Thiazolidones are related to thiazoles as shown below:

![Thiazole](image1)  ![Thiazolidine](image2)  ![2-Thiazolidone](image3)

4-Thiazolidone  2,4-Thiazolidone  Rhodonine
Or
3-Mercapto-4-thiazolidone

The above hetero nuclei have attained great importance as they are present in naturally occurring substances and also in synthetic substances of immense value. 2-Aminothiazole is an intermediate in the preparation of sulphahtiazole, one of the important members of the series of the sulpha drugs (63).

![Sulphahtiazole](image4)

Sulphahtiazole
Or
2-Sulphanilamidothiazole
Sulphasuxidine is N-succinyl derivative of sulphathiazole (60).

\[
\text{HOOC-CH}_2-\text{CH}_2-\text{CO-NH-C}_6\text{H}_4-\text{SO}_2-\text{NH-C}
\]

Sulphasuxidine

It is of value in bacillary dysentery (67).

In 1935, Williams et al., demonstrated the existence of the simple thiazole ring in vitamin B\textsubscript{1} (103).

\[
\text{HN}_3-\text{C-CH}_2-\text{CH}_2-\text{OH}
\]

\[
\text{Cl}
\]

\[
\text{C-CH}_2-\text{CH}_2-\text{OH}
\]

\[
\text{C-CH}_3
\]

\[
\text{CH}_2-\text{C}
\]

\[
\text{C-CH}_3
\]

\[
\text{NH}_2-\text{HCl}
\]

**Vitamin B\textsubscript{1}**

Promizole contains 2-aminothiazole ring. It has been tested in animals and men, and up to 40 per cent of lepers lost their positive skin reaction for lepra bacilli (28).

\[
\text{H}_2-\text{C}
\]

\[
\text{N}
\]

\[
\text{C-CH}_2-\text{CH}_2-\text{OH}
\]

\[
\text{S}
\]

**Promizole**
2-Mercaptobenzothiazole known as 'Captax' is widely used as vulcanization accelerator (33).

\[ \text{H}_2\text{C} \quad \text{N} \quad \text{H} \]

2-Mercaptobenzothiazole
(Captax)

Thiazolidine ring is present in penicillin C, one of the most important antibiotics (15).

\[ \text{C}_6\text{H}_5\text{-CH}_2\text{-CONH-CH}=\text{CH-COOC} \]

Penicillin C.

Some thiazolidine derivatives have been shown to possess bacteriostatic properties against Mycobacterium tuberculosis (36).

2-Mercapto-4-thiazolidone is known as rhodanine.

\[ \text{S} \quad \text{CH}_2 \quad \text{N} \quad \text{CH} \]

Rhodanine
Several 3-(substituted benzyl) rhodanines have been shown to exhibit strong antifungal activity (12).

2-Imino-4-thiazolidone i.e. pseudothiohydantoin or isothiohydantoin is isomeric with 2-thiohydantoin.

\[
\begin{align*}
\text{2-Thiohydantoin} & \quad \text{Pseudothiohydantoin} \\
\begin{array}{c}
\text{SC} \\
\text{NH} \\
\text{NH} \\
\text{CO}
\end{array} & \quad \begin{array}{c}
\text{S} \\
\text{NH} \\
\text{HH} \\
\text{CO}
\end{array}
\end{align*}
\]

Or

2-Imino-4-thiazolidone

Recently several thiazolidone derivatives have been prepared, which show a wide variety of physiological properties.

Anticonvulsant (electroshock) activity has been observed in the case of 2-phenyl-3-methyl (or ethyl)-4-thiazolidone. 2-(p-chlorophenyl)-3-methyl- and 2-(2-furyl)-3-methyl-4-thiazolidones are also active against nitrazol induced convulsions (100). Similar activity has been observed by Chen et al., in the case of 2-phenyl-3-ethyl-4-thiazolidone (14).

2-Aryl-3-alkylaminoalkyl-4-thiazolidone possesses a high degree of activity in producing sciatic nerve block in guinea pigs and spinal anesthesia in rabbits (93).

Lucena and Hoppe report that 3-(alkyl, dialkyl and cycloalkylaminoalkyl)-2-phenyl-4-thiazolidone derivatives possess local anesthetic activity (49). Surrey and Cutler prepared
1:1-dioxides of 2-halophenyl-4-thiazolidones and found them to possess amebicidal activity (95). Satzinger prepared amides of 4-thiazolidones and found them to possess analgesic and sedative activity (83). Same author also prepared substituted bis-(4-thiazolidones) having analgesic, sedative and choleretic properties (84).

Where:
\[
A^\alpha = \text{CH}_2 \cdot \text{CH}_2^-
\]

\[
= \text{CH}_2 \cdot \text{CH(OH)} \cdot \text{CH}_2^-
\]

\[
= \text{NcN} \cdot \text{(CH}_2 \cdot \text{CH}_2)^2^-
\]

Warner-Lambert pharmaceutical company prepared 2-cyano-4-thiazolidones and found them to possess analgesic, sedative and antiphlogistic activity (102). Sheikh and Thaker synthesised 3-aryl-5-(3-methylbutyl)-2-mercapto-4-thiazolidones as potential anticonvulsants (85). Surrey prepared 3-(2-oxa-zolidinone-3-yl)-4-thiazolidones which showed psychomotor stimulant, psychomotor depressant and barbiturate potentiating activity (96). Same author also prepared 4-thiazolidones and their oxides which were found to possess psychomotor stimulant, anticonvulsant and barbiturate potentiating activity (97).
McLemore et al., isolated an antibiotic from the culture broths of strains of streptomyces (55). It is (-)-2-(carboxy-pentyl)-4-thiazolidone (actithiazic acid) and is active in vitro against Mycobacterium tuberculosis.

\[
\text{HOOC-(CH}_2)_5\text{-H}
\]

\[\text{S} \quad \text{CH}_2 \quad \text{NH} \quad \text{Cu}\]

Actithiazic acid

Pennington et al., prepared compounds closely related to actithiazic acid (65).

2-(2-Naphthyl)imino-4-thiazolidone and its 5-arylidene derivatives completely inhibit the spore germination of Alternaria polandu Ayyangar at a concentration of 50 p.p.m. Their dibromides inhibit completely the spore germination at a concentration of 6-8 p.p.m. (80).

Mercury derivatives of 2-arylimino-4-thiazolidones are active against Escherichia coli and S. aureus in dilution up to 1:40000 (81). Acetoxymercury derivatives of 2-(p-chlorophenyl) imino-4-thiazolidones exhibit antibacterial and fungicidal activity (82). 2-Aryl-3-phenylamino and 2-aryl-3-ureido-4-thiazolidones have been found to possess appreciable bacteriostatic activity against Salmonella typhi, Escherichia coli, Staphylococcus pyogenes aureus and streptococcus equi (30). 2- \([(\text{Arsenosobenzoyl})-\text{aryl}]\)-imino-4-thiazolidone also shows amebicidal activity (37).
5-Arylazo-3-aryl-2-arylimino-4-thiazolidones (70),
2-(4-aryltiazol-2-yl)imino-3-aryl-4-thiazolidones (86),
2-arylimino-5-methyl-4-thiazolidones, 3-alkyl-2-(2-benzo-
thiazolyl)imino-4-thiazolidones (11), 2-arylimino-3-aryl-
-4-thiazolidones and 2-arylimino-3-aryl-5-(p-tolylazo)-4-
thiazolidones (87) have been prepared to study their
fungicidal activity.

N,N-Ethylidene bis-4-methyl-2-oxazolidone possesses
anthelmintic, insecticidal, fungicidal and bactericidal
activity (32).

Rout et al., and Shergawa et al., have prepared several
2-arylimino-4-thiazolidones and condensed them with aldehydes
with a view to studying their physiological properties (78,
9, 10).

Mizzoni prepared 2-phenylimino-3-phenyl-4-thiazolidone
and its derivatives and reported them as antitubercular or
antileprotic agents (57). Several 4-thiazolidone derivatives
have been found by Mizzoni and Bismann to be antitubercular
agents (27, 56). 2-Hydroxyimino-3-phenyl-4-thiazolidone has
been found to be active against Mycobacterium tuberculosis(98).

Rodriguez Perez, Montaqui, Candela and Carreras found
pseudothiohydantoin to have antithyroid action similar to that
of thioacetil (77). 2-(p-n-Alkoxaryl) pseudothiohydantoins
are useful as intermediates for dyes, photographic sensitizers,
sedatives and spasmpreventives (13).

1-2-Bis-(2-phenylthiazolidin-4-one-3-yl) ethanol exhibits radiation protective properties (8). 2-Arylimino-4-thiazolidones and their 5-arylidene derivatives are useful as light stabilizers for plastics (43). 2-Imino-4-oxothiazolidine-5-acetic acid(16), 2-benzylimino-4-thiazolidones (99), 2-arylimino-5-phenyl-4-thiazolidones (71), 5-alkyl/benzyl-2-arylimino-4-thiazolidones (73), 3-benzyl-2-arylimino-4-thiazolidones(39), 5-alkyl/aryl-2-arylimino-4-thiazolidones (74), 2-aryl-3-benzyl-4-thiazolidones (72), 2-aryl-3-aryloxyethyl-4-thiazolidones (64), 5-alkyl-2-a/β-arylalkylmino-4-thiazolidones (40), 2-(pyridyl/2-/3-methylpyridyl/2-thiazolyl) imino-3-benzyl-4-thiazolidones and 2-arylimino-3-β-aryloxyethyl-4-thiazolidones (58) and 2-alkoxybenzylimino-4-thiazolidones and α,ω-bis-(2-arylimino-4-thiazolidone-3-yl) alkanes (88) have been synthesised. Some of them possess antibacterial and antifungal activity. Similar derivatives of N,N'-bis-(2-hydroxyethyl) derivatives of ethylene diamine containing thioamide group are reported as potential antituberculous agents (66).

p-Bis-(2-imino-4-thiazolidone-N^2-yl) benzene and its derivatives (68), bis-thiazolidones from mercapto acetic acid (59) and bicyclic derivatives of oxazolone and thiazolone(89) have also been reported. α,ω-bis-(2-arylthiazolidin-4-one-3-yl) alkanes have been prepared from alkylene diamines (61).
PRESENT WORK

The above indicates the importance of 2,3 disubstituted thiazolidiones. Basic amides from desyl amines have shown local anaesthetic and antispasmodic activity (64, 96a, 104). Thiazolidiones have been shown to exhibit anticonvulsant, local anaesthetic, analgesic, sedative and other interesting activities. It was therefore interesting to attach desyl group on thiazolidone ring. With this in view some 2-aryl-3-desyl thiazolidiones have been prepared by using the reaction shown below.

\[ R \cdot C_6H_4CHO + R' \cdot C_6H_4-CH \cdot CH_2 \cdot C_6H_5 \quad NH_2 \]

\[ + \]

\[ \text{HS} \quad \text{COOH} \]

\[ \text{CH}_2 \]

\[ R \cdot C_6H_4 \cdot CH \quad N \quad CH \cdot CH_2 \cdot C_6H_5 \]

\[ \text{S} \quad \text{CO} \quad C_6H_4 \cdot R' \]

\[ \text{CH}_2 \]

Where

\[ R = \text{H}; 2-\text{Cl}; 4-\text{Cl}; 2,4-(\text{Cl})_2; 3,4-(\text{Cl})_2; 4-\text{OCH}_3. \]

\[ R' = \text{H}; 4-\text{Cl}; 4-\text{CH}_3; 3,4-(\text{CH}_3)_2; 2,5-(\text{CH}_3)_2; 4-\text{OCH}_3; 4-\text{OC}_2\text{H}_5. \]
THEORETICAL

PART II
THEORETICAL PART-II

A few of the important methods for the preparation of 4-thiazolidone derivatives are described below:

(I) Davies, Ramsay and Stove claimed to have prepared 2-phenyl-4-thiazolidone by heating a mixture of thioglycolamide and benzaldehyde at 52°C (21).

\[
\text{C}_6\text{H}_5\text{CHO} + \text{HS-CH}_2 + \text{H}_2\text{NCO} \rightarrow \text{C}_6\text{H}_5\text{HCONH}-\text{CO} + \text{H}_2\text{O}
\]

(II) Surrey and Cutler obtained 2-substituted-4-thiazolidones by heating a mixture of an appropriate aldehyde or a ketone with thioglycolic acid and ammonia or an ammonium salt such as ammonium acetate or carbonate (95). The use of ammonium carbonate as the source of ammonia and benzene as solvent, were found to be very convenient.

\[
\text{R-CHO} + \text{NH}_3 + \text{HS-CH}_2 + \text{HCOOH} \rightarrow \text{R-HCONH}-\text{CO} + 2\text{H}_2\text{O}
\]

They postulated the following mechanism for the above reaction.
(i) \[ R-\text{CHO} + \text{NH}_3 \rightarrow R-\text{CH}-\text{NH} + \text{H}_2\text{O} \]

(ii) \[ R-\text{CH}==\text{CH} \ + \ \text{HS-CH}_2 \text{S-CH}_2 \text{COOC} \rightarrow R-\text{H} \text{CH}==\text{CH} \text{S-CH}_2 \text{COOC} + \text{H}_2\text{O} \]

Formation of thioglycolamide as the principal intermediate in this sequence is ruled out, since these authors found that the amide reacts with aromatic aldehyde under conditions employed, to give only a small yield of 4-thiazolidone. They were not able to repeat the work of Davies et al., (21).

(III) Pennington et al., have prepared 2-substituted-4-thiazolidones from thioglycolamide and aldehyde or ketone in presence of catalytic amounts of p-toluene sulphonic acid(65). They have shown the compound of Davies et al., to be a hemimercaptal (21).

(IV) (a) 2,3-Disubstituted-4-thiazolidones have been prepared by Surrey (90). Substituted 2,3-diphenyl-4-thiazolidones were prepared from Schiff's bases and thioglycolic acid with benzene as solvent.
The water liberated in the reaction is distilled off and the amount collected is a measure of the progress of the reaction. The use of ethyl thioglycolate was found to give lower yields of 4-thiazolidiones.

Erlemeyer and Oberlin reacted Schiff's bases from tuberculostatic aromatic amines with thioglycolic acid and obtained 4-thiazolidone derivatives (29).

Marteni obtained 2,3-disubstituted thiazolidiones from Schiff's bases and thioglycolic acid in benzene as solvent (53).

(b) Surrey used the same method for the preparation of 3-alkyl (and aralkyl)-2-aryl derivatives of 4-thiazolidones (91).

(c) Surrey obtained a series of 2-aryl-3-dialkyl-aminocarbonyl derivatives of 4-thiazolidones by reaction between benzylidene dialkylaminoalkylamine and methyl thioglycolate (92). The
reactants are refluxed in Skellysolve E and methylalcohol collected is a measure of the progress of the reaction.

Troutman and Long prepared 2-aryl-3-alkyl- and 2-hetero-3-alkyl derivatives of 4-thiazolidones by the use of thioglycolic acid and anil (100).

\[
R-\text{CHO} + H_2N-R_1 \rightarrow R-\text{CH}=N-R_1
\]

They found that the use of thioglycolic ester was more suitable with benzylidene alkylamines, while with benzylidene-anilines the ester gave poor yields. The thiazolidones were
oxidised to 1:1-dioxides by hydrogen peroxide or potassium-permanganate in acetic acid (91).

\[
\text{R-CH} \quad \text{Oxidation} \quad \text{R-CH}
\]

(c) Surrey prepared 2-aryl-3-alkylaminoalkyl derivatives of thiazolidones by reaction between Schiff's bases and methyl thioglycolate (93).

\[
\text{Ar-CH} + \text{H}_2\text{N-}\text{CH}_2\text{H}_n\text{NH-R} \rightarrow \text{Ar-CH} = \text{CH-CH}_2\text{H}_n\text{NH-R}
\]

\[
\text{Ar-CH} + \text{HS-CH}_2 \quad \text{COOH}_3
\]

\[
\text{Ar-CH} + \text{COOH}_3 \rightarrow \text{Ar-CH} \quad \text{COOH}_3
\]

\[
\text{Ar-CH} + \text{CH}_3\text{OH}
\]

(V) Surrey prepared 3-ureido-4-thiazolidone by reaction of
thioglycolic acid with semicarbazone (94).

\[
\begin{align*}
R' & \quad \text{C} \quad \text{R} \quad \text{N} \quad \text{H} \quad \text{NH-CO-NH}_2 \\
\text{R} & \quad \text{C} \quad \text{R'} \quad \text{S} \quad \text{CH}_2 \\
\text{COOH} & \quad \text{N} \quad \text{NH-CO-NH}_2 \\
\text{HS-CH}_2 & \quad \text{R'} \quad \text{S} \quad \text{CH}_2 \\
& \quad \text{N} \quad \text{NH-CO-NH}_2 \\
& \quad \text{HS} \quad \text{R'} \quad \text{S} \quad \text{R} \\
& \quad \text{H}_2\text{O}
\end{align*}
\]

p-Toluene sulphonic acid was found to have catalytic effect on the reaction.

(VI) Rhodamines which are 2-mercapt-4-thiazolidones have been prepared by (i) condensation of dithiocarbamates with monochloroacetic acid (35), (ii) condensation of primary amines with dicarboxymethyl trithiocarbonate (34) and (iii) condensation of mustard oil with thioglycolic acid (4).

(i) \( R-\text{NH}_2 + \text{CS}_2 + \text{NH}_3 \rightarrow R-\text{NH-C-SNH}_4 \)

Dithiocarbamate

(ii) \( R-\text{NH}_2 + \text{S=C} \rightarrow R-\text{N=S-C=CH}_2 \)

+ HSCCH\text{2}COOH

(iii) \( R-\text{NCS} + \text{HSCCH}_2\text{COOH} \rightarrow R-\text{N=S-C=CH}_2 \)

+ HSCCH\text{2}COOH
2-Imino-4-thiazolidones-pseudothiohydantoins

These are the substances which were prepared quite early in the development of thiazolidone chemistry.

2-Imino-4-thiazolidone was for the first time prepared by Maly and simultaneously by Volhard and Andreasch by melting thiourea with monochloracetic acid (51, 101, 4).

\[
\begin{align*}
\text{NH} &= \text{C} \quad \text{Cl-CH}_2 \quad \rightarrow \quad \text{HC-CH}_2 \quad + \quad \text{H}_2\text{O} \\
\text{NH}_2 &\quad \text{SH} \quad \text{HOOC} &\quad \text{H}_2\text{COOH}
\end{align*}
\]

The correct structure, however, was established by Liebermann and Lange in 1879 (45, 46). Andreasch in support synthesised it from thioglycolic acid and cyanamide (3).

\[
\begin{align*}
\text{N} &= \text{C} \quad \text{HS-CH}_2 \quad \rightarrow \quad \text{HC-CH}_2 \quad \text{COOH} \\
\text{NH}_2 &\quad \text{HOOC} \quad \text{NH}_2 &\quad \text{HOOC} \quad \text{NH}_2 \quad \text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{NH} &= \text{C} \quad \text{SH} \quad \text{CH}_2 \\
\text{NH} &= \text{C} \quad \text{COOH}
\end{align*}
\]

\[+ \quad \text{H}_2\text{O}\]

There has been some confusion in the literature about 2-imino-4-thiazolidone-pseudothiohydantoin—which has been confused with 2-thiohydantoin.
The difference between 2-thiohydantoin and pseudothiohydantoin was first recognised by Liebermann (45,46). Further study of the structural differences was made by Aschan and by Dixon (7,24).

One of the principal methods for the preparation of 2-imino-4-thiazolidone derivatives is through the interaction of an appropriate thiourea with monochloroacetic acid (2). This method, with slight modification in the condition of the reaction, is applicable to the synthesis of a variety of substituted 2-imino-4-thiazolidones.

Ray and Fernandes studied the interaction of thiocarbonamide with monochloroacetic acid in aqueous solution at room temperature (75). They obtained formamidinethiol-acetic acid (I) which on heating gave rise to Volhard's iso-thiohydantoin (II).

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} \\
\begin{array}{c}
\text{NH}_2 \\
\text{NH} = \text{C} \\
\text{S} \quad \text{CH}_2 \\
\text{COOH}
\end{array} & \quad \begin{array}{c}
\text{NH}_2 \\
\text{NH} = \text{C} \\
\text{S} \quad \text{CH}_2 \\
\text{COOH}
\end{array}
\end{align*}
\]

2-Phenylimino-4-thiazolidone was prepared by Mayer and also by Andreasch by reaction between phenylthiourea and ethylchloroacetate (54,5). The correct constitution, however was established by Liebermann and Voeltzkov and Lange (47,42).
Desel, Hunter and Kopper condensed arylthiocarbamides with monochloroacetic acid in acetone solution and obtained hydrochloride salts of aryl formamidinethiolic acids (23). The salts, when hydrolysed by water, liberated the free acid, which cyclised with the elimination of water yielding pseudothiohydantoin when heated in glacial acetic acid solution.

\[
\begin{align*}
\text{R-NH-C} & \xrightarrow{\text{S}} \text{R-N=C} & \xrightarrow{\text{SH}} & \text{Cl-CH}_2 \\
\text{NH}_2 & & \text{NH}_2 & \text{HOOC} \\
\end{align*}
\]

\[
\begin{align*}
\text{R-N=C} & \xrightarrow{\text{S}} \text{R-N=C} & \xrightarrow{\text{CH}_2} & \text{HCl} & \text{COOH} \\
\text{NH}_2 & & \text{NH}_2 & \\
\end{align*}
\]

\[
\begin{align*}
\text{R-N=C} & \xrightarrow{\text{S}} \text{R-N=C} & \xrightarrow{\text{CH}_2} & \text{H}_2O & \text{HCl} \\
\text{NH} & & \text{CO} & \\
\end{align*}
\]

Nicolet and Bate have condensed \(\alpha\)-haloeno derivatives of long chain aliphatic acids (or esters) with thiourea in alcoholic solution and obtained iminothiazolidone derivatives(62).

Markley and Reid investigated the method of Lange for the preparation of diphenyl pseudothiohydantoin (52, 42). Mann and Markley and later Kingsbury and Markley observed that the reaction conditions markedly affected not only the yield but also the compound which was formed (31, 41). No explanation of these
observations could be obtained from the papers of Andreasch, Liebermann and Lange and Liebermann who previously prepared diphenyl pseudothiohydantoin (1,46, 44). Best yields were obtained with short heating, small ratio of solvent to reactants, a slight excess of monochloroacetic acid and addition of sufficient sodium acetate to remove hydrogen chloride from the reaction as rapidly as formed. They obtained diphenyl pseudothiohydantoin in 82 per cent yield in presence of sodium acetate in acetic acid as solvent. In ethyl alcohol, without sodium acetate, a mixture of diphenyl pseudothiohydantoin and 3-phenyl-2,4-thiazolidone is formed, whereas with acetic acid as solvent in absence of sodium acetate only 2,4-thiazolidone is formed.

Davis and Dains have prepared 2-imino-4-thiazolidone derivatives by

(a) condensation of R-NH-CO-CH₂Cl with KCN (22,43,76).

(b) from monoarylthiourea and ethyl chlorooacetate in alcoholic solution with equimolecular quantity of pyridine (18,76).

Eberly and Dains have prepared the labile 2-imino-3-allyl-4-thiazolidone hydrochloride by the condensation of allyl-thiourea and monochloroacetic acid by warming in water or in alcoholic solution (26).

5,5-Dialkyl-2-imino-4-thiazolidones can be prepared by the condensation of dialkyl substituted α-bromo acetic acids
with thiourea (25).

Das and Rout condensed p-tolythiourea with monochloroacetic acid in absolute alcohol in presence of anhydrous sodium acetate (19). They found rectified spirit quite unsuitable, as a compound soluble in water and acidic in nature was obtained. Pujari and Rout condensed in a similar manner p-chlorophenylthiourea with monochloroacetic acid and obtained 2-(p-chlorophenyl) imino-4-thiazolidone (69). Das and Rout also prepared 2-(α-naphthyl)imino-4-thiazolidone (20). Rout and Mahapatra prepared in a similar manner 2-(β-naphthyl)imino-4-thiazolidone (80). Mahapatra and Rout prepared 2-arylimino-4-thiazolidones by (a) condensing arythiourea with monochloroacetic acid in absolute alcohol in presence of anhydrous sodium acetate and (b) condensing arythioureas with ethyl chloroacetate in absolute alcohol using sodium ethoxide as the condensing agent (50). Both the methods gave identical products and the yields were almost the same. Rout prepared 2-(p-nitrophenyl)imino-4-thiazolidone by the condensation of appropriate thiourea with monochloroacetic acid in presence of sodium acetate in absolute alcohol (79).

Bhargava prepared 2-arylimino-3-aryl-4-thiazolidones derivatives by condensation of corresponding symmetrical diarylthioureas with monochloroacetic acid in presence of anhydrous sodium acetate in ethyl alcohol (9).

Bhargava and Kaul prepared 2-(o-toly)imino-3-o-toly-4-thiazolidones by the condensation of appropriate thiourea with
monochloroacetic acid (10). When monochloroacetic acid is slightly in excess over the required molecular quantity and the time of reflux is about three hours, the highest yield is obtained. The secondary formation of 3-o-tolyl-2,4-thiazolidone is successfully suppressed by the addition of a sufficient quantity of anhydrous sodium acetate, which removes hydrogen chloride in situ.

When an unsymmetrically substituted thiourea is condensed with monochloroacetic acid, there is a possibility of obtaining isomeric thiazolidones.

\[
R-NHCS\equiv H-R' + C_2H_4COOH \rightarrow R'-\text{N}=\text{C} \quad \text{S} \quad \text{CH}_2 \\
\text{OR}
\]

In many cases only one of the two isomers is formed (17). Davis and Dains have condensed R-(alkyl or benzy1)-R'- (phenyl)-thiourea with ethyl chloroacetate in presence of pyridine and established the constitution of the product as 3-alkyl/benzy1-2-erylimino-4-thiazolidone (22). They hydrolysed the benzal derivatives of the corresponding thiazolidones, when 5-benzal-
-3-alkyl/benzyl-2,4-thiazolidone and arylamine were obtained.

\[
R\text{-NHCSNH-}R' + \text{ClCH}_2\text{COOC}_2\text{H}_5 \rightarrow R\text{-N}\text{C}=\text{CH-}R' + \text{R''-CHO}
\]

\[
\begin{align*}
R\text{-N}\text{C}=\text{CH-}R'' & \rightarrow \text{HCl} \rightarrow \\
& \text{HOH} \rightarrow \\
& \text{O=CO} \\
& \text{N} \\
& \text{CO} \\
& \text{R'} \\
& + \text{R'.NH}_2
\end{align*}
\]

Where: \( R \) and \( R'' \) = Aryl and \( R' \) = Alkyl or benzyl.

Kharidia and Trivadi prepared 2-benzylimino-4-thiazolidone derivatives by the condensation of appropriate thiourea with monochloroacetic acid in presence of anhydrous sodium acetate in absolute alcohol (38).

Arakelian and Dunn prepared 2-imino-4-oxo-5-thiazolidine-acetic acid and its derivatives by the interaction of thiourea
with maleic or fumaric acid (6).

Contractor and Trivedi prepared 2-aryl/benzylimino-3-aryl/benzyl/naphthyl-4-oxo-5-thiazolidine-acetic acids by the condensation of appropriate thiourea with maleic anhydride (16).
I have used Friedel-Crafts reaction for the preparation of substituted desoxybenzoins in the present work.

<table>
<thead>
<tr>
<th>Name of desoxybenzoin</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desoxybenzoin</td>
<td>Friedel-Crafts reaction</td>
</tr>
<tr>
<td>4-Chloro desoxybenzoin</td>
<td>(Herlekar and Nargund Journal of the Karnataka University Vol. II (No.1.), 58, (1957); Chem. Abstr., 53, 14051 (1959).)</td>
</tr>
<tr>
<td>4-Methyl desoxybenzoin</td>
<td></td>
</tr>
<tr>
<td>3,4-Dimethyl desoxybenzoin</td>
<td></td>
</tr>
<tr>
<td>2,5-Dimethyl desoxybenzoin</td>
<td></td>
</tr>
<tr>
<td>4'-Ethoxy desoxybenzoin</td>
<td></td>
</tr>
<tr>
<td>4-Ethoxy desoxybenzoin</td>
<td></td>
</tr>
</tbody>
</table>
1,2-DIARYLETHYLAMINES:

I have used Leuckart reaction for the preparation of 1,2-diarylethylamines in the present work.

<table>
<thead>
<tr>
<th>Name of the 1,2-diarylethylamines</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Diphenylethylamine</td>
<td>Leuckart reaction (Nerlekar and Margund, Journal of the Karnataka University, Vol. II (No. 1), 50, 1957; Chem. Abstr., 53, 14051 (1959)).</td>
</tr>
<tr>
<td>1-(4-Chlorophenyl)-2-phenylethylamine</td>
<td></td>
</tr>
<tr>
<td>1-(3,4-Dimethylphenyl)-2-phenylethylamine</td>
<td></td>
</tr>
<tr>
<td>1-(2,5-Dimethylphenyl)-2-phenylethylamine</td>
<td></td>
</tr>
<tr>
<td>1-(4-Methylphenyl)-2-phenylethylamine</td>
<td></td>
</tr>
<tr>
<td>1-(4-Methoxyphenyl)-2-phenylethylamine</td>
<td></td>
</tr>
<tr>
<td>1-(4-Ethoxyphenyl)-2-phenylethylamine</td>
<td></td>
</tr>
</tbody>
</table>
Several 2-aryl-3-desyl-4-thiazolidones have been prepared by the condensation of Schiff’s bases (obtained by the interaction of the corresponding desyl amines and aldehydes) and thio-glucolic acid in dry benzene.

\[ R \cdot C_6H_4CHO + R' \cdot C_6H_4-CH-CH_2-C_6H_5 \]

\[ + \]

\[ \text{HS} \quad \text{CCOH} \]

\[ \text{CH}_2 \]

\[ \Downarrow \]

\[ R \cdot C_6H_4-CH-CH-CH_2-C_6H_5 \]

\[ \text{S} \quad \text{CO} \quad \text{C}_6H_4-R' \]

\[ \text{CH}_2 \]

Where:

\( R = \text{H; 2-Cl; 4-Cl; 2,4-(Cl)_2; 3,4-(Cl)_2; 4-OCH}_3 \).

\( R' = \text{H; 4-Cl; 4-CH}_3; 3,4-(CH}_3)_2; 2,5-(CH}_3)_2; 4-OCH}_3; 4-OC_2H_5 \).

Compounds prepared are shown in the table.
### TABLE C-I

2-ARYL-3-DESYL-4-THIAZOLIDONES

![Chemical Structure]

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>R'</th>
<th>D.P. degree C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H</td>
<td>H</td>
<td>123</td>
</tr>
<tr>
<td>2.</td>
<td>2-Cl</td>
<td>H</td>
<td>153</td>
</tr>
<tr>
<td>3.</td>
<td>4-Cl</td>
<td>H</td>
<td>175</td>
</tr>
<tr>
<td>4.</td>
<td>H</td>
<td>4-Cl</td>
<td>285</td>
</tr>
<tr>
<td>5.</td>
<td>4-Cl</td>
<td>4-Cl</td>
<td>200</td>
</tr>
<tr>
<td>6.</td>
<td>3,4-(Cl) &lt;sub&gt;2&lt;/sub&gt;</td>
<td>4-Cl</td>
<td>185</td>
</tr>
<tr>
<td>7.</td>
<td>4-OC&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;</td>
<td>4-Cl</td>
<td>196</td>
</tr>
<tr>
<td>8.</td>
<td>H</td>
<td>4-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>115</td>
</tr>
<tr>
<td>9.</td>
<td>2-Cl</td>
<td>4-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>203</td>
</tr>
<tr>
<td>10.</td>
<td>H</td>
<td>3,4-(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>119</td>
</tr>
<tr>
<td>11.</td>
<td>2-Cl</td>
<td>3,4-(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>103</td>
</tr>
<tr>
<td>12.</td>
<td>4-Cl</td>
<td>3,4-(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>96</td>
</tr>
<tr>
<td>No.</td>
<td>R</td>
<td>R'</td>
<td>H.P. degree C</td>
</tr>
<tr>
<td>-----</td>
<td>------------</td>
<td>------------</td>
<td>---------------</td>
</tr>
<tr>
<td>13.</td>
<td>2,4-(Cl)₂</td>
<td>3,4-(CH₃)₂</td>
<td>147</td>
</tr>
<tr>
<td>14.</td>
<td>H</td>
<td>2,5-(CH₃)₂</td>
<td>128</td>
</tr>
<tr>
<td>15.</td>
<td>4-Cl</td>
<td>2,5-(CH₃)₂</td>
<td>130</td>
</tr>
<tr>
<td>16.</td>
<td>2,4-(Cl)₂</td>
<td>2,5-(CH₃)₂</td>
<td>145</td>
</tr>
<tr>
<td>17.</td>
<td>H</td>
<td>4-OCH₃</td>
<td>99</td>
</tr>
<tr>
<td>18.</td>
<td>4-Cl</td>
<td>4-OCH₃</td>
<td>160</td>
</tr>
<tr>
<td>19.</td>
<td>H</td>
<td>4-O₂H₅</td>
<td>148</td>
</tr>
<tr>
<td>20.</td>
<td>2-Cl</td>
<td>4-O₂H₅</td>
<td>105</td>
</tr>
<tr>
<td>21.</td>
<td>4-Cl</td>
<td>4-O₂H₅</td>
<td>116</td>
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<tr>
<td>22.</td>
<td>2,4-(Cl)₂</td>
<td>4-O₂H₅</td>
<td>152</td>
</tr>
<tr>
<td>23.</td>
<td>3,4-(Cl)₂</td>
<td>4-O₂H₅</td>
<td>175</td>
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<tr>
<td>24.</td>
<td>4-OCH₃</td>
<td>4-O₂H₅</td>
<td>175</td>
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</tbody>
</table>
EXPERIMENTAL

PART II
**EXPERIMENTAL PART-II**

Desoxybenzoins required for the preparation of 1,2-diarylethylamines were prepared as described in experimental part I.

![Structure Diagram]

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>M.P./degree C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.</td>
<td>4-CH₃</td>
<td>110</td>
<td>Weiss, Monatshefte fur Chemie., 40, 394 (1919).</td>
</tr>
<tr>
<td>4.</td>
<td>3,4-(CH₃)₂</td>
<td>95</td>
<td>Nage, Ber., 24, 3540 (1891).</td>
</tr>
<tr>
<td>6.</td>
<td>4-OCH₃</td>
<td>77</td>
<td>Torres, C., Anales. Soc. espaf. fis. quim., 24, 82-90 (1926).</td>
</tr>
<tr>
<td>7.</td>
<td>4-OCH₂H₅</td>
<td>105-106</td>
<td>-DO-</td>
</tr>
</tbody>
</table>
GENERAL METHOD FOR THE PREPARATION OF
1,2-DIARYLETHYLamines BY LEUCKART REACTION:

Formic acid (21 ml.) was slowly added to ammonium carbonate
(21.5 g.), placed in a three necked round bottomed flask, fitted
with a thermometer and a distillation bend attached to a condenser,
for simultaneous distillation. After complete addition of formic
acid, the thermometer was raised gradually to 165°, and heating
continued till the removal of water from the reaction mixture was
complete. Desoxybenzoin (0.1 mole) was added in one lot to this
reaction mixture and heating once again resumed. The temperature
was slowly raised to 165° and maintained at that temperature for
four hours. The reaction mixture was then poured in water and the
resulting solid formyl derivative was hydrolysed with 12 percent
hydrochloric acid. In some cases, the amine was isolated as the
hydrochloride, but where the hydrochloride was not obtained with
case, the hydrolysed solution was basified and the liberated base
was extracted with ether. [(Merckar and Nargund, Journal of the
Karmatak University, Vol. II (No.1), 58, 1957; Chem. Abstr. 53,
14051 (1959).]
Following 1,2-diarylethylamines were prepared by this method in 60 per cent yield.

![Chemical structure](attachment:image)

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>M.P. of Hydrochloride degree C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H</td>
<td>( B.P. of amine 175/15 m.m. )</td>
<td>Sieglitz, Ber. 55, 2040 ( 1922 ).</td>
</tr>
<tr>
<td>3.</td>
<td>3,4-(CH₃)₂</td>
<td>214-218</td>
<td>-DO-</td>
</tr>
<tr>
<td>4.</td>
<td>2,5-(CH₃)₂</td>
<td>202-204</td>
<td>-DO-</td>
</tr>
<tr>
<td>7.</td>
<td>4-OC₆H₅</td>
<td>203-204</td>
<td>-DO-</td>
</tr>
</tbody>
</table>
GENERAL METHOD FOR THE PREPARATION OF
2-ARYL-3-DESYL-4-ThIAZOLIDONES:

A mixture of aldehyde (0.02 mole) and desylamine (0.02 mole) in dry benzene (25 ml.) was refluxed with a Dean and Stark water separator. After the theoretical quantity of water was separated (4-5 hours), thioglycolic acid (2.0 g.) was added and refluxing was continued, till no more water separated [(Surrey, et al., J. Am. Chem. Soc., 69. 2911 (1947)].

The residue, after removal of benzene, was taken up in ether, washed with sodium bicarbonate solution to remove any acid formed during the reaction, with dilute hydrochloric acid (1:1) to remove unreacted desylamine, with sodium bisulphite solution (10 per cent) to remove unreacted aldehyde and finally with water. The ether solution was dried over anhydrous sodium sulphate. The oily residue, obtained after removal of ether, deposited crystals on long standing.

Thiazolidones (Yield about 60 per cent) were crystallised from alcohol.

Compounds prepared are shown in the following table:
### Table C-11

2-Aryl-3-benzyl-4-thilidones:

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>R'</th>
<th>M.P. degree C</th>
<th>Molecular Formula</th>
<th>Per cent Sulphur Found</th>
<th>Required</th>
<th>Per cent Carbon Found</th>
<th>Required</th>
<th>Per cent Nitrogen Found</th>
<th>Required</th>
<th>Per cent Hydrogen Found</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H</td>
<td>H</td>
<td>123</td>
<td>C\textsubscript{23}H\textsubscript{21}O\textsubscript{3}S</td>
<td>9.0</td>
<td>8.9</td>
<td>76.7</td>
<td>76.9</td>
<td>3.7</td>
<td>3.9</td>
<td>6.0</td>
<td>5.8</td>
</tr>
<tr>
<td>2.</td>
<td>2-Cl</td>
<td>H</td>
<td>153</td>
<td>C\textsubscript{23}H\textsubscript{20}O\textsubscript{3}Cl\textsubscript{1}S</td>
<td>8.2</td>
<td>8.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>4-Cl</td>
<td>H</td>
<td>175</td>
<td>C\textsubscript{23}H\textsubscript{20}O\textsubscript{3}Cl\textsubscript{1}S</td>
<td>6.0</td>
<td>6.1</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>H</td>
<td>4-Cl</td>
<td>285</td>
<td>C\textsubscript{23}H\textsubscript{20}O\textsubscript{3}Cl\textsubscript{1}S</td>
<td>6.2</td>
<td>6.1</td>
<td>70.3</td>
<td>70.1</td>
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<td>3.6</td>
<td>5.4</td>
<td>5.1</td>
</tr>
<tr>
<td>5.</td>
<td>4-Cl</td>
<td>4-Cl</td>
<td>200</td>
<td>C\textsubscript{23}H\textsubscript{19}O\textsubscript{3}Cl\textsubscript{2}S</td>
<td>7.4</td>
<td>7.5</td>
<td></td>
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<td></td>
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<tr>
<td>6.</td>
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<td>4-Cl</td>
<td>185</td>
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<td>6.7</td>
<td>6.9</td>
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</tr>
<tr>
<td>7.</td>
<td>4-OCH\textsubscript{3}</td>
<td>4-Cl</td>
<td>196</td>
<td>C\textsubscript{24}H\textsubscript{22}O\textsubscript{3}Cl\textsubscript{1}S</td>
<td>7.7</td>
<td>7.6</td>
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<tr>
<td>8.</td>
<td>H</td>
<td>4-CH\textsubscript{3}</td>
<td>115</td>
<td>C\textsubscript{24}H\textsubscript{23}O\textsubscript{3}S</td>
<td>8.0</td>
<td>8.6</td>
<td>77.0</td>
<td>77.2</td>
<td>3.5</td>
<td>3.8</td>
<td>6.4</td>
<td>6.2</td>
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<tr>
<td>No.</td>
<td>R</td>
<td>R'</td>
<td>M.P. degree C</td>
<td>Molecular Formula</td>
<td>% S found</td>
<td>% S required</td>
<td>% C found</td>
<td>% C required</td>
<td>% N found</td>
<td>% N required</td>
<td>% H found</td>
<td>% H required</td>
</tr>
<tr>
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<tr>
<td>9.</td>
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<td>4-CH₃</td>
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<tr>
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<td>8.3</td>
<td>77.8</td>
<td>77.5</td>
<td>3.4</td>
<td>3.6</td>
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<td>6.5</td>
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<tr>
<td>11.</td>
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<td>7.6</td>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>15.</td>
<td>4-Cl</td>
<td>2,5-(Cl)₂</td>
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<td>7.6</td>
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<td>17.</td>
<td>H</td>
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<td>8.0</td>
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<td>74.0</td>
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<td>3.6</td>
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<tr>
<td>No.</td>
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<td>R'</td>
<td>H.P. degree C</td>
<td>Molecular Formula</td>
<td>Per cent Sulphur Found</td>
<td>Per cent Carbon Found</td>
<td>Per cent Nitrogen Found</td>
<td>Per cent Hydrogen Found</td>
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<td>7.6</td>
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<tr>
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</tr>
<tr>
<td>21.</td>
<td>4-Cl</td>
<td>4-OCH₃</td>
<td>116</td>
<td>C₂₅H₂₄O₂NC₁S</td>
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<td>7.3</td>
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<tr>
<td>22.</td>
<td>2,4-(Cl)₂</td>
<td>4-OCH₃</td>
<td>152</td>
<td>C₂₅H₂₃O₂NC₁₂S</td>
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<td>6.8</td>
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<td>23.</td>
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<td>C₂₅H₂₃O₂NC₁₂S</td>
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PART - II
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