SECTION IV

SYNTHESIS OF 8-METHYL-3-ARYL-2-MERCAPTO QUINAZOL-4-ONES

The preparation of 3-methylanthranilic acid has been already described in Part I.

I : (a) CONDENSATION OF 3-METHYLANTHRANILIC ACID WITH MONO-PHENYLTHIOUREA : FORMATION OF 8-METHYL-3-PHENYL-2-MERCAPTO-QUINAZOL-4-ONES :

3-Methylanthranilic acid (1.5 g; 0.01 mol) and mono-phenylthiourea (1.5 g; 0.01 mol) were finely ground together and placed in a 100-ml r.b.-flask. The flask was then fitted with a long glass-tube as an air-condenser and heated in an oil-bath at 170-80° for an hour and a half. A brown cake was obtained on cooling. It was extracted twice with warm (40-50° C) aqueous sodium hydroxide solution (5%; 50 ml each time) and filtered. Almost negligible amount of residue that remained was discarded. The filtrate was cooled on adding ice and was acidified with cold dilute (1:1) hydrochloric acid. The white solid obtained was washed with sodium carbonate solution (5%; 25 ml) followed by water to remove unreacted anthranilic acid, if any. It was then crystallised from ethanol, pale yellow prismatic needles, m.p. 196°. Yield : 0.8 g.

Analysis : (a) 0.1186 g. substance gave 0.1022 g. BaSO₄.

Found : S, 11.80 per cent

C₁₅H₁₂O₂N₄S requires S, 11.99 per cent
(b) 0.0924 g. substance on Kjeldahl determination required 14.1 ml of 0.0483 N sulphuric acid.

Found: N, 10.32 per cent

\( \text{C}_{15}\text{H}_{12}\text{ON}_{2}\text{S} \) requires N, 10.45 per cent

(b) **Condensation of 3-Methylantranilic acid with Phenyl isothiocyanate: Formation of 3-Methyl-3-phenyl-2-mercapto-quinazol-4-one**

3-Methylantranilic acid (0.75 g; 0.005 mol) was dissolved in ethanol (30 ml) and a solution of phenyl isothiocyanate (0.7 g; 0.005 mol) in ethanol (10 ml) was added to it in a 250-ml distilling flask whose side-arm was plugged. It was refluxed for an hour in boiling water-bath, and ethanol was distilled off. The brown residue that remained in the flask when treated as in (a) above, gave a solid. It was crystallised from ethanol, pale yellow prismatic needles, m.p. and mixed m.p. with compound obtained in (a) above, 196°. Yield: 0.45 g.

(c) **8-Methyl-3-phenyl-2-thiophenyl-quinazol-4-one**: 8-Methyl-3-(0.5 g) was suspended in dry bromobenzene (10 ml) in a 50-ml r.b.-flask and anhydrous potassium carbonate (0.5 g) and a pinch of copper powder were added to it. The flask was then fitted with a long glass tube as an air-condenser and heated in oil-bath at a temperature 165-70° for a period of five hours. The reaction mixture was then transferred to a 250-ml r.b.-flask and unreacted bromobenzene steam-distilled off. The solid obtained was collected and acrystallised from acetone, colourless long fibrous needles, m.p. 160°.

**Analysis**: 0.1520 g. substance gave 0.1006 g. BaSO₄.

Found: S, 9.07 per cent

\( \text{C}_{27}\text{H}_{16}\text{ON}_{2}\text{S} \) requires S, 9.30 per cent
(d) 8-Methyl-3-phenyl-2-thiobenzoyl-quinazol-4-one : 8-Methyl-3-phenyl-2-mercapto-quinazol-4-one (0.5 g) was dissolved in sodium hydroxide solution (10 %; 30 ml) and benzoyl chloride (0.5 g) was added to it. The reaction mixture was then left at room temperature for about six hours during which occasional shaking was done several times. The product separated was filtered, washed with water and crystallised from acetone, colourless small needles, m.p. 153°.

Analysis:

0.1382 g. substance gave 0.0880 g. BaSO₄.

Found: S, 8.74 per cent

C₂₂H₁₆O₂N₂S requires S, 8.60 per cent

(e) Oxidation of 8-Methyl-3-phenyl-2-mercapto-quinazol-4-one:

Formation of 8-Methyl-3-phenyl-quinazol-2:4-dione:

8-Methyl-3-phenyl-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aq. NaOH (10 %; 50 ml) and hydrogen peroxide (6 vol.; 10 ml) was added to it. The reaction mixture was stirred for two hours at room temperature and filtered. The filtrate (bluish-violet fluorescence) was cooled and acidified with cold dilute hydrochloric acid (1:1). The product separated was filtered and crystallised from acetone-alcohol mixture, light yellow short needles, m.p. 265°. It was found to be identical with an authentic sample synthesized below.

(f) Condensation of 3-Methylanthranilic acid with Mono-phenylurea:

Formation of 8-Methyl-3-phenyl-quinazol-2:4-dione:

3-Methylanthranilic acid (0.75 g) and mono-phenylurea (0.7 g) were ground together and placed in a 100-ml r.b.-flask fitted with a long tube. A brown mass obtained after heating this mixture at 170-80° for 1.5 hours in an oil-bath was treated as in (a) and the white product
obtained was crystallised from acetone-alcohol mixture, light yellow short needles, m.p. and mixed m.p. with the oxidation product obtained in (e) above, 265°.

Analysis: 0.0686 g. substance on Kjeldahl determination required 10.0 ml of 0.0532 g. N sulphuric acid.

Found: N, 10.86 per cent

\[C_{15}H_{12}O_2N_2\] requires N, 11.11 per cent

II: (a) CONDENSATION OF 3-METHYLANTHRANILIC ACID WITH MONO-o-TOLYLTHIOUREA: FORMATION OF 3-METHYL-3-(o-TOLYL)-2-MERCAPTO-QUINAZOL-4-ONE:

3-Methylanthranilic acid (1.5 g) and mono-o-tolylthiourea (1.7 g) were ground together and heated at 170-80° for 1.5 hours, when a brown mass was obtained. The solid obtained on working it up as before was crystallised from ethanol-acetone mixture, pale yellow thick prismatic needles, m.p. 182°. Yield 0.85 g.

Analysis: (a) 0.1160 g. substance gave 0.0990 g. BaSO₄.

Found: S, 11.71 per cent

\[C_{16}H_{14}ON_2S\] requires S, 11.35 per cent

(b) 0.0816 g. substance on Kjeldahl determination required 9.4 ml of 0.0483 N sulphuric acid.

Found: N, 9.77 per cent

\[C_{16}H_{14}ON_2S\] requires N, 9.93 per cent

(b) Condensation of 3-Methylanthranilic acid with o-Tolyl isothiocyanate: Formation of 3-Methyl-3-(o-tolyl)-2-mercapto-quinazol-4-one:

A mixture of 3-methylanthranilic acid (0.75 g) and o-tolyl isothiocyanate (0.75 g) containing ethanol as solvent was refluxed for one hour
and worked up as before. A product thus obtained was crystallised from ethanol-acetone mixture, pale yellow thick prismatic needles, m.p. and mixed m.p. with the product obtained in (a) above, 182°. Yield : 0.45 g.

(c) **8-Methyl-3-(o-tolyl)-2-thiophenyl-quinazol-4-one** : To a solution of 8-methyl-3-(o-tolyl)-2-mercapto-quinazol-4-one (0.5 g) in dry bromobenzene (15 ml) were added anhydrous potassium carbonate (0.5 g) and a pinch of copper powder. It gave a product on treatment as before, which was crystallised from acetone, colourless long fibrous needles, m.p. 173°.

**Analysis** :

<table>
<thead>
<tr>
<th>Substance</th>
<th>BaSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1592 g</td>
<td>0.1070 g</td>
</tr>
</tbody>
</table>

Found : S, 9.22 per cent

\[ C_{22}H_{18}O_{2}N_{2}S \] requires S, 8.94 per cent

(d) **8-Methyl-3-(o-tolyl)-2-thiobenzoyl-quinazol-4-one** : 8-Methyl-3-(o-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aq. NaOH and benzoyl chloride (0.5 g) was added to it. Product obtained on similar treatment as before was crystallised from acetone, colourless short needles, m.p. 147°.

**Analysis** :

<table>
<thead>
<tr>
<th>Substance</th>
<th>BaSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1466 g</td>
<td>0.0896 g</td>
</tr>
</tbody>
</table>

Found : S, 8.38 per cent

\[ C_{23}H_{18}O_{2}N_{2}S \] requires S, 8.29 per cent

(e) **Oxidation of 8-Methyl-3-(o-tolyl)-2-mercapto-quinazol-4-one** :

**Formation of 8-Methyl-3-(o-tolyl)-quinazol-2:4-dione** :

8-Methyl-3-(o-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised with hydrogen peroxide in alkaline medium as before and the solid obtained was crystallised from acetone, light yellow small prismatic needles, m.p. 226°. It was found to be identical with the product synthesized as under.
(f) Condensation of 3-Methylanthranilic acid with Mono-o-tolylurea: Formation of 8-Methyl-3-(o-tolyl)-quinazol-2,4-dione:

A mixture of 3-methylanthranilic acid (0.75 g) and mono-o-tolylurea (0.75 g) was heated at 170-80° for 1.5 hours and the brown mass that obtained was worked up as before. The product was crystallised from acetone, light yellow small prismatic needles, m.p. and the mixed m.p. with the oxidation product obtained in (e) above, 226°. Dokunikhin and Gaeva (J. Gen. Chem. U.S.S.R., 1953, 23, 606; Chem. Abstr., 1954, 48, 7018) who obtained this compound by following different route report m.p. 225-27°.

Analysis: 0.0818 g. substance on Kjeldahl determination required 8.5 ml of 0.0532 N sulphuric acid.

Found: N, 10.40 per cent

C\(_{16}\)H\(_{14}\)O\(_2\)N\(_2\) requires N, 10.53 per cent

III: (a) Condensation of 3-Methylantranilic acid with mono-m-tolylthiourea: Formation of 8-Methyl-3-(m-tolyl)-2-mercapto-quinazol-4-one:

3-Methylantranilic acid (1.5 g) and mono-m-tolylthiourea (1.7 g) were heated together as before and the product obtained on similar treatment was crystallised from acetone, pale yellow small prismatic needles, m.p.167°. Yield: 0.75 g.

Analysis: (a) 0.1258 g. substance gave 0.1024 g. BaSO\(_4\).

Found: S, 11.17 per cent

C\(_{16}\)H\(_{14}\)ON\(_2\)S requires S, 11.35 per cent

(b) 0.0882 g. compound on Kjeldahl determination required 10.2 ml of 0.0483 N sulphuric acid.

Found: N, 9.83 per cent

C\(_{16}\)H\(_{14}\)ON\(_2\)S requires N, 9.93 per cent
(b) Condensation of 3-Methylanthranilic acid with m-Tolyl isothiocyanate: Formation of 8-Methyl-3-(m-tolyl)-2-mercapto-quinazol-4-one:

A mixture of 3-methylanthranilic acid (0.75 g) and m-tolyl isothiocyanate (0.75 g) was refluxed in ethanol and the product obtained as before was crystallised from acetone, pale yellow small prismatic needles, m.p. and mixed m.p. with the product obtained in (a), 167°. Yield: 0.45 g.

(c) 8-Methyl-3-(m-tolyl)-2-thiophenyl-quinazol-4-one: 8-Methyl-3-(m-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was suspended in dry bromobenzene (10 ml) and anhydrous potassium carbonate (0.5 g) and a pinch of copper powder were added to it. The product obtained as before was crystallised from acetone, pale yellow long glistening needles, m.p. 164°.

Analysis: 0.1416 g. substance gave 0.0946 g. \( \text{BaSO}_4 \).

Found: S, 9.15 per cent \( \text{C}_{22}\text{H}_{18}\text{ON}_{2}\text{S} \) requires S, 8.94 per cent

(d) 8-Methyl-3-(m-tolyl)-2-thiobenzoyl-quinazol-4-one: 8-Methyl-3-(m-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aq. NaOH and benzoyl chloride was added to it. The product obtained on treating the mixture as before was crystallised from acetone, dull-white short needles, m.p. 173°.

Analysis: 0.1474 g. substance gave 0.0874 g. \( \text{BaSO}_4 \).

Found: S, 8.13 per cent \( \text{C}_{23}\text{H}_{18}\text{O}_{2}\text{N}_{2}\text{S} \) requires S, 8.29 per cent
(e) Oxidation of 8-Methyl-3-(m-tolyl)-2-mercapto-quinazol-4-one:
Formation of 8-Methyl-3-(m-tolyl)-quinazol-2:4-dione:

8-Methyl-3-(m-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised by alkaline hydrogen peroxide as before. The product obtained was crystallised from acetone, yellowish cubes, m.p. 242°. It was found to be identical with the authentic compound synthesized as under.

(f) Condensation of 3-Methylanthranilic acid with Mono-m-tolylurea:
Formation of 8-Methyl-3-(m-tolyl)-quinazol-2:4-dione:

3-Methylanthranilic acid (0.75 g) was ground with mono-m-tolylurea (0.75 g) and the mixture was treated as before. The solid obtained was crystallised from acetone, yellowish cubes, m.p. and mixed m.p. with the oxidation product obtained in (e) above, 242°.

Analysis: 0.0790 g. substance on Kjeldahl determination required 8.1 ml of 0.0532 N sulphuric acid.

Found: N, 10.25 per cent
C_{16}H_{14}O_{2}N_{2} requires N, 10.53 per cent

IV: (a) Condensation of 3-Methylanthranilic acid with Mono-p-tolylthiourea:
Formation of 8-Methyl-3-(p-tolyl)-2-mercapto-quinazol-4-ones:

3-Methylanthranilic acid (1.5 g) and mono-p-tolylthiourea (1.7 g) were heated together and the product obtained as before was crystallised from ethanol, pale yellow short needles, m.p. 230°. Yield: 0.8 g.

Analysis: (a) 0.0936 g. substance on Kjeldahl determination required 13.4 ml of 0.0483 N sulphuric acid.

Found: N, 9.68 per cent
C_{16}H_{14}O_{2}N_{2}S requires N, 9.93 per cent
(b) 0.1340 g. substance gave 0.1082 g. BaSO₄.

Found : S, 11.08 per cent

\[ \text{C}_{16}\text{H}_{14}\text{O}_{2}\text{N}_{2}\text{S} \text{ requires } S, 11.35 \text{ per cent} \]

(b) Condensation of 3-Methylantranilic acid with p-Tolyl isothiocyanate : Formation of 8-Methyl-3-(p-tolyl)-2-mercaptoquinazol-4-one :

3-Methylantranilic acid (0.75 g) and p-tolyl isothiocyanate (0.75 g) were refluxed together in ethanol as before and the product obtained was crystallised from ethanol, pale yellow short needles, m.p. and mixed m.p. with the product obtained in (a), 230°. Yield : 0.45 g.

(c) 8-Methyl-3-(p-tolyl)-2-thiophenyl-quinazol-4-one : A solution of 8-methyl-3-(p-tolyl)-2-mercapto-quinazol-4-one (0.5 g) in bromobenzene (15 g) was heated with anhydrous potassium carbonate (0.5 g) and a pinch of copper powder. The product obtained as before was crystallised from acetone, dull-white long needles, m.p. 201°.

Analysis : 0.1492 g. compound gave 0.0948 g. BaSO₄.

Found : S, 8.71 per cent

\[ \text{C}_{22}\text{H}_{18}\text{O}_{2}\text{N}_{2}\text{S} \text{ requires } S, 8.94 \text{ per cent} \]

(d) 8-Methyl-3-(p-tolyl)-2-thiobenzoyl-quinazol-4-one : To 8-methyl-3-(p-tolyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g) and the reaction mixture was worked up as before. The product separated was collected and crystallised from acetone, white short needles, m.p. 177°.

Analysis : 0.1394 g. substance gave 0.0804 g. BaSO₄.

Found : S, 7.91 per cent

\[ \text{C}_{23}\text{H}_{18}\text{O}_{2}\text{N}_{2}\text{S} \text{ requires } S, 8.29 \text{ per cent} \]
(e) Oxidation of 8-Methyl-3-(p-tolyl)-2-mercapto-quinazol-4-one:
Formation of 8-Methyl-3-(p-tolyl)-quinazol-2:4-dione:

8-Methyl-3-(p-tolyl)-2-mercapto-quinazol-4-one (0.5 g) gave on oxidation with alkaline hydrogen peroxide as before, which was crystallised from ethanol, pale yellow short prismatic needles, m.p. 286°. It was found to be identical with the product obtained on direct synthesis as under.

(f) Condensation of 3-Methylantranilic acid with Mono-p-tolylurea:
Formation of 8-Methyl-3-(p-tolyl)-quinazol-2:4-dione:

3-Methylantranilic acid (0.75 g) was heated with mono-p-tolylurea (0.75 g) as before. The product obtained was crystallised from ethanol, pale yellow short prismatic needles, m.p. and mixed m.p. with the oxidation product obtained in (e) above, 286°.

Analysis: 0.0864 g. substance on Kjeldahl determination required 8.9 ml of 0.0532 N sulphuric acid.

Found: N, 10.32 per cent
C_{16}H_{14}O_{2}N_{2} requires N, 10.53 per cent

V: (a) Condensation of 3-Methylantranilic acid with Mono-o-anisylthiourea: Formation of 8-Methyl-3-(o-anisyl)-2-mercapto-quinazol-4-one:

3-Methylantranilic acid (1.5 g) and mono-o-anisylthiourea (1.8 g) were heated together at 170-80° for an hour and a half and the product obtained as before was crystallised from acetone, pale yellow short needles, m.p. 220°. Yield: 0.8 g.

Analysis: (a) 0.1290 g. substance gave 0.0998 g. BaSO_{4}.

Found: S, 10.58 per cent
C_{16}H_{14}O_{2}N_{2}S requires S, 10.74 per cent
(b) 0.0796 g. substance on Kjeldahl determination required 10.8 ml of 0.0483 N sulphuric acid.

Found : N, 9.14 per cent
C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>S requires N, 9.40 per cent

(b) Condensation of 3-Methylanthranilic acid with o-Anisyl isothiocyanate : Formation of 8-Methyl-3-(o-anisyl)-2-mercapto-quinazol-4-one :

A mixture of 3-methylanthranilic acid (0.75 g) and o-anisyl isothiocyanate (0.8 g) was refluxed in ethanol for an hour. The product obtained as before was crystallised from acetone, m.p. and mixed m.p. with the product synthesized as in (a) above, 220°. Yield 0.45 g.

(c) 8-Methyl-3-(o-anisyl)-2-thiophenyl-quinazol-4-one : A solution of 8-methyl-3-(o-anisyl)-2-mercapto-quinazol-4-one (0.5 g) in bromobenzene (15 ml) was heated in presence of anhydrous potassium carbonate (0.5 g) and a pinch of copper powder as before. The product obtained was crystallised from acetone, dull-white long needles, m.p. 207°.

Analysis : 0.1390 g. substance gave 0.0882 g. BaSO<sub>4</sub>.

Found : S, 8.70 per cent
C<sub>22</sub>H<sub>18</sub>O<sub>2</sub>N<sub>2</sub>S requires S, 8.55 per cent

(d) 8-Methyl-3-(o-anisyl)-2-thiobenzoyl-quinazol-4-one : To 8-methyl-3-(o-anisyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g) and the product obtained as before was crystallised from acetone, dull-white short needles, m.p. 168°.

Analysis : 0.1512 g. substance gave 0.0912 g. BaSO<sub>4</sub>.

Found : S, 8.28 per cent
C<sub>23</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub>S requires S, 7.96 per cent
(e) Oxidation of 8-Methyl-3-(o-anisyl)-2-mercapto-quinazol-4-one:
   Formation of 8-Methyl-3-(o-anisyl)-quinazol-2:4-dione:

8-Methyl-3-(o-anisyl)-2-mercapto-quinazol-4-one (0.5 g) was
oxidised with hydrogen peroxide in alkaline medium as before. The
product obtained was crystallised from ethanol, pale yellow short
prismatic needles, m.p. 263°. It was found to be identical with the
authentic sample synthesized as under.

(f) Condensation of 5-Methylanthranilic acid with Mono-o-anisyl-
urea: Formation of 8-Methyl-3-(o-anisyl)-quinazol-2:4-dione:

3-Methylanthranilic acid (0.75 g) was heated with mono-o-anisyl-
urea (0.8 g) and the product obtained on similar treatment as before
was crystallised from ethanol, pale yellow short prismatic needles,
m.p. 261-62°. Mixed m.p. with the oxidation product obtained in (e)
above remains undepressed.

Analysis: 0.0914 g. substance on Kjeldahl determination required
12.0 ml of 0.0532 N sulphuric acid.

   Found: N, 9.78 per cent
   C_{16}H_{14}O_{3}N_{2} requires N, 9.93 per cent

VI: (a) CONDENSATION OF 3-METHYLANTHRANILIC ACID WITH MONO-
p-ANISYLTHIOUREA: FORMATION OF 8-METHYL-3-(p-ANISYL)-
2-MERCAPTO-QUINAZOL-4-ONES:

A mixture of 3-methylanthranilic acid (1.5 g) and mono-p-anisyl-
thiourea (1.8 g) were heated as before. The product obtained was
crystallised from ethanol, pale yellow small prismatic needles, m.p.
238°. Yield 0.85 g.
Analysis: (a) 0.1368 g. substance gave 0.1046 g. BaSO$_4$.

Found: S, 10.35 per cent  

$C_{16}H_{14}O_2N_2S$ requires S, 10.74 per cent

(b) 0.0718 g. compound on Kjeldahl determination required 9.8 ml of 0.0483 N sulphuric acid.

Found: N, 9.23 per cent  

$C_{16}H_{14}O_2N_2S$ requires N, 9.40 per cent

(b) Condensation of 3-Methylantranilic acid with p-Anisyl isothiocyanate: Formation of 8-Methyl-3-(p-anisyl)-2-mercapto-quinazol-4-one:

To the solution of 3-methylantranilic acid (0.75 g) in ethanol (30 ml) was added an ethanolic solution of p-anisyl isothiocyanate (0.8 g in 10 ml ethanol) and the mixture was refluxed for an hour. The product obtained as before was crystallised from ethanol, pale yellow small prismatic needles, m.p. and mixed m.p. with the product obtained in (e) above, 238°. Yield: 0.45 g.

(c) 8-Methyl-3-(p-anisyl)-2-thiophenyl-quinazol-4-one: To the solution of 8-methyl-3-(p-anisyl)-2-mercapto-quinazol-4-one (0.5 g) in dry bromobenzene (15 ml) was added anhydrous potassium carbonate as well as a little copper powder and the mixture was treated as before. The product obtained was crystallised from acetone, light yellow short needles, m.p. 214°.

Analysis: 0.1306 g. substance gave 0.0840 g. BaSO$_4$.

Found: S, 8.81 per cent  

$C_{22}H_{18}O_2N_2S$ requires S, 8.55 per cent

(d) 8-Methyl-3-(p-anisyl)-2-thiobenzoyl-quinazol-4-one: 8-Methyl-3-(p-anisyl)-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aq. NaOH
and benzoyl chloride (0.5 g) was added to it. The product obtained on working it up as before was crystallised from acetone, white short needles, m.p. 181°.

**Analysis:**
0.1318 g. substance gave 0.0790 g. BaSO₄.

Found: S, 8.09 per cent

C₂₃H₁₈O₃N₂S requires S, 7.96 per cent

(e) Oxidation of 8-Methyl-3-(p-anisyl)-2-mercapto-quinazol-4-one:

**Formation of 8-Methyl-3-(p-anisyl)-quinazol-2,4-dione:**

8-Methyl-3-(p-anisyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised by alkaline hydrogen peroxide and the product obtained as before was crystallised from ethanol, light yellow short needles, m.p. 253°. It was found to be identical with the authentic sample synthesized as under.

(f) Condensation of 3-Methylantranilic acid with Mono-p-anisyl-urea:

**Formation of 8-Methyl-3-(p-anisyl)-quinazol-2,4-dione:**

3-Methylantranilic acid (0.75 g) was treated with mono-p-anisyl-urea (0.8 g) as before and the product obtained was crystallised from ethanol, yellowish short needles, m.p. and mixed m.p. with the oxidation product obtained in (e) above, 253°.

**Analysis:**
0.0784 g. substance on Kjeldahl determination required 10.2 ml of 0.0532 N sulphuric acid.

Found: N, 9.69 per cent

C₁₆H₁₄O₃N₂ requires N, 9.93 per cent

VII: (a) **CONDENSATION OF 3-METHYLANTRANILIC ACID WITH MONO-o-CHLOROPHENYLTHIOUREA:**

**FORMATION OF 8-METHYL-3-2-MERCAPTO-QUINAZOL-4-ONES:**
3-Methylantranilic acid (1.5 g) and mono-o-chlorophenylthiourea (1.9 g) were heated together and the product obtained as before was crystallised from ethanol, pale yellow small prismatic needles, m.p. 201-02°. Yield : 0.75 g.

Analysis : (a) 0.1330 g. substance gave 0.1002 g. BaSO₄.

Found : S, 10.31 per cent
\( \text{C}_{15}\text{H}_{11}\text{ON}_{2}\text{SCl} \) requires S, 10.58 per cent

(b) 0.0678 g. substance on Kjeldahl determination required 9.1 ml of 0.0483 N sulphuric acid.

Found : N, 9.04 per cent
\( \text{C}_{15}\text{H}_{11}\text{ON}_{2}\text{SCl} \) requires N, 9.26 per cent

(b) Condensation of 3-Methylantranilic acid with o-Chlorophenyl isothiocyanate : Formation of 8-Methyl-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one :

3-Methylantranilic acid (0.75 g) and o-chlorophenyl isothiocyanate (0.85 g) were refluxed in ethanol for one hour and the product obtained on working up the reaction mixture as before was crystallised from pale yellow small prismatic needles, ethanol, m.p. 202. Mixed m.p. with the product obtained in (a) remains undepressed. Yield : 0.4 g.

(c) 8-Methyl-3-(o-chlorophenyl)-2-thiophenyl-quinazol-4-one : A solution of 8-methyl-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) in dry bromobenzene (10 ml) was heated with anhydrous potassium carbonate (0.5 g) and a little copper powder. The product obtained as before was crystallised from acetone, pale yellow thick plates, m.p. 138°.

Analysis : 0.1372 g. substance gave 0.0868 g. BaSO₄.

Found : S, 8.67 per cent
\( \text{C}_{21}\text{H}_{15}\text{ON}_{2}\text{SCl} \) requires S, 8.45 per cent
(d) 8-Methyl-3-(o-chlorophenyl)-2-thiobenzoyl-quinazol-4-one: To 8-methyl-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g) with vigorous shaking. The product obtained as before was crystallised from acetone, white short needles, m.p. 143°.

Analysis: 0.1306 g. substance gave 0.0772 g. BaSO₄.

Found: S, 8.11 per cent

C₂₂H₁₅O₂N₂SCl requires S, 7.87 per cent

(e) Oxidation of 8-Methyl-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one:

Formation of 8-Methyl-3-(o-chlorophenyl)-quinazol-2:4-dione:

8-Methyl-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) gave on oxidation with alkaline hydrogen peroxide a product as before, which was crystallised from ethanol, pale yellow small prismatic needles, m.p. 247°. It was found to be identical with the product prepared by direct synthesis as under.

(f) Condensation of 3-Methylanthranilic acid with Mono-o-chlorophenylurea:

Formation of 8-Methyl-3-(o-chlorophenyl)-quinazol-2:4-dione:

3-Methylanthranilic acid (0.75 g) and mono-o-chlorophenylurea (0.85 g) were heated together as before and the product obtained by similar treatment was crystallised from ethanol, pale yellow small prismatic needles, m.p. and mixed m.p. with the oxidation product obtained in (e), 247°.

Analysis: (a) 0.0818 g. compound gave 0.0404 g. AgCl.

Found: Cl, 12.22 per cent

C₁₅H₁₁O₂N₂Cl requires Cl, 12.39 per cent
(b) 0.0860 g. substance on Kjeldahl determination required 11.0 ml of 0.0532 N sulphuric acid.

Found : N, 9.51 per cent

\[ C_{15}H_{11}ON_2Cl \] requires N, 9.77 per cent

VIII : (a) **CONDENSATION OF 3-METHYLANTHRANILIC ACID WITH MONO-
(m-CHLOROPHENYLTHIOUREA) : FORMATION OF 8-METHYL-3-
(m-CHLOROPHENYL)-2-MERCAPTO-QUINAZOL-4-ONE :**

3-Methylantranilic acid (1.5 g) was heated with mono-m-chloro-
phenylthiourea (1.9 g) as before. The product obtained was crystallised
from ethanol, light yellow grains, m.p. 218°. Yield : 0.7 g.

**Analysis** : (a) 0.1422 g. substance gave 0.1082 g. \( \text{BaSO}_4 \).

Found : S, 10.46 per cent

\[ C_{15}H_{11}ON_2SCL \] requires S, 10.58 per cent

(b) 0.0832 g. substance on Kjeldahl determination required 12.01 ml of 0.0483 N sulphuric acid.

Found : N, 9.00 per cent

\[ C_{15}H_{11}ON_2SCL \] requires N, 9.26 per cent

(b) **Condensation of 3-Methylantranilic acid with m-Chlorophenyl
isothiocyanate : Formation of 8-Methyl-3-(m-chlorophenyl)-
2-mercapto-quinazol-4-one :**

3-Methylantranilic acid (0.75 g) and m-chlorophenyl isothiocyanate
(0.85 g) when refluxed together in ethanol as before gave a product
which was crystallised from ethanol, m.p. and mixed m.p. with the
compound obtained in (a) above, 218°. Yield : 0.4 g.

(c) **8-Methyl-3-(m-chlorophenyl)-2-thiophenyl-quinazol-4-one :** A
solution of 8-methyl-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one
(0.5 g) in dry bromobenzene (15 ml) was heated with anhydrous potassium
carbonate (0.5 g) and a little amount of copper powder. The product
obtained on treatment as before was crystallised from acetone, light
yellow shining needles, m.p. 170°.

**Analysis** : 0.1580 g. substance gave 0.0990 g. \( \text{BaSO}_4 \).
(d) 8-Methyl-3-(m-chlorophenyl)-2-thiobenzoyl-quinazol-4-one: To 8-Methyl-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g) and the product obtained as before was crystallised from acetone, white short needles, m.p. 172°.

Analysis: 0.1424 g. substance gave 0.0852 g. BaSO₄.

Found: S, 8.20 per cent
C₂₂H₁₅O₂N₂SCl requires S, 7.87 per cent

(e) Oxidation of 8-Methyl-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one: Formation of 8-Methyl-3-(m-chlorophenyl)-quinazol-2:4-dione:

8-methyl-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised using hydrogen peroxide in alkaline medium as before and the product thus obtained was crystallised from ethanol, dull-white small needles, m.p. 284°. It was found to be identical with the product directly synthesized by following a different route as under.

(f) Condensation of 3-Methylanthranilic acid with Mono-m-chlorophenylurea: Formation of 8-Methyl-3-(m-chlorophenyl)-quinazol-2:4-dione:

A mixture of 3-methylanthranilic acid (0.75 g) and mono-m-chlorophenylurea (0.85 g) on treatment as before gave a product which was crystallised from ethanol, dull-white small needles, m.p. and mixed m.p. with the oxidation product obtained in (e) above, 284°.

Analysis: (a) 0.0802 g. substance on Kjeldahl determination required 10.4 ml of 0.0532 N sulphuric acid.

Found: N, 9.66 per cent
C₁₅H₁₁O₂N₂Cl requires N, 9.77 per cent
(b) 0.1182 g. substance gave 0.0598 g. AgCl.

Found : Cl, 12.51 per cent

\[ C_{15}H_{11}O_2N_2Cl \text{ requires } \text{Cl, 12.39 per cent} \]

IX : (a) **CONDENSATION OF 3-METHYLANTHRANILIC ACID WITH MONO-**

**p-CHLOROPHENYLTHIOUREA : FORMATION OF 8-METHYL-3-**

(p-CHLOROPHENYL)-2-MERCAPTO-QUINAZOL-4-ONE **:**

3-Methylantranilic acid (1.5 g) and mono-p-chlorophenylthiourea (1.9 g) were treated as before and the product obtained was crystallised from acetone, light yellow glistening long needles, m.p. 246°. Yield : 0.8 g.

**Analysis :** (a) 0.1410 g. substance gave 0.1066 g. BaSO₄.

Found : S, 10.37 per cent

\[ C_{15}H_{11}ON_2SCl \text{ requires } S, 10.58 \text{ per cent} \]

(b) 0.0832 g. substance on Kjeldahl determination required 13.3 ml of 0.0483 N sulphuric acid.

Found : N, 9.18 per cent

\[ C_{15}H_{11}ON_2SCl \text{ requires } N, 9.26 \text{ per cent} \]

(b) **Condensation of 3-Methylantranilic acid with p-Chlorophenyl isothiocyanate : Formation of 8-Methyl-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one :**

3-Methylantranilic acid (0.75 g) and p-chlorophenyl isothiocyanate (0.85 g) when refluxed in ethanol as before gave a product which was crystallised from ethanol, light yellow glistening long needles, m.p. and mixed m.p. with the product obtained in (a) above, 246°. Yield : 0.4 g.

(c) 8-Methyl-3-(p-chlorophenyl)-2-thiophenyl-quinazol-4-one ;
8-Methyl-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was suspended in dry bromobenzene (10 ml) and anhydrous potassium carbonate and a little copper powder were added to it. The product obtained on treatment as before was crystallised from acetone, white long shining needles, m.p. 222°.

Analysis: 0.1518 g. compound gave 0.0920 g. BaSO$_4$.

Found : S, 8.31 per cent

C$_{21}$H$_{15}$O$_2$N$_2$SCl requires S, 8.45 per cent

(d) 8-Methyl-3-(p-chlorophenyl)-2-thiobenzoyl-quinazol-4-one: To 8-methyl-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH (10%; 30 ml) was added benzoyl chloride (0.5 g). The product obtained on working it up as before was crystallised from acetone, white short needles, m.p. 183°.

Analysis: 0.1492 g. substance gave 0.0838 g. BaSO$_4$.

Found : S, 7.71 per cent

C$_{22}$H$_{15}$O$_2$N$_2$SCl requires S, 7.87 per cent

(e) Oxidation of 8-Methyl-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one: Formation of 8-Methyl-3-(p-chlorophenyl)-quinazol-2:4-dione:

8-Methyl-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised with hydrogen peroxide in alkaline medium as before. The product obtained was crystallised from ethanol, light yellow long needles, m.p. 296°. It was found to be identical on comparison with an authentic sample achieved by direct synthesis by following different route as described below.

(f) Condensation of 3-Methylanthranilic acid with Mono-p-chlorophenylurea : Formation of 8-Methyl-3-(p-chlorophenyl)-quinazol-2:4-dione:
3-Methylanthrаниlic acid (0.75 g) when heated with mono-p-chlorophenylurea (0.8 g) as before gave a product which on crystallisation from ethanol gave light yellow long needles, m.p. and mixed m.p. with the product obtained on oxidation of 8-methyl-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one by alkaline hydrogen peroxide as referred to above, 296°.

**Analysis**: (a) 0.0772 g. compound on Kjeldahl determination required 9.9 ml of 0.0532 N sulphuric acid.

  Found: N, 9.54 per cent
  \( \text{C}_{15}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl} \text{ requires N, 9.77 per cent} \)

(b) 0.0890 g. substance gave 0.0448 g. AgCl.

  Found: Cl, 12.46 per cent
  \( \text{C}_{15}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl} \text{ requires Cl, 12.39 per cent} \)