hydrochloride by the interaction of 1-aryl-2-S-benzyl-3-amidinoisothiocarbamide and \(t\)-butylisocyanodichloride.

**Synthesis of thioglucosidic group containing 6-membered heterocyclic compounds:**

Bedekar and Paranjape\(^8\) have synthesised a 3-aryl-2,6-diphenylimido-4-S-tetra-\(o\)-acetyl-D-glucopyranosyl-1,3,5-thiadiazine by the interaction of 1,5-diaryl-2-S-tetra-\(o\)-acetyl-D-glucopyranosyl-2,4-isodithiobiuret and \(N\)-phenylisocyanodichloride.
3-Aryl-2,6-diphenylimido-4-S-tetra-o-acetyl-D-glucopyranosyl-2,3-dihydro-1,3,5-thiadiazine, hydrochloride

\[ \text{(49)} \]

\[ \text{(50)} \]

**Synthesis of nucleosides containing 6-membered heterocyclic compounds:**

Berad\(^5^9\) has reported the interaction of N-phenylisocyanodichloride and 1-aryl/H-2-S-benzyl-5-tetra-o-acetyl-\(\beta\)-D-glucopyranosyl-2,4-isodithiobiuret leading to 2-phenylimino-3-aryl/H-4-S-benzyl-6-tetra-o-acetyl-\(\beta\)-D-glucopyranosylimino-2,3-dihydro-1,3,5-thiadiazine, hydrochloride (50).

**Chemical Structures:**

- **(2b)**: N-phenyl isocyanodichloride
- **(51)**: 2-Phenylimino-3-aryl/H-4-S-benzyl-6-tetra-o-acetyl-\(\beta\)-D-glucopyranosylimino-2,3-dihydro-1,3,5-thiadiazine, hydrochloride

Where, \(R = \text{phenyl, } p\)-tolyl, \(o\)-chiorophenyl, \(p\)-chlorophenyl and hydrogen

\(\text{Bz} = \text{benzyl}\)

M. E. Sheike, Ph.D. Thesis... 19
Lately, Berad has reported the formation of 1,3,5-triazino-benzothiazole involving the interaction of 1-benzothiazolo-2-yl-3-tetra-o-acetyl-\(\beta\)-D-glucopyranosylthiocarbamide and N-phenylisocyanodichloride.

\[
\text{Ph} \quad \text{N} = \text{C} < \text{Cl} \quad + \quad \begin{array}{c}
\text{R} \\
\text{Cl}
\end{array}
\]

\((2b)\)

N-phenyl isocyanodichloride

\[
\rightarrow
\quad \begin{array}{c}
\text{R} \\
\text{C}
\end{array}
\]

1-Tetra-o-acetyl-\(\beta\)-D-glucopyranosyl-3-(substituted) benzothiazolythiocarbamide

\[
\text{N} - \text{Ph} \quad 2\text{HCl}
\]

\((52)\)

4H,4-Thio-2-tetra-o-acetyl-\(\beta\)-D-glucopyranosylimino-1,3,5-triazino (2,1-6) 6,7- or 8-substituted benzothiazole

Aparajit has reported the formation of 5-aryl/alkylimino-3-\(\beta\)-butyl-2-S-\(\beta\)-butyl-4-phenylimino-6-thiotetrahydro-s-triazine (53); by the interaction of N-\(\beta\)-butyl-S-\(\beta\)-butyl-5-aryl/alkyl-2,4-isodithiobiuret and N-phenylisocyanodichloride.

\[
\text{Ph} \quad \text{N} = \text{C} < \text{Cl} \quad + \quad \begin{array}{c}
\text{Tb} \\
\text{NH} \\
\text{C}
\end{array}
\]

\((2b)\)

N-phenyl isocyanodichloride

\[
\rightarrow
\quad \begin{array}{c}
\text{Tb} \\
\text{C}
\end{array}
\]

5-Aryl/alkyl-3-\(\beta\)-butyl-2-S-\(\beta\)-butyl-4-phenylimino-6-thiotetrahydro-s-triazine

M. E. Sheike, Ph.D. Thesis...
Bhaskar and Berad have synthesised 3-thio-4-p-aryl/alkyl-5-phenylimino-6-phenylthiazole-(2,3-b)-s-triazine (55) by the interaction of 1-(4-phenylthiazol-2-yl)-3-aryl/alkylthiocarbamide with N-phenylisocyanodichloride.

\[
\text{Ph - N = C} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} + \text{Ph - C} \begin{array}{c} \text{N - H} \\ \text{N - H} \end{array} \text{C} = \text{S} \rightarrow \text{Ph - C} \begin{array}{c} \text{N - R} \\ \text{N - R} \end{array} \text{C} = \text{S}
\]

Where, \( R \) : aryl/alkyl

Deohate and Berad have synthesised 2,6-diphenylimino-4-(substituted) aryl/alkyl ideneamino-2,3-dihydro-1,3,5-thiadiazine (56a) which were successfully isomerised into s-triazine (57) by the interaction of N-phenylisocyanodichloride and 1-(substituted)-aryl/alkyl-ideneamidino-3-phenylthiocarbamide.

\[
\text{R' - CH = N - C} \begin{array}{c} \text{NH} \\ \text{S} \end{array} \rightarrow \text{R' - CH = N - C} \begin{array}{c} \text{N} \\ \text{R} \end{array} \text{C} = \text{S}
\]

M. E. Shelke, Ph.D. Thesis...
General Introduction

\[
\text{dil \( \text{NH}_2\text{OH} \)}
\]

\[
\text{5\% NaOH in ethanol}
\]

M. E. Shelke, Ph.D. Thesis ... 22
References

1. J. Clarke

"The Chemistry of Penicillin",
Prication Univ. Press, (1949).


Indian Patent, 142, 048 (1977);


Indian Patent, 142, 046 (1977);


Arch. Pharm (Weinheim), 335(9), 438 (2002).

5. K. Alfred and A. Tantaway


6. B. Helmut, K. Willi, K. Wolfgang, M. Edger and R. Peter

Ger Offen, 2, 630/849 (1978);

7. H. Moriga and H. Tatsta

Japan Patent, 77, 111/584 (1977);

8. L. M. Pugacheva

U.S.S.R. Patent, 466, 263 (1975);

9. D. T. Tayade


10. D. T. Tayade


11. M. G. Paranjape

"Studies in the Chemistry of Isothiocyanate (Senfol) Oxides, Sulphides and related Heterocycles"
12. C. P. Joshua  
   "Chemistry of Hetor's Base",  

13. V. K. Varma  
   "Contribution to Organic Chemistry of  
   Nitrogen and Sulphur Compounds",  

14. P. K. Shrivastava  
   "Bases Related with Thiourea",  

15. S. N. Pandeya  
   "Interaction of 2-chlorobenzothiazole- 
   amidine chlorides and acetone with  
   (1965).

16. Y. R. Rao  
   "Isomeric changes involving Amidino  
   and Thioamidino groups with special  
   reference to Nitrogen, Sulphur, Hetero- 
   cycles and related Chemistry", Ph.D.  

17. Miss. I. D. Bedekar  
   "Chemistry of Tetra-o-acetyl-D-glucopyranosyl bromide, synthesis of certain  
   Acetylated Thioglucosides", Ph.D. Thesis,  
   Nagpur University, Nagpur (1983).

18. B. N. Berad  
   "Organic Chemistry of Nitrogen, Sulphur  
   and Oxygen containing compounds,  
   synthesis of N-glucosylated nitrogen  
   and sulphur containing 5 and 6  
   membered heterocyclic compounds",  
   Ph.D. Thesis, Nagpur University,  

19. D. T. Tayade  
   "A contribution to the chemistry of  
   Nitrogen and Sulphur containing  
   heteroacyclic and heterocyclic  
   compounds", Ph.D. Thesis, Amravati  
   University, Amravati (1996).
20. Miss. R. S. Deshmukh
   "Synthesis and structural chemistry of pyrazoles, thiazolidines, dithia-

21. C. S. Bhaskar
   "Synthesis and study of nitrogen and sulphur containing 5 and 6 membered

22. B. Bielsten and A. Keller
   Ber., 16, 1074 (1883).

23. L. Hagg and J. Liebig
   Ann, 122, 122 (1862).

24. D. Hallwach and J. Liebig
   Ibid, 153, 293 (1870).

25. M. Bamberger
   Inaugural Dissertation Berline, (1880).

   Ber., 6, 1374 (1873); 8, 703 (1875).

27. J. Liebig
   Ann, 122, 22 (1862).

28. F. Kurzer

29. J. Kaiser and B. Elmer

30. A. Ostrogovich
   Rend, Acca Lincer (5), 21, 213 (1912).

31. H. J. LinDholm
   Ber., 49, 156-60 (1913).

32. L. Bamberger and A. Ostrogovich
   Gazz, Chim, ital, 44 II, 562 (1914).

33. Smolka Friendreich

34. D. Nagy
   U.S. 2, 481, 526 (1949).

35. M. Wystrach and S. Erickson

36. B. Rathke
   Ber., 18, 3120 (1885).

37. A. Keller
   Ber., 24, 2512 (1891).
<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s)</th>
<th>Title</th>
<th>Institution and Year</th>
</tr>
</thead>
</table>