CHAPTER VI

REACTIONS OF S-ALKYLISODITHIOBIUREAS AND DITHIOBIUREAS

INTRODUCTION

Oxidation of 1-arylthioureas, 81-83 1,3-diarylthioureas, 48,55,109-111 1-alkyl-3-aryltioureas, 40,114,116 1,1-alkylaryltioureas, 45,46,100,105-107 1-alkylthioureas, 75,77 1,3-dialkylthioureas 80 and binary mixtures of differently substituted thioureas 117-121 in polar medium has been found to yield 1,2,4-thiadiazole derivatives as the final product except in a few cases, where the thiadiazole underwent isomerisation to benzothiazolylguanidines. The thiadiazoles were shown to be formed by the oxidation of the intermediate amidinothiourea. In the oxidation of the amidinothiourea, the thiol form of the thiocarbonyl group and the nitrogen which was in the third position from the thiocarbonyl group are involved. Oxidations of a few other similar systems have also been reported. Thus the oxidation of 1-substituted-4-S-alkyl(or aryl)-iso-2,4-dithiobiuret (1) yielded a 1,2,4-thiadiazole derivative 165(2). 1,5-Diaryl-2-S-alkylisodithiobiurets (3) on oxidation yielded only the related benzothiazolyl isothioureas 172(4). The oxidation of thiobiuret (5) yielded 1,2,4-thiadiazol-3-one 79(6).
The oxidation of dithiobiureas (7) and (8) also has been investigated. The products reported in these cases are 2-amino(or arylamino)-5-substituted amino-1,3,4-thiadiazoles (9) or (10).\(^{176,177}\) Recently the oxidation of 1-(N,N'-diarylamidino)thiosemicarbazide (11) has also been reported.\(^{178}\) The product formed was 1,2,4-triazole (12) with elimination of sulphur. Since isodithiobiureas also contain an enolizable thioketo group and an amino group three atoms apart in the chain, it was anticipated that the oxidation of these might yield a thiatriazine or a triazole derivative.

\[
\begin{align*}
R'NH-C-NH-C-SR^3 & \xrightarrow{R^2=H} N-C-SR^3 \\
S & NR^2
\end{align*}
\tag{1}
\]

\[
\begin{align*}
ArNH-C-NH-C=NAr & \rightarrow \\
S & SR^1
\end{align*}
\tag{3}
\]

\[
\begin{align*}
ArNH-C-NH-C-NHAr & \rightarrow \\
S & O
\end{align*}
\tag{5}
\]
S-Alkylisodithiobiureas (13) required for these could be prepared either by the condensation of S-alkylisothiosemicarbazide with isothiocyanate, a reaction analogous to the condensation of S-alkylisothiourea with isothiocyanate. This reaction does not appear to have been investigated. Here the condensation of the isothiocyanate could occur at position 1 or position 4 of the isothiosemicarbazide and yield isodithiobiuret (14) or the isomeric isodithiobiurea derivative (13). Since the hydrazino group is more basic it is likely that the condensation might occur at the hydrazino nitrogen. Another method which could be adopted for the preparation of isodithiobiureas is the alkylation of dithiobiureas. Here the
alkylation could occur at either of two thioketo groups. If the product formed from both the above reactions are one and the same, the product would be 5-S-alkylisodithio-
biurea (13).

\[
\begin{align*}
\text{NH}_2\text{-NH-C}=\text{NH} + \text{RNCS} & \rightarrow \text{RNH-C-NH-C}=\text{NNH} \quad \text{RNH-C-NH}=\text{NNH} \quad \text{RNH-C-NH}=\text{NH} \\
\text{SR}^1 & \quad \text{SR}^1 \\
(14) & \quad (13)
\end{align*}
\]

RESULTS AND DISCUSSIONS

Condensation of S-benzylisothiosemicarbazide with phenyl isothiocyanate yielded a product which was extremely labile. Crystallisation from warm solvents resulted in the elimination of benzyl mercaptan and formation of a triazole derivative (15). Therefore it was crystallised in cold by dissolving in cold acetone and adding petroleum ether. Determination of melting point with a slow rate of heating obscures the correct melting point due to gradual eliminative decomposition to triazole. Therefore melting point was determined under a fast rate of heating (3-5°/min). Product from different lots gave concordent melting points.

\[
(13) \quad \text{R'SH} \rightarrow \quad \text{RN-C-NH}_2 \\
\quad \text{HS-C} \equiv \text{N} \quad \equiv \text{N} \\
(15)
\]
The corresponding S-methyl and S-ethyl derivatives were also prepared. These were also found to undergo eliminative cyclisation on attempted crystallisation from warm solvents. Therefore, these also were purified by the same method adopted for S-benzyl derivative.

Oxidation of these isodithiobiureas in acidic ethanolic medium with hydrogen peroxide did not proceed to yield the thiatriazine derivative. Instead 2-alkyl(or aryl) amino-5-alkyl mercapto-1,3,4-thiadiazoles (16) were formed.

Several of these isodithiobiureas were prepared by condensing the S-alkylisothiosemicarbazide and isothiocyanate. All these compounds were found to be very labile and they underwent eliminative cyclisation similar to the phenyl analogue. The S-alkylisodithiobiurea derivatives formed from different alkyl halides in boiling ethanol gave the same triazole irrespective of the nature of the S-alkyl group. This observation therefore implies that the initial condensation product has a 1-aryl-5-S-alkylisodithiobiurea structure (13).

Since the free S-alkylisodithiobiureas were unstable, preparation of their salts were attempted by alkylating the dithiobiureas with alkyl halides in neutral solvents. In these alkylations also the reaction did not follow expected course. Instead, the reaction yielded 2-alkyl(or aryl)amino-5-alkyl mercapto-1,3,4-thiadiazoles (16).
Since these thiadiazoles were obtained in the alkylation reactions, it was thought that the isodithiobiurea salt formed was the one which underwent eliminative cyclisation to the thiadiazole derivative. Therefore to study the behaviour of isodithiobiurea obtained by the condensation of phenyl isothiocyanate with S-alkylisothiocyanate, they were heated in hydrochloric acid. It was found to undergo cyclisation with the elimination of ammonia yielding the thiadiazole derivative, identical with the one obtained when 1-aryldithiobiurea was heated with alkyl chloride.

Reaction of the isodithiobiureas under alkaline conditions was also examined. The products obtained in each of these cases were identical with the product obtained by heating the related isodithiobiurea in neutral solvents, viz., 4-alkyl(or aryl)-3-amino-5-mercapto-1,2,4-triazole.

The observation that the thiadiazoles were obtained by the oxidation of isodithiobiureas does not warrant the formation of an intermediate thiatriazine as these oxidations were carried out in acidic solution. The thiadiazole was
formed in all probability by an eliminative cyclisation and not by an oxidative cyclisation.

Oxidation of 1-phenyldithiobiurea with either hydrogen peroxide or iodine in warm ethanolic medium yielded the expected 1,3,4-thiadiazole (9) with the elimination of sulphur. Similarly the oxidation of 1-p-tolyl, 1-methyl and 1-ethyldithiobiureas was also carried out. The structure (9)

\[
\text{RNH-C-NHNH-C-NH}_2 \quad \rightarrow \quad \text{N-N} \quad \text{RNH-C-S-C-NH}_2
\]

\[(17)\]

\[
\text{R = } \text{Ph, p-CH}_3\text{C}_6\text{H}_4, \text{C}_2\text{H}_5, \text{ and CH}_3
\]

is assigned to the alkyl analogues by analogy with that of aryl derivatives. No intermediate could be isolated from these oxidation reactions. Oxidation of dithiobiureas suspended in non-polar solvents like chloroform or carbon tetrachloride with bromine yielded semisolid materials which could not be induced to crystallise. When these oxidation products were treated with aqueous ethanol they extruded sulphur and yielded the thiadiazoles. Probably the intermediate, which extruded sulphur on treatment with ethanol is a six-membered disulphide. Such extrusion is seen in the case of oxidation of 1-(N,N'-diarylamidino)thiosemicarbazide.178
EXPERIMENTAL

I. INTERACTION OF S-ALKYLISOTHIOSEMICARBAZIDES WITH
ISOTHIOCYANATES: FORMATION OF 1-ALKYL(OR ARYL)-5-S-
ALKYLISODITHIOBIUREAS (13)

The details of a typical preparation are as follows.

S-Benzylisothiosemicarbazide was prepared by refluxing thiosemicarbazide (4.6g, 0.05 mol) with benzyl chloride (6.3g, 0.05 mol) in ethanol (20 ml) for 30 min. The 5-S-benzylthiosemicarbazide hydrochloride formed in solution was diluted with water (150 ml), phenylisothiocyanate and sodium carbonate (2.6g, 0.025 mol) were added in a slow stream with stirring. During the addition of phenylisothiocyanate and sodium carbonate, the reaction mixture turned pink in colour. The stirring was continued for another 30 min; when a powdery white substance started separating. This was collected and washed with petroleum ether to remove any unreacted phenyl isothiocyanate. The residue was then dried. The substance was dissolved in acetone, and treated with charcoal and filtered. To this filtrate petroleum ether (40-60°C) was added until a faint turbidity appeared. On keeping, colourless shining crystals separated. These crystals of 1-phenyl-5-S-benzylisodithiobiurea were collected, washed with acetone-petroleum ether mixture and dried. Several lots were prepared in this fashion and their melting points were
determined by rapid heating. All gave identical melting points, 136° with decomposition. Their t.l.c. also showed only single spot.

The p-toly, methyl and ethyl analogues also were prepared following the above procedure.

S-Methylisothiosemicarbazide and S-ethylisothiosemicarbazide hydroiodides were prepared by reacting thiosemicarbazide with methyl iodide and ethyl iodide respectively. These isothiosemicarbazides were condensed with phenyl, p-tolyl, methyl and ethyl isothiocyanates. The procedure adopted for the condensation was the same as that of phenyl-benzyl analogue. Purification of these isodithiobiureas were also effected by the same procedure described above. The isodithiobiureas prepared in this way are listed in Table I.

II. FORMATION OF 4-ALKYL(OR ARYL)-3-AMINO-5-MERCAPTO-1,2,4-TRIAZOLEs (15)

(a) 3-Amino-5-mercapto-4-phenyl-1,2,4-triazole

1-Phenyl-5-S-benzylisodithiobiurea (13; R = Ph; R' = benzyl) was dissolved in ethanol and the solution was refluxed on a water-bath for 10-15 min. Benzyl mercaptan was found to evolve during the reaction. Then the solution was cooled when a white powdery substance separated. It was collected and dried. This substance was found to dissolve in alkali.
Hence it was purified by dissolving in alkali and reprecipitating. The product was crystallised from ethanol, m.p. 271°. It was identified as 3-amino-5-mercapto-4-phenyl-1,2,4-triazole (lit.184 m.p. 264-66°).

The S-methyl and S-ethyl analogues also yielded the same triazole when refluxed in ethanol. Methyl mercaptan and ethyl mercaptan respectively were found to evolve during the reaction.

p-Tolyl, ethyl and methylisodithiobiureas listed in Table II were also subjected to cyclisation by refluxing in ethanol and their characteristics are listed below:

(b) 3-Amino-5-mercapto-4-p-tolyl-1,2,4-triazole, prisms from ethanol, m.p. 280-82° (decom)(lit.184 m.p. 277-280°).
   (Found: C,52.5; H,4.7; S,15.1; Calc.for C₉H₁₀N₄S. C,52.4; H,4.8; S,15.5%).

(c) 3-Amino-4-ethyl-5-mercapto-1,2,4-triazole, needles from ethanol, m.p. 198° (decom) (lit.185 m.p. 195-8°). (Found: C,33.1; H,5.8; S,22.0; Calc.for C₄H₈N₄S: C,33.3; H,5.5; S,22.2%).

(d) 3-Amino-5-mercapto-4-methyl-1,2,4-triazole, crystals from aqueous ethanol, m.p. 168° (lit.185 m.p. 269-72°) (Found: C,27.2; H,4.7; S,24.1. Calc.for C₂H₆N₄S: C,27.6; H,4.6; S,24.6%).
III. OXIDATION OF 1-ALKYL(OR ARYL)-5-S-ALKYLISODITHIOBIUREAS: FORMATION OF 2-ALKYL(OR ARYL)AMINO-5-ALKYLMERCAPO-1,3,4-THIADIAZOLE (16)

To a solution of 1-phenyl-5-S-benzylisodithiobiurea (3.2g, 0.01 mol) in ethanol containing concentrated hydrochloric acid (1.2 ml, 32%, 0.01 mol), hydrogen peroxide was added (1.2 ml, 30%, 0.01 mol). After warming for 15 min. the reaction mixture was basified. The precipitate formed was collected and crystallised from ethanol when shining needles were obtained m.p. 143\degree. This was identified as 2-amino-5-benzylmercapto-1,3,4-thiadiazole by comparison with an authentic sample prepared by known methods.\(^{186,187}\) (lit. m.p. 141\degree and 145\degree).

The other substituted isodithiobiureas listed in Table I were also treated as described in the above experiment and in each case the product obtained was identified as 5-alkylmercapto-2-substituted amino-1,3,4-thiadiazoles. These are listed in Table II.

IV. PREPARATION OF 1-ALKYL(OR ARYL)DITHIOBIUREAS

(a) 1-Phenylldithiobiurea

A suspension of powdered thiosemicarbazide (4.6g, 0.05 mol) and sodium hydroxide (2g, 0.05 mol) in acetonitrile (50 ml) was stirred and treated dropwise with phenyl isothiocyanate (6.8g, 0.05 mol). A transient green colour
was formed during the addition of isothiocyanate. On stirring for about an hour a homogeneous solution was obtained. It was diluted with water (125 ml), treated with activated charcoal and filtered. Acidification of the filtrate with dilute hydrochloric acid yielded a white precipitate (83%). It was collected and crystallised from ethanol as shining leaflets, m.p. 182°C. It was identified as 1-phenyldithiobiurea, (lit. \textsuperscript{188} m.p.180°C). (Found: C,42.1; H,4.2; S,28.0. Calc. for $C_8H_{10}N_4S_2$: C,42.4; H,4.4; S,28.3%).

The other 1-aryl and 1-alkyl substituted dithiobiureas also were prepared following the above procedure. The melting points and analysis of the dithiobiureas so prepared are given below:

(b) 1-\textsuperscript{t}-Tolyldithiobiurea (86%); shining leaflets from ethanol, m.p. 195°C. (Found: C,45.1; H,4.8; S,26.3; Calc. for $C_9H_{12}N_4S_2$: C,45.0; H,5.0; S,26.6%).

(c) 1-Ethylidithiobiurea (22%), shining leaflets from aqueous ethanol, m.p. 202°C. (Found: C,26.7; H,5.2; S,35.7. $C_4H_{10}N_4S_2$ requires C,26.9; H,5.6; S,35.9%).

(d) 1-Methylidithiobiurea (15%), shining leaflets from aqueous ethanol, m.p. 221°C. (Found: C,21.8; H,4.8; S,38.8. $C_3H_8N_4S_2$ requires C,21.9; H,4.8; S,39%).
The yield of the products in all these cases were found to be better than what was observed when thiosemicarbazide and the corresponding isothiocyanate were refluxed in ethanol.

V. ALKYLATION OF 1-ALKYL(OR ARYL)DITHIIOBIUREAS: FORMATION OF 2-ALKYL(OR ARYL)AMINO-5-ALKYLMercAPTO-1,3,4-THIADIAZOLE (16).

(a) 2-Anilino-5-benzylmercapto-1,3,4-thiadiazole

A solution of 1-phenyldithiobiurea (5.8g, 0.025 mol) was refluxed with one equivalent of benzyl chloride (3.2g, 0.025 mol) in ethanol (20 ml) for 30 min. The reaction mixture was diluted with water and cooled, when colourless shining crystals of 2-anilino-5-benzylmercapto-1,3,4-thiadiazole started separating. It was collected and crystallised from ethanol, m.p. 143\degree. It did not show any depression in melting when mixed with 2-anilino-5-benzylmercapto-1,3,4-thiadiazole obtained in an earlier experiment.

A solution of 1-phenyldithiobiurea in ethanol was refluxed with methyl iodide or ethyl iodide. In these experiments also 2-anilino-5-alkylmercapto-1,3,4-thiadiazoles were formed. Other dithiobiureas also were subjected to alkylation with benzyl chloride, methyl iodide or ethyl iodide. Ethanol was used as the solvent when ethyl and benzyl halides were used and methanol for methyl iodide. All the thiadiazoles
obtained are listed in Table II.

VI. REACTION OF ISODITHIOBIUREAS IN PRESENCE OF ALKALI: FORMATION OF 4-ALKYL(OR ARYL)-3-AMINO-5-MERCAPTO-1,2,4-TRIAZOLEs (15)

(a) 3-Amino-5-mercapto-4-phenyl-1,2,4-triazole

A solution of 1-phenyl-5-S-benzylisodithiobiurea (3.2 g, 0.01 mol) in ethanol was treated with sodium hydroxide (10%, 2 ml) and warmed on a water-bath for 30 min. Benzyl mercaptan was found to evolve during the reaction. On cooling and neutralising the reaction mixture with hydrochloric acid, a precipitate was formed. It was collected, washed with water and crystallised from ethanol, m.p. 271°. It was identified as 3-amino-5-mercapto-4-phenyl-1,2,4-triazole (lit.184 m.p. 264-66°).

p-Tolyl, ethyl and methyl isodithiobiureas listed in Table I were also subjected to treatment with alkali. The triazoles obtained in these cases did not show any depression in melting point when mixed with the triazoles obtained by refluxing the isodithiobiureas in ethanol.

VII. REACTION OF ISODITHIOBIUREAS IN PRESENCE OF ACID: FORMATION OF 2-ALKYL(OR ARYL)AMINO-5-ALKYLMERCAPTO-1,3,4-THIADIAZOLEs (16)

In a typical experiment a solution of 1-phenyl-5-S-
benzylisodithiobiurea (3.2 g, 0.01 mol) in ethanol was refluxed for 5 min. in presence of hydrochloric acid (1.2 ml, 32%, 0.01 mol). The reaction mixture was diluted with water and cooled. The precipitate obtained was collected and crystallised from ethanol to give 2-anilino-5-benzylmercapto-1,3,4-thiadiazole, m.p. 143°. It did not show any depression in melting point when mixed with 2-anilino-5-benzylmercapto-1,3,4-thiadiazole obtained earlier.

The other isodithiobiureas also were refluxed in ethanol in presence of hydrochloric acid and the thiadiazoles obtained are listed in Table II.

VIII. OXIDATION OF 1-ALKYL(OR ARYL)DITHIIOBIUREAS: FORMATION OF 2-AMINO-5-ALKYL(OR ARYL)AMINO-1,3,4-THIADIAZOLE (17)

(a) 2-Amino-5-phenylamino-1,3,4-thiadiazole.

To a suspension of 1-phenyldithiobiurea (5.6 g, 0.025 mol) in 50% ethanol containing concentrated hydrochloric acid (3 ml, 32%, 0.025 mol), hydrogen peroxide (3 ml, 30%) was added slowly with stirring. The dithiobiurea dissolved and sulphur began to separate. The reaction mixture was kept at 80-90°C for fifteen minutes to complete separation of sulphur. Separated sulphur was removed by filtration, the filtrate was diluted with water (150 ml) and basified with aqueous ammonia. The precipitate formed was collected
and extracted with dilute hydrochloric acid. The acidic extracts were basified and the product collected (2.9g, 60%) was crystallised from aqueous ethanol when colourless leaflets of 2-amino-5-phenylamino-1,3,4-thiadiazole were obtained, m.p. 210° (lit. 176, m.p. 205°) (Found: C, 49.9; H, 4.2; S, 16.8. Calc. for C8H8N4S: C, 50.0; H, 4.1; S, 16.6%).

(b) 2-Amino-5-p-tolylamino-1,3,4-thiadiazole

1-p-Tolylidithiobiurea (6g, 0.025 mol) when oxidised as in the above experiment yielded 2-amino-5-p-tolylamino-1,3,4-thiadiazole (3.2g, 61%), which on crystallisation from aqueous ethanol gave shining leaflets m.p. 207° (lit. 177 m.p. 203°). (Found: C, 52.1; H, 5.0; S, 15.8. Calc. for C9H10N4S: C, 52.4; H, 4.8; S, 15.5%).

(c) 2-Amino-5-ethylamino-1,3,4-thiadiazole

When the oxidation of 1-ethylidithiobiurea (4.7g, 0.025 mol) was carried out as described above and the solution basified, the thiadiazole did not precipitate. Therefore the solution was treated with picric acid. The picrate (5.4g, 58%) was crystallised from ethanol when yellow needles were obtained m.p. 222°. (Found: C, 32.1; H, 2.8; S, 8.1. C4H8N4S. C6H3N2O7 requires C, 32.1; H, 2.9; S, 8.5%).
(d) 2-Amino-5-methylamino-1,3,4-thiadiazole

The oxidation of 1-methyldithiobiurea (4.1g, 0.025 mol) and working up as in the above experiment yielded the picrate of 2-amino-5-methylamino-1,3,4-thiadiazole (4.7g, 52%). On crystallisation from ethanol yellow leaflets were obtained, m.p. 224°. (Lit. \(^\text{183}\) m.p. 218-221°) (Found: C, 30.1; H, 2.1; S, 8.5. Calc. for \(\text{C}_3\text{H}_5\text{N}_4\text{S}\). \(\text{C}_6\text{H}_3\text{N}_2\text{O}_7\) C, 30.0; H, 2.5; S, 8.9%).
### TABLE I
1-ALKYL/ARYL-5-S-ALKYL ISODITHIIOBIUREAS (13)

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Yield</th>
<th>M.p. °C</th>
<th>Formula</th>
<th>Element analysis</th>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>C</td>
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<tr>
<td>Ph</td>
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<td>65</td>
<td>136</td>
<td>C_{15}H_{16}N_{4}S_{2}</td>
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<td></td>
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<td>28</td>
<td>129</td>
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<td></td>
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<tr>
<td></td>
<td>Methyl</td>
<td>15</td>
<td>112</td>
<td>C_{4}H_{10}N_{4}S_{2}</td>
<td>26.8</td>
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1. Crystallised from acetone by addition of petroleum ether.
2. Crystallised from diethyl ether by addition of petroleum ether.
<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Yield %</th>
<th>M.p. °C</th>
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<td></td>
<td></td>
<td>C%</td>
<td>H%</td>
<td>S%</td>
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<td>Benzyl</td>
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<td>84</td>
<td>143*</td>
<td>C_{15}H_{13}N_{2}S_{2}</td>
<td>Found 60.1</td>
<td>4.4</td>
<td>21.2</td>
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<td>Ph</td>
<td>Ethyl</td>
<td>63</td>
<td>139</td>
<td>C_{10}H_{11}N_{3}S_{2}</td>
<td>Found 50.2</td>
<td>4.4</td>
<td>26.8</td>
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<tr>
<td></td>
<td>Methyl</td>
<td>61</td>
<td>126*</td>
<td>C_{9}H_{9}N_{3}S_{2}</td>
<td>Found 48.1</td>
<td>3.8</td>
<td>28.2</td>
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<td>139*</td>
<td>C_{16}H_{15}N_{3}S_{2}</td>
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<td>135*</td>
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<td>88**</td>
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<td>R'</td>
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<td>M.p. °C</td>
<td>Formula</td>
<td>Analysis</td>
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<td>H%</td>
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1. Crystallised from aqueous ethanol.

* Ref: 187 gives m.p. 145°
* Ref: 187 gives m.p. 127°
* Ref: 186 gives m.p. 141°
* Ref: 186 gives m.p. 118-20°
* Ref: 187 gives m.p. 140-42°
* Ref: 187 gives m.p. 175-77°

** Freund and Kuh, *Ber.*, 1890., 22, 2831 gives m.p. 88°