SECTION II

SYNTHESIS OF 7-CHLORO-3-ARYL-2-MERCAPTO-
QUINAZOL-4-ONES

4-Chloroanthranilic acid required for this work was prepared by the following sequence of reactions.

(i) 4-Chloro-2-acetamino toluene : A mixture of 4-chloro-o-toluidine (42.6 g) and acetic anhydride (33.6 g) was heated in a 250-ml round bottomed flask on water-bath for two hours. The pinkish product that separated on pouring the reaction mixture on crushed ice was collected and crystallised from dilute alcohol, colourless needles, m.p. 130-31°. (Bamberger, Annalen, 1925, 441, 303; Raiford, Am. Chem. Journal, 1911, 46, 453). Yield : 30 g.

(ii) 4-Chloro-N-acetylanthranilic acid : A mixture of 4-chloro-2-acetamino toluene (37 g), magnesium sulphate (20 g) and a solution of potassium permanganate (65 g) in water (1.3 litre) was heated in a 2-litre r.b.-flask equipped with mechanical stirrer and placed in a water-bath till the colour of the permanganate disappeared. It was then filtered hot and the filtrate was concentrated and finally acidified with hydrochloric acid. The white product that separated was collected and crystallised from boiling water, white small needles, m.p. 214°. (Cohen, Monatsh, 1901, 22, 485; Heller and Hessel, J. prak.t. Chem., 1929, 120(ii), 71). Yield : 19 g.

(iii) 4-Chloroanthranilic acid : 4-Chloro-N-acetylanthranilic acid (10 g) and hydrochloric acid (1:1; 100 ml) were heated together
on wire-gauze for about three hours. The brown reaction mixture was cooled and made just alkaline with sodium hydroxide (10%). On just acidification with acetic acid, it gave light pinkish solid. It was filtered and crystallised from dilute ethanol, light yellow needles, m.p.236°. Yield : 5 g. (Cohen, loc.cit.; Hunn, J. Am. Chem. Soc., 1923, 45, 1027).

I. (a) CONDENSATION OF 4-CHLOROANTHRANILIC ACID WITH MONO-PHENYLTHIOUREA : FORMATION OF 7-CHLORO-3-PHENYL-2-MERCAPTO-QUINAZOL-4-ONE :

An intimate mixture of 4-chloroanthranilic acid (1.7 g; 0.01 mol) and mono-phenylthiourea (1.5 g; 0.01 mol) was placed in a 100-ml round bottomed flask. The flask was then fitted with a long glass tube to serve as an air-condenser and heated at a temperature of 180-90° in an oil-bath for two hours. A brown mass obtained on cooling the reaction mixture was extracted twice with warm (about 40-50° C) sodium hydroxide solution (5% ; 50 ml each time) and filtered. The residue was almost negligible. The filtrate was cooled by adding ice and carefully acidified with cold dilute hydrochloric acid (1:1). The white product that separated was filtered, washed with sodium carbonate solution (5%; 25 ml) and water (25 ml) to remove unreacted anthranilic acid, if any. It was then crystallised from ethanol-acetone mixture, white short needles, m.p.328-30°. Yield : 0.8 g.

Analysis : (a) 0.1180 g. substance gave 0.0940 g. BaSO₄.

Found : S, 10.92 per cent

C₁₄H₉NO₂SCl requires S, 11.09 per cent

(b) 0.0802 g. substance on Kjeldahl determination required 12.00 ml of 0.04612 N sulphuric acid.
Found: N, 9.67 per cent  
\( C_{14}H_{10}N_{2}SCl \) requires N, 9.93 per cent

(b) Condensation of 4-Chloroanthranilic acid with Phenyl isothiocyanate: Formation of 7-Chloro-3-phenyl-2-mercapto-quinazol-4-one:

4-Chloroanthranilic acid (0.85 g; 0.005 mol) was dissolved in ethanol (30 ml) and an ethanolic solution of phenyl isothiocyanate (0.7 g; 0.005 mol in 10 ml ethanol) was added to it. The reaction mixture was refluxed for one hour and then alcohol was distilled off. The brown solid that remained was extracted as above and filtered. The white solid obtained on acidification of the filtrate was treated with sodium carbonate solution (5%, 25 ml) and then washed with water to remove unreacted anthranilic acid, if any. It was crystallised from ethanol-acetone mixture, white short needles, m.p. 329-30°. Mixed m.p. with the product obtained in (a) remains undepressed. Yield: 0.35 g.

(c) 7-Chloro-3-phenyl-2-thiophenyl-quinazol-4-one: 7-Chloro-3-phenyl-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 finely divided copper powder were added. It was then kept at a temperature of 165-70° for five hours and unreacted bromobenzene removed by steam distillation. The solid obtained was filtered and crystallised from acetone, white long needles, m.p. 218°.

Analysis: 0.1472 g. substance gave 0.0954 g. BaSO₄.

Found: S, 8.89 per cent  
\( C_{20}H_{13}ON_{2}SCl \) requires S, 8.78 per cent
(d) **7-Chloro-3-phenyl-2-thiobenzoyl-quinazol-4-one**: 7-Chloro-3-phenyl-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aqueous sodium hydroxide (10%, 30 ml) and benzoyl chloride (0.5 g) added to it with vigorous shaking. The reaction mixture was then kept at room temperature for six hours with occasional shaking during the period. The solid that separated was washed with water, filtered and crystallised from acetone, white small needles, m.p. 187°.

**Analysis**: 0.1502 g. substance gave 0.0856 g. BaSO₄.

Found: S, 7.80 per cent

C₂₁H₁₃O₂N₂SCl requires S, 8.15 per cent

(e) **Oxidation of 7-Chloro-3-phenyl-2-mercapto-quinazol-4-one**:

**Formation of 7-Chloro-3-phenyl-quinazol-2:4-dione**:

7-Chloro-3-phenyl-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aqueous sodium hydroxide (10%; 50 ml) and hydrogen peroxide (6 vol.; 10 ml) was added to it. This solution was stirred at room temperature (30° C) for two hours and filtered. The filtrate (bluish violet fluorescence) was cooled and acidified with cold dilute (1:1) hydrochloric acid when a solid separated. It was crystallised from ethanol, white short needles, m.p. 300°. It was found to be identical with an authentic sample synthesized as described below.

(f) **Condensation of 4-Chloroanthranilic acid with Monophenylurea**:

**Formation of 7-Chloro-3-phenyl-quinazol-2:4-dione**:

A mixture of 4-chloroanthranilic acid (0.85 g) and mono-phenylurea (0.7 g) was heated in a 100-ml r.b.-flask fitted with a long tube as air-condenser and heated at 180-90° for two hours. A brown mass that obtained was extracted with aqueous sodium hydroxide (5%; 100 ml) as
before. The product obtained on acidification of the alkaline extract was collected and crystallised from ethanol, white short needles, m.p. 299-300°. Mixed m.p. with the oxidation product obtained in (e) remains undepressed.

Analysis : (a) 0.0660 g. substance on Kjeldahl determination required 11.4 ml of 0.0418 N sulphuric acid.

    Found : N, 10.11 per cent

    C₁₄H₉O₂N₂Cl requires N, 10.28 per cent

(b) 0.1942 g. substance gave 0.0994 g. AgCl.

    Found : Cl, 12.67 per cent

    C₁₄H₉O₂N₂Cl requires Cl, 13.03 per cent

II : (a) **CONDENSATION OF 4-CHLOROANTHRANILIC ACID WITH MONO-o-TOLYLTHIOUREA : FORMATION OF 7-CHLORO-3-(o-TOLYL)-2-MERCAPTO-QUINAZOL-4-ONE** :

4-Chloroanthranilic acid (1.7 g) and mono-o-tolylthiourea (1.7 g) were ground together and heated at 180-90° for two hours. A brown mass obtained on cooling gave white solid on treatment as before. It was crystallised from ethanol, white short needles, m.p. 304°. Yield : 0.75 g.

Analysis : (a) 0.1348 g. substance gave 0.1024 g. BaSO₄.

    Found : S, 10.41 per cent

    C₁₅H₁₁O₂N₂SCl requires S, 10.58 per cent

(b) 0.0618 g. substance on Kjeldahl determination required 8.9 ml of 0.04612 N sulphuric acid.

    Found : N, 9.30 per cent

    C₁₅H₁₁O₂N₂SCl requires N, 9.38 per cent

(b) **Condensation of 4-Chloroanthranilic acid with o-Tolyl isothiocyanate : Formation of 7-Chloro-3-(o-tolyl)-2-mercapto-quinazol-4-one** :
4-Chloroanthranilic acid (0.85 g) was dissolved in ethanol (30 ml) and an ethanolic solution of o-tolyl isothiocyanate (0.75 g in 10 ml) was added to it. The reaction mixture, on working up as before, gave a white product. It was crystallised from ethanol, white short needles, m.p. and mixed m.p. with the product obtained in (a) is 304°. Yield : 0.4 g.

(c) 7-Chloro-3-(o-tolyl)-2-thiophenyl-quinazol-4-one : To a solution of 7-chloro-3-(o-tolyl)-2-mercapto-quinazol-4-one (0.5 g) in bromobenzene (15 ml) was added anhydrous potassium carbonate (0.5 g) and a pinch of copper powder. The product obtained on treatment as before was crystallised from acetone, dull-white thick needles, m.p.188°.

Analysis : 0.1394 g. substance gave 0.0844 g. BaSO_4.
Found : S, 8.29 per cent

C_{21}H_{15}^\text{ON}_2^\text{S}Cl requires S, 8.45 per cent

(d) 7-Chloro-3-(o-tolyl)-2-thiobenzoyl-quinazol-4-one : 7-Chloro-3-(o-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aq. NaOH (10 %; 30 ml) and benzoyl chloride (0.5 g) was added to it. Solid obtained on keeping the reaction mixture as before was collected and crystallised from acetone, white small needles, m.p.152°.

Analysis : 0.1320 g. substance gave 0.0730 g. BaSO_4.
Found : S, 7.58 per cent

C_{22}H_{15}^\text{ON}_2^\text{S}Cl requires S, 7.87 per cent

(e) Oxidation of 7-Chloro-3-(o-tolyl)-2-mercapto-quinazol-4-one : Formation of 7-Chloro-3-(o-tolyl)-quinazol-2,4-dione :

7-Chloro-3-(o-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised with hydrogen peroxide (6 vol.; 10 ml) in alkaline medium as before. The product obtained was crystallised from ethanol, white grains, m.p.
296°. It was identical with an authentic product prepared as under.

(f) Condensation of 4-Chloroanthranilic acid with Mono-o-tolylurea: Formation of 7-Chloro-3-(o-tolyl)-quinazol-2:4-dione:

4-Chloroanthranilic acid (0.85 g) and mono-o-tolyl-urea (0.75 g) were heated together at 180-90° for two hours, when a brown mass was obtained. It was worked up as before and the white solid obtained was crystallised from ethanol; white grannules, m.p. and mixed m.p. with the oxidation product obtained in (e), 296°.

Analysis: (a) 0.0822 g. substance on Kjeldahl determination required 13.5 ml of 0.0418 N sulphuric acid.

- Found: N, 9.61 per cent
  \[\text{C}_{15}\text{H}_{11}\text{O}_{2}\text{N}_{2}\text{Cl} \text{ requires } N, 9.77 \text{ per cent}\]

(b) 0.1820 g. substance gave 0.0878 g. AgCl.

- Found: Cl, 11.93 per cent
  \[\text{C}_{15}\text{H}_{11}\text{O}_{2}\text{N}_{2}\text{Cl} \text{ requires } \text{Cl}, 12.39 \text{ per cent}\]

III: (a) Condensation of 4-Chloroanthranilic Acid with Mono-m-Tolylthiourea: Formation of 7-Chloro-3-(m-tolyl)-2-mercaptquinazol-4-one:

4-Chloroanthranilic acid (1.7 g) and mono-m-tolylthiourea (1.7 g) were heated together at 180-90° for two hours and the reaction mixture was worked up as before. The solid obtained was crystallised from ethanol, white grains, m.p. 238-39°. Yield 0.7 g.

Analysis: (a) 0.1410 g. substance gave 0.1062 g. BaSO₄.

- Found: S, 10.33 per cent
  \[\text{C}_{15}\text{H}_{11}\text{ON}_{2}\text{S} \text{ requires } \text{S}, 10.58 \text{ per cent}\]

(b) 0.0730 g. substance on Kjeldahl determination required 10.3 ml of 0.04612 N sulphuric acid.

- Found: N, 9.11 per cent
  \[\text{C}_{15}\text{H}_{11}\text{ON}_{2}\text{S} \text{ requires } N, 9.38 \text{ per cent}\]
(b) Condensation of 4-Chloroanthranilic acid with m-Tolyl isothiocyanate: Formation of 7-Chloro-3-(m-tolyl)-2-mercaptoquinazol-4-one:

4-Chloroanthranilic acid (0.85 g) and m-tolyl isothiocyanate (0.75 g) when refluxed in ethanol as before gave a white solid. It was crystallised from ethanol, white grains, m.p. and mixed m.p. with the product obtained in (a), 238-39°. Yield: 0.4 g.

(c) 7-Chloro-3-(m-tolyl)-2-thiophenyl-quinazol-4-one: To the solution of 7-chloro-3-(m-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 and the reaction mixture was treated as before. The product obtained was crystallised from acetone, white short needles, m.p. 196°.

Analysis: 0.1580 g. substance gave 0.0944 g. BaSO₄.

Found: S, 8.20 per cent
C₂₁H₁₅ON₂SCl requires S, 8.45 per cent

(d) 7-Chloro-3-(m-tolyl)-2-thiobenzoyl-quinazol-4-one: To the solution of 7-chloro-3-(m-tolyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g) and the solid obtained as before was crystallised from acetone, white short needles, m.p. 167°.

Analysis: 0.1480 g. substance gave 0.0844 g. BaSO₄.

Found: S, 7.82 per cent
C₂₂H₁₅O₂N₂SCl requires S, 7.87 per cent

(e) Oxidation of 7-Chloro-3-(m-tolyl)-2-mercapto-quinazol-4-one: Formation of 7-Chloro-3-(m-tolyl)-quinazol-2:4-dione:
7-Chloro-3-(m-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised by means of hydrogen peroxide in alkaline medium as before. The solid that obtained on acidification was crystallised from acetone, white grains, m.p. 288°. It was found to be identical with the product synthesized as under.

(f) Condensation of 4-Chloroanthranilic acid with Mono-m-tolyl-urea : Formation of 7-Chloro-3-(m-tolyl)-quinazol-2:4-dione :

4-Chloroanthranilic acid (0.85 g) and mono-m-tolylurea (0.75 g) were heated together at 180-90° for two hours, and the reaction mixture was worked up as before. White solid obtained was crystallised from acetone, white granules, m.p. 287°. Mixed m.p. with the product obtained by oxidation in (e) remains undepressed.

Analysis : (a) 0.0706 g. substance on Kjeldahl determination required 11.6 ml of 0.0418 N sulphuric acid.

\[ \text{Found : } N, \ 9.62 \text{ per cent} \]
\[ C_{15}H_{11}O_{2}N_{2}Cl \text{ requires } N, \ 9.77 \text{ per cent} \]

(b) 0.1902 g. substance gave 0.0936 g. AgCl.

\[ \text{Found : } Cl, \ 12.18 \text{ per cent} \]
\[ C_{15}H_{11}O_{2}N_{2}Cl \text{ requires } Cl, \ 12.39 \text{ per cent} \]

IV : (a) CONDENSATION OF 4-CHLOROANTHRANILIC ACID WITH MONO-p-TOLYLTHIOUREA : FORMATION OF 7-CHLORO-3-(p-TOLYL)-2-MERCAPTO-QUINAZOL-4-ONE :

4-Chloroanthranilic acid (1.7 g) and mono-p-tolylthiourea (1.7 g) were heated together at 180-90° for two hours. The reaction mixture, on working up as before, gave a solid which on crystallisation from acetone gave white grains, m.p. 322°. Yield 0.7 g.
Analysis: (a) 0.1432 g. substance gave 0.1086 g. BaSO₄.  
Found: S, 10.42 per cent  
C₁₅H₁₁O₂N₂SCl requires S, 10.58 per cent  
(b) 0.0712 g. substance on Kjeldahl determination required 10.2 ml of 0.04612 N sulphuric acid.  
Found: N, 9.24 per cent  
C₁₅H₁₁O₂N₂SCl requires N, 9.38 per cent  

(b) Condensation of 4-Chloroanthranilic acid with p-Tolyl isothiocyanate: Formation of 7-Chloro-3-(p-tolyl)-2-mercaptoquinazol-4-one:

4-Chloroanthranilic acid (0.85 g) and p-tolyl isothiocyanate (0.75 g) when refluxed together in ethanol as before gave a product which was crystallised from acetone, m.p. 323°. Mixed m.p. with the product obtained in (a) remains undepressed. Yield: 0.4 g.

(c) 7-Chloro-3-(p-tolyl)-2-thiophenyl-quinazol-4-one: 7-Chloro-3-(p-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was suspended in trumo- benzene (10 ml) and anhydrous potassium carbonate (0.5 g) and a pinch of copper powder were added to it. The product obtained on working up the reaction mixture as before was crystallised from acetone, white short needles, m.p. 204°.

Analysis: 0.1542 g. substance gave 0.0934 g. BaSO₄.  
Found: S, 8.30 per cent  
C₂₁H₁₅O₂N₂SCl requires S, 8.45 per cent  

(d) 7-Chloro-3-(p-tolyl)-2-thiobenzoyl-quinazol-4-one: To 7-Chloro-3-(p-tolyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g). The solid separated on working it up as before was crystallised from acetone, white short needles, m.p. 193°.
Analysis : 0.1478 g. substance gave 0.0834 g. BaSO₄.
Found : S, 7.70 per cent
C₂₂H₁₅O₂N₂SCl requires S, 7.87 per cent

(e) Oxidation of 7-Chloro-3-(p-tolyl)-2-mercapto-quinazol-4-one :
Formation of 7-Chloro-3-(p-tolyl)-quinazol-2:4-dione :

7-Chloro-3-(p-tolyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised with hydrogen peroxide in alkaline medium and the solid thus obtained was crystallised from ethanol, white short needles, m.p. 302°. It was found to be identical with an authentic sample synthesized as under.

(f) Condensation of 4-Chloroanthranilic acid with Mono-p-tolyl-
urea : Formation of 7-Chloro-3-(p-tolyl)-quinazol-2:4-dione :

4-Chloroanthranilic acid (0.85 g) was heated with mono-p-tolylurea (0.75 g) at 180-90° for two hours. The product obtained as before was crystallised from ethanol, white short needles, m.p. 302-303°. Mixed m.p. with the oxidation product obtained in (e) above remains undepressed.

Analysis : (a) 0.0730 g. substance on Kjeldahl determination required 12.0 ml of 0.0418 N sulphuric acid.
Found : N, 9.62 per cent
C₁₅H₁₁O₂N₂Cl requires N, 9.77 per cent
(b) 0.1786 g. substance gave 0.0876 g. AgCl.
Found : Cl, 12.12 per cent
C₁₅H₁₁O₂N₂Cl requires Cl, 12.39 per cent

V : (a) CONDENSATION OF 4-CHLOROANTHRANILIC ACID WITH MONO-
o-ANISYLTHIOUREA : FORMATION OF 7-CHLORO-3-(o-ANISYL)-
2-MERCAPTO-QUINAZOL-4-ONE :

4-Chloroanthranilic acid (1.7 g) was heated with mono-o-anisyl-
thiourea (1.8 g) at 180-90° for two hours. White solid obtained on working up the reaction mixture as before was crystallised from ethanol, white short needles, m.p. 298°. Yield: 0.7 g.

Analysis: (a) 0.1382 g. substance gave 0.0984 g. BaSO₄.

Found: S, 9.78 per cent

\[ \text{C}_{15}\text{H}_{11}\text{O}_2\text{N}_2\text{S} \text{Cl requires S, 10.05 per cent} \]

(b) 0.0832 g. substance on Kjeldahl determination required 11.3 ml of 0.04612 N sulphuric acid.

Found: N, 8.77 per cent

\[ \text{C}_{15}\text{H}_{11}\text{O}_2\text{N}_2\text{S} \text{Cl requires N, 8.90 per cent} \]

(b) Condensation of 4-Chloroanthranilic acid with o-Anisyl isothiocyanate: Formation of 7-Chloro-3-(o-anisyl)-2-mercapto-quinazol-4-one:

4-Chloroanthranilic acid (0.85 g) and o-anisyl isothiocyanate (0.8 g) when refluxed together in ethanol as before gave a solid, which on crystallisation from ethanol gave white short needles, m.p. 297-98°. Mixed m.p. with the product obtained in (a) above remains undepressed. Yield: 0.35 g.

(c) 7-Chloro-3-(o-anisyl)-2-thiophenyl-quinazol-4-one: 7-Chloro-3-(o-anisyl)-2-mercapto-quinazol-4-one (0.5 g) was suspended in bromobenzene (10 ml) and anhydrous potassium carbonate and a pinch of copper powder were added to it. The solid obtained on treatment as before was crystallised from acetone, white long needles, m.p. 178°.

Analysis: 0.1424 g. substance gave 0.0872 g. BaSO₄.

Found: S, 8.39 per cent

\[ \text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_2\text{S} \text{Cl requires S, 8.11 per cent} \]
(d) **7-Chloro-3-(o-anisyl)-2-thiobenzoyl-quinazol-4-one**: To 7-chloro-3-(o-anisyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g). The product obtained as before was collected and crystallised from acetone, dull-white short needles, m.p. 171°.

**Analysis**: 0.1392 g. substance gave 0.0740 g. BaSO₄.

Found: S, 7.30 per cent

C_{22}H_{15}O_{3}N_{2}SCl requires S, 7.57 per cent

(e) **Oxidation of 7-Chloro-3-(o-anisyl)-2-mercapto-quinazol-4-one**:

**Formation of 7-Chloro-3-(o-anisyl)-quinazol-2:4-dione**:

7-Chloro-3-(o-anisyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised with alkaline hydrogen peroxide as before. The solid obtained was crystallised from ethanol, white short needles, m.p. 279°. It was found to be identical with the authentic sample synthesized as under.

(f) **Condensation of 4-Chloroanthranilic acid with Mono-o-anisylurea**:

**Formation of 7-Chloro-3-(o-anisyl)-quinazol-2:4-dione**:

4-Chloroanthranilic acid (0.85 g) when heated with mono-o-anisylurea (0.8 g) as before gave a product which on crystallisation from ethanol gave white short needles, m.p. 279-80°. Mixed m.p. with the oxidation product in (e) above, remains undepressed.

**Analysis**: (a) 0.0840 g. substance on Kjeldahl determination required 13.0 ml of 0.0418 N sulphuric acid.

Found: N, 9.06 per cent

C_{15}H_{11}O_{3}N_{2}Cl requires N, 9.26 per cent

(b) 0.1934 g. substance gave 0.0898 g. AgCl.

Found: Cl, 11.48 per cent

C_{15}H_{11}O_{3}N_{2}Cl requires Cl, 11.73 per cent
VI : (a) CONDENSATION OF 4-CHLOROANTHRANILIC ACID WITH MONO-
p-ANISYLTHIOUREA : FORMATION OF 7-CHLORO-3-(p-ANISYL)-
2-MERCAPTO-QUINAZOL-4-ONE :

An intimate mixture of 4-chloroanthranilic acid (1.7 g) and mono-
p-anisylthiourea (1.8 g) was heated at 180-90° for two hours and the
product obtained on treatment as before was crystallised from ethanol,
white short needles, m.p.318°. Yield : 0.8 g.

Analysis : (a) 0.1396 g. substance gave 0.1008 g. BaSO₄.

   Found : S, 9.90 per cent.
   C₁₅H₁₁O₂N₂SCl requires S, 10.05 per cent

(b) 0.0636 g. substance on Kjeldahl determination required
   8.5 ml of 0.04612 N sulphuric acid.

   Found : N, 8.63 per cent
   C₁₅H₁₁O₂N₂SCl requires N, 8.90 per cent

(b) Condensation of 4-Chloroanthranilic acid with p-anisyl isothio-
cyanate : Formation of 7-Chloro-3-(p-anisyl)-2-mercapto-
quinazol-4-one :

4-Chloroanthranilic acid (0.85 g) together with p-anisyl isothio-
cyanate (0.8 g) when refluxed in ethanol, as before, gave a product,
which on crystallisation from ethanol gave white short needles, m.p.
and mixed m.p. with the product obtained as in (a) above, 318°.
Yield : 0.4 g.

(c) 7-Chloro-3-(p-anisyl)-2-thiophenyl-quinazol-4-one : A solution
of 7-chloro-3-(p-anisyl)-2-mercapto-quinazol-4-one (0.5 g) in bromo-
benzene (15 ml) when treated with anhydrous potassium carbonate (0.5 g)
in presence of a pinch of copper powder as before gave a product which
was crystallised from acetone, pale yellow short needles, m.p.196°.
**Analysis**: 0.1380 g. compound gave 0.0828 g. BaSO₄.

Found: S, 8.23 per cent

\[ C_{21}H_{15}O_2N_2S \] requires S, 8.11 per cent

(d) **7-Chloro-3-(p-anisyl)-2-thiobenzoyl-quinazol-4-one**: 7-Chloro-3-(p-anisyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was treated with benzoyl chloride (0.5 g) and the product obtained as before was crystallised from acetone, white small needles, m.p. 183°C.

**Analysis**: 0.1534 g. substance gave 0.0862 g. BaSO₄.

Found: S, 7.70 per cent

\[ C_{22}H_{15}O_2N_2S \] requires S, 7.57 per cent

(e) **Oxidation of 7-Chloro-3-(p-anisyl)-2-mercapto-quinazol-4-one**: Formation of 7-Chloro-3-(p-anisyl)-quinazol-2:4-dione:

7-Chloro-3-(p-anisyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised with alkaline hydrogen peroxide as before. The product obtained was crystallised from ethanol, white grains, m.p. 270°C. It was found to be identical with the authentic sample synthesized as described below.

(f) **Condensation of 4-Chloroanthranilic acid with Mono-p-anisylurea**: Formation of 7-Chloro-3-(p-anisyl)-quinazol-2:4-dione:

4-Chloroanthranilic acid (0.85 g) when treated with mono-p-anisylurea (0.8 g) as before gave a product, which was crystallised from ethanol, white grains, m.p. 271°C. Mixed m.p. with the product obtained on oxidation as in (e) remains undepressed.

**Analysis**: (a) 0.1964 g. substance gave 0.0944 g. AgCl.

Found: Cl, 11.90 per cent

\[ C_{15}H_{11}O_3N_2Cl \] requires Cl, 11.73 per cent
(b) 0.0726 g. substance on Kjeldahl determination required 11.3 ml of 0.0418 N sulphuric acid.

Found: N, 9.11 per cent

\[ \text{C}_{15}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl} \] requires N, 9.26 per cent

VII: (a) CONDENSATION OF 4-CHLOROANTHRANILIC ACID WITH MONO-o-CHLOROPHENYLTHIOUREA : FORMATION OF 7-CHLORO-3-(o-CHLOROPHENYL)-2-MERCAPTO-QUINAZOL-4-ONE :

4-Chloroanthranilic acid (1.7 g) and mono-o-chlorophenylthiourea (1.9 g) were heated together at 180-90° for two hours. The product obtained on working up the reaction mixture as before was crystallised from ethanol, dull-white short needles, m.p. 307°. Yield: 0.85 g.

Analysis: (a) 0.1412 g. substance gave 0.1010 g. \( \text{BaSO}_4 \).

Found: S, 9.78 per cent

\[ \text{C}_{14}\text{H}_8\text{O}_2\text{S}_2\text{Cl}_2 \] requires S, 9.91 per cent

(b) 0.0662 g. substance on Kjeldahl determination required 8.0 ml of 0.04612 N sulphuric acid.

Found: N, 7.80 per cent

\[ \text{C}_{14}\text{H}_8\text{O}_2\text{S}_2\text{Cl}_2 \] requires N, 8.02 per cent

(b) Condensation of 4-Chloroanthranilic acid with o-Chlorophenyl isothiocyanate : Formation of 7-Chloro-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one :

4-Chloroanthranilic acid (0.85 g) and o-chlorophenyl isothiocyanate (0.85 g) when refluxed in ethanol as before gave a product which crystallised from ethanol, white short needles, m.p. 308°. Mixed m.p. with the product synthesized in (a) remains undepressed.

(c) 7-Chloro-3-(o-chlorophenyl)-2-thiophenyl-quinazol-4-one :

7-Chloro-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was
suspended in bromobenzene (10 ml) and anhydrous potassium carbonate (0.5 g) and a pinch of finely divided copper powder were added to it. The product obtained as before was crystallised from acetone, white shining needles, m.p. 167°.

Analysis: 0.1462 g. substance gave 0.0842 g BaSO₄.

Found: S, 7.89 per cent

\( \text{C}_{20}\text{H}_{12}\text{O}_{2}\text{N}_{2}\text{SCl}_{2} \) requires S, 8.02 per cent

(d) 7-Chloro-3-(o-chlorophenyl)-2-thiobenzoyl-quinazol-4-one:

7-Chloro-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was dissolved in aq. NaOH (10 %; 30 ml) and benzoyl chloride (0.5 g) was added to it. The solid that separated on keeping the reaction mixture for six hours was crystallised from acetone, dull-white short needles, m.p. 166°.

Analysis: 0.1486 g. substance gave 0.0800 g. BaSO₄.

Found: S, 7.38 per cent

\( \text{C}_{21}\text{H}_{12}\text{O}_{2}\text{N}_{2}\text{SCl}_{2} \) requires S, 7.49 per cent

(e) Oxidation of 7-Chloro-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one:

Formation of 7-Chloro-3-(o-chlorophenyl)-quinazol-2:4-dione:

7-Chloro-3-(o-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised with hydrogen peroxide as before. The product obtained as usual was crystallised from ethanol, white grains, m.p. 313°. It was found to be identical with the product obtained as under.

(f) Condensation of 4-Chloroanthranilic acid with Mono-o-chlorophenylurea:

Formation of 7-Chloro-3-(o-chlorophenyl)-quinazol-2:4-dione:
4-Chloroanthranilic acid (0.85 g) and mono-o-chlorophenylurea (0.85 g) when heated together at 180°-90° for two hours and worked up as before gave a product which was crystallised from ethanol, white grains, m.p. and mixed m.p. with the oxidation product obtained as in (e) above, 313°.

Analysis: (a) 0.0686 g. substance on Kjeldahl determination required 10.5 ml of 0.0418 N sulphuric acid.

Found: N, 8.96 per cent
C₁₄H₈O₂N₂Cl₂ requires N, 9.14 per cent

(b) 0.1208 g. substance gave 0.0926 g. AgCl.

Found: Cl, 18.96 per cent
C₁₄H₈O₂N₂Cl₂ requires Cl, 19.19 per cent

VIII: (a) CONDENSATION OF 4-CHLOROANTHRANILIC ACID WITH MONO-
m-CHLOROPHENYLTHIOUREA : FORMATION OF 7-CHLORO-3-
(m-CHLOROPHENYL)-2-MERCAPTO-QUINAZOL-4-ONE :

A mixture of 4-chloroanthranilic acid (1.7 g) and mono-m-chlorophenylthiourea (1.9 g) was heated as before. The product obtained on similar treatment as before was crystallised from ethanol, white grains, m.p. 293°. Yield: 0.75 g.

Analysis: (a) 0.1430 g. substance gave 0.1012 g. BaSO₄.

Found: S, 9.67 per cent
C₁₄H₈ON₂SCl₂ requires S, 9.91 per cent

(b) 0.0704 g. substance on Kjeldahl determination required 8.6 ml of 0.04612 N sulphuric acid.

Found: N, 7.88 per cent
C₁₄H₈ON₂SCl₂ requires N, 8.02 per cent
(b) Condensation of 4-Chloroantranilic acid with m-Chlorophenyl isothiocyanate: Formation of 7-Chloro-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one:

4-Chloroantranilic acid (0.85 g) and m-chlorophenyl isothiocyanate (0.85 g) were refluxed in ethanol and the product obtained as before was crystallised from ethanol, white grains, m.p. 292-93°. Mixed m.p. with the product obtained in (a) above remains undepressed. Yield: 0.35 g.

(c) 7-Chloro-3-(m-chlorophenyl)-2-thiophenyl-quinazol-4-one: A solution of 7-chloro-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) in bromobenzene (15 ml) was heated with anhydrous potassium carbonate (0.5 g) and a pinch of copper powder. The solid obtained on working up the reaction as before was crystallised from acetone, pale yellow short needles, m.p. 164°.

Analysis: 0.1418 g. substance gave 0.0856 g. BaSO₄.
Found: S, 8.28 per cent
C₂₀H₁₂O₂N₂SCl₂ requires S, 8.02 per cent

(d) 7-Chloro-3-(m-chlorophenyl)-2-thiobenzoyl-quinazol-4-one: To 7-chloro-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g). The product obtained on treatment as before was crystallised from acetone, white small needles, m.p. 178°.

Analysis: 0.1360 g. substance gave 0.0714 g. BaSO₄.
Found: S, 7.20 per cent
C₂₁H₁₂O₂N₂SCl₂ requires S, 7.49 per cent
(e) **Oxidation of 7-Chloro-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one:**  
**Formation of 7-Chloro-3-(m-chlorophenyl)-quinazol-2:4-dione:**

7-Chloro-3-(m-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised in alkaline hydrogen peroxide and the product obtained as before was crystallised from ethanol, white short needles, m.p. 311°. It was found to be identical on comparison with the product obtained as under.

(f) **Condensation of 4-Chloroanthranilic acid with Mono-m-chlorophenylurea:**  
**Formation of 7-Chloro-3-(m-chlorophenyl)-quinazol-2:4-dione:**

4-Chloroanthranilic acid (0.85 g) when heated with mono-m-chlorophenylurea (0.85 g) as before gave a product which was crystallised from ethanol, white short needles, m.p. 311-12°. The mixed m.p. with the oxidation product obtained in (e) remains undepressed. Dokunikhin and Gaeva (J. Gen. Chem., U.S.S.R., 1953, 23, 606; Chem. Abstr., 1954, 48, 7018) and Kizber and Glagoleva (ibid., 1953, 23, 1028; Chem. Abstr., 1954, 48, 8790) who prepared this compound following different routes report melting points 309-311° and 312° respectively.

**Analysis:**  
0.1180 g. substance gave 0.0900 g. AgCl.  
*Found:* Cl, 18.86 per cent  
*Calculated for C₁₄H₈O₂N₂Cl₂:* Cl, 19.19 per cent

IX: **Condenstion of 4-Chloroanthranilic Acid with Mono-p-chlorophenylthiourea:**  
**Formation of 7-Chloro-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one:**

A mixture of 4-chloroanthranilic acid (1.7 g) and mono-p-chloro-
phenylthiourea (1.9 g) when treated as before gave a product which was crystallised from ethanol, white grains, m.p. 300°. Yield: 0.8 g.

Analysis: (a) 0.1396 g. substance gave 0.1002 g. BaSO₄.

Found: S, 9.81 per cent

C₁₄H₇O₁N₂Cl₂ requires S 9.91 per cent

(b) 0.0770 g. substance on Kjeldahl determination required 9.3 ml of 0.04612 N sulphuric acid.

Found: N, 7.80 per cent

C₁₄H₇O₁N₂Cl₂ requires N, 8.02 per cent

(b) Condensation of 4-Chloroanthranilic acid with p-Chlorophenyl isothiocyanate: Formation of 7-Chloro-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one:

4-Chloroanthranilic acid (0.85 g) and p-chlorophenyl isothiocyanate (0.85 g) when refluxed in ethanol as before, gave a product which was crystallised from ethanol, white grains, m.p. 300°. Mixed m.p. with the product obtained in (a) above remains undepressed. Yield: 0.4 g.

(c) 7-Chloro-3-(p-chlorophenyl)-2-thiophenyl-quinazol-4-one:
7-Chloro-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was heated with anhydrous potassium carbonate and a pinch of copper powder in dry bromobenzene (10 ml). The product obtained on working up the reaction mixture as before was crystallised from acetone, pale yellow short needles, m.p. 197°.

Analysis: 0.1520 g. substance gave 0.0912 g. BaSO₄.

Found: S, 8.23 per cent

C₂₀H₁₂O₂N₂SCl₂ requires S, 8.02 per cent
(d) 7-Chloro-3-(p-chlorophenyl)-2-thiobenzoyl-quinazol-4-one: To 7-chloro-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) in aq. NaOH was added benzoyl chloride (0.5 g) and solid obtained on treatment as before was crystallised from acetone, white short needles, m.p. 168°.

Analysis: 0.1472 g. substance gave 0.0824 g. BaSO₄.

Found: S, 7.67 per cent  
\( \text{C}_{21}\text{H}_{12}\text{O}_2\text{N}_2\text{S} \text{Cl}_2 \) requires S, 7.49 per cent

(e) Oxidation of 7-Chloro-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one:
Formation of 7-Chloro-3-(p-chlorophenyl)-quinazol-2:4-one:

7-Chloro-3-(p-chlorophenyl)-2-mercapto-quinazol-4-one (0.5 g) was oxidised by hydrogen peroxide as before. The product obtained as usual was crystallised from ethanol, white short needles, m.p. 298°. It was found to be identical with the product synthesized as under.

(f) Condensation of 4-Chloroanthranilic acid with Mono-p-chlorophenylurea:
Formation of 7-Chloro-3-(p-chlorophenyl)-quinazol-2:4-dione:

4-Chloroanthranilic acid (0.85 g) and mono-p-chlorophenylurea (0.5 g) when heated together and treated as before gave a product which was crystallised from ethanol, white short needles, m.p. and mixed m.p. with the oxidation product obtained in (e), 298°.

Analysis:  
(a) 0.0770 g substance on Kjeldahl determination required 11.5 ml of 0.0418 N sulphuric acid.

\( \text{Found: N, 8.82 per cent} \)
\( \text{C}_{14}\text{H}_{8}\text{O}_2\text{N}_2\text{Cl}_2 \text{ requires N, 9.14 per cent} \)

(b) 0.1354 g. substance gave 0.1056 g. AgCl.

\( \text{Found: Cl, 19.50 per cent} \)
\( \text{C}_{14}\text{H}_{8}\text{O}_2\text{N}_2\text{Cl}_2 \text{ requires Cl, 19.19 per cent} \)