EXPERIMENTAL
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I SYNTHESES OF SYBSTITUTED - OXOQUINAZOLINES
(SUBSTITUTION IN PYRIMIDINE RING)

1 N-Acetylanthranilic acid

A mixture of anthranilic acid (13.7 gms, 0.1 mole) and acetic anhydride three times its weight of anthranilic acid (42 ml) was refluxed on a water bath for 6 hours. On completion, the melt is cooled and poured over crushed ice. The product separated on stirring, was filtered and crystallised from ethanol to give brown coloured needles. Melting point 185°C, yield 99%.

(Bogert reported m.p. 186°C)

Found : N : 10.21%

C_{9}H_{9}NO_{3} requires : N : 10.22%

2 2-Methyl-3,1,4-benzoxazone

A mixture of N-acetylanthranilic acid (5 gm, 0.02 mole) and acetic anhydride, three times its weight of N-acetylanthranilic acid (15 ml) was boiled for few minutes. The reaction mixture was filtered hot through a cotton plug. The hot filtrate on cooling, gave colourless needles. Melting point 86°C, yield 66%.

(Zentmeyer reported m.p. 85°C)

Found : N : 6.44%

C_{11}H_{9}NO_{4} requires : N : 6.40%
2-Methyl-3(H)-4-ketoquinazoline

It was obtained by the action of ammonia on 2-methyl-3,1,4-benzoxazone. By boiling (0.5 gms, 0.003 mole) of 2-methyl-3,1,4 benzoxazone with slight excess of ammonia dissolved in 95% alcohol for 30 minutes. When all excess of ammonia was evolved the reaction mixture was filtered hot which on cooling, gave white product which is filtered, and recrystallised from ethanol to furnish white needles. Melting point 235°C, yield 50%.

Found : C : 67.49%, H:5.02% and N : 17.48%

\(\text{C}_9\text{H}_6\text{N}_2\text{O}\) requires : C : 67.5%, H : 5.0% and N : 17.5%

2-Methyl-3-phenyl-4-ketoquinazoline

A mixture of 2-methyl-3,1,4-benzoxazone (0.5 gm, 0.003 mole) and freshly distilled aniline (2 ml) was taken in a dry hard glass tube and heated on a water bath till a homogenous mixture is formed. It was then cooled and treated with dilute hydrochloric acid (2 ml) to remove the unreacted aniline. The residue was extracted with ethanol which gave colourless plates, Melting point 170°C, yield 41%.

Found : C : 76.30%, H:5.0% and N : 11.88%

\(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\) requires : C : 76.27%, H : 5.08% and N : 11.87%
3-Amino-2-methyl-4-ketoquinazoline
Hydrazine hydrate (50%, 2ml) was slowly added with stirring to a cooled mixture of 2-methyl-3,1,4-benzoxazone (0.5 ml, 0.003 moles) and ethanol (10 ml). The reaction mixture was refluxed for 2 hours on a water bath. On completion, filtered hot, which on cooling furnished pale yellow needles, melting point 150°C, yield 81%. (Bogert reported m.p. 152°C)

Found : C : 61.70%, H:5.10% and N:24.05%
C_{9}H_{9}ON_{3} requires : C : 61.71%, H : 5.14% and N : 24.0%

3-Anilino-2-methyl-4-ketoquinazoline
2-Methyl-3,1,4-benzoxazone (0.5 gms, 0.005 mole) is dissolved in 20 ml methanol and mixed with slightly more than equimolar amount of phenylhydrazine (0.5 gm, 0.005 mole). The reaction mixture was refluxed for 2 hours on a water bath. On completion, filtered hot, which on cooling furnished pale yellow needles. Melting point 176°C, yield 18%.

Found : C : 71.69%, H:5.15% and N : 16.70%
C_{15}H_{13}ON_{3} requires : C : 71.71%, H : 5.17% and N : 16.73%
N-Propionylanthranilic acid

A mixture of anthranilic acid (6.85 gms, 0.05 mole) and excess of propionic anhydride (20 ml) almost three times its weight of anthranilic acid was refluxed on a water bath for 10 hours. On completion, the brown mass was cooled and poured over crushed ice. The product separated on stirring was filtered and crystallised from boiling water, to furnish white fluffy needles. Melting point 121°C, yield 85%.

Found : N : 7.49%
C\textsubscript{10}H\textsubscript{11}O\textsubscript{3}N requires : N : 7.46%

2-Ethyl-3,1,4-benzoxazine

A mixture of N-propionylanthranilic acid (5 gm, 0.02 mole) and acetic anhydride (15 ml) three times its weight of N-propionylanthranilic acid was taken in a beaker and covered with a watchglass. The reaction mixture was boiled for few minutes and filtered hot through a cotton plug. The hot filtrate on cooling, furnished colourless plates. Melting point 88°C, yield 54%.

(Zentmyer reported m.p. 86°C)

Found : N : 8.05%
C\textsubscript{10}H\textsubscript{9}O\textsubscript{2}N requires : N : 8.0%
2-Ethyl-3(H)-4-Ketoquinazoline

It was obtained by the action of ammonia on 2-ethyl-3,1,4-benzoxazone. By boiling 2-ethyl-3,1,4-benzoxazone (0.5 gm, 0.002 mole) with slight excess of ammonia dissolved in 95°C methanol, for 30 minutes.

When all excess of ammonia is driven off it is filtered hot, which on cooling furnished with white shining flakes, Melting point 231°C, Yield 26% (Zentmyer reported m.p. 233°C)²

Found : C : 68.90%, H : 5.75% and N : 16.09%

C₁₀H₁₀N₂O requires : C : 68.96%, H : 5.74% and N : 16.14%

2-Ethyl-3-phenyl-4-ketoquinazoline

Equimolar mixture of 2-ethyl-3,1,4-benzoxazone (0.5 gm, 0.002 mole) and freshly prepared aniline (0.002 mole) is taken in a hard glass tube and heated to 150°C for 30 minutes. The mass was treated with dilute hydrochloric acid and extracted with ethanol to give pale yellow needles. Melting point 125°C, yield 33%.

(Zentmyer reported m.p. 125°C)²

Found : C : 76.81%, H : 5.5% and N : 11.24%

C₁₆H₁₄N₂O requires : C : 76.8%, H : 5.6% and N : 11.2%
11 3-Amino-2-ethyl-4-ketoquinazoline

Hydrazine hydrate (50%, 2ml) was slowly added with stirring to a cooled mixture of 2-ethyl-3,1,4-benzo-

xazone (0.5 gms, 0.003 mole) and ethanol (10 ml)

The reaction mixture was refluxed for 2 hrs. On a water bath. On completion, filtered hot, which on cooling, furnished colourless needles.

Melting Point 140°C, yield 20%

Found : C : 63.41%, H : 5.5% and N : 22.24%

C_{10}H_{11}N_{3}O requires : C : 63.43%, H : 5.8% and N : 22.22%

12 3-Anilino-2-ethyl-4-ketoquinazoline

A mixture of 2-ethyl -3,1,4-benzoazone (0.5 gms 0.002 mole) and slight excess of phenylhydrazine (0.5 gms, 0.005 mole) was refluxed for 3 hrs. on a water bath using methanol as a solvent. On completion filtered hot. The hot filterate on cooling furnished pale yellow needles.

Melting Point 163°C, yield 34%

Found : C : 72.40%, H : 5.61% and N : 17.58%

C_{16}H_{15}N_{3}O requires C : 72.45%, H : 5.6% and N : 17.56%
13 N-Butyrylanthranilic Acid

A mixture of anthranilic acid (6.85 gms, 0.05 mole) and excess of butyric anhydride (20 ml) almost three times its weight of anthranilic acid was refluxed on a water bath for 12 hours. On completion, the brown mass was cooled and poured over crushed ice. The product obtained on stirring was filtered and crystallised from boiling water to give white cottony needles. Melting Point 120°C, yield 79%.

Found : N : 6.74%

C_{13}H_{13}NO_2 requires : N : 6.74%

14 2-Propyl-3,1,4-benzoxazone

A mixture of N-butyrylanthranilic acid (5 gm, 0.02 mole) and excess of acetic anhydride (15 ml) almost three times its weight of N-butyrylanthranilic acid was taken in a beaker and covered with a watch glass. The reaction mixture was boiled for few minutes and filtered hot, which on cooling, furnished cream coloured needles. Melting Point 60°C, yield 55%.

Found : N : 9.71%

C_{11}H_{11}NO_2 requires : N : 9.76%
2-Propyl-3(H)-4-ketoquinazoline
It was obtained by boiling a mixture of 2-propyl-3,1,4-benzoxazone (0.5 gms, 0.002 mole) with slight excess of ammonia in 95% methanol for 30 minutes. When all excess of ammonia was evolved it was filtered hot. The hot filtrate on cooling, furnished white needles. Melting Point 200°C, yield 39%.

Found : C : 70.1%, H :  6.30% and 
        N : 14.80%

C\textsubscript{11}H\textsubscript{12}N\textsubscript{2}O requires : C : 70.2%, H : 6.33% and 
        N : 14.89%

2-Propyl-3-phenyl-4-ketoquinazoline
Equimolar mixture of 2-propyl-3,1,4-benzoxazone (0.5 gm, 0.002 mole) and freshly prepared aniline (0.002 mole) is taken in a hard glass tube and heated to 150°C for 30 minutes. The fused mass obtained was treated with dilute hydrochloric acid and extracted with ethanol, which gave white needles, Melting point 120°C, yield 43%.

Found : C : 76.68%, H : 6.0 % and 
        N : 10.59%

C\textsubscript{17}H\textsubscript{16}N\textsubscript{2}O requires : C : 76.69%, H : 6.01% and 
        N : 10.53%
17 3-Amino-2-propyl-4-ketoquinazoline

Hydrazine hydrate (50%, 2 ml) was slowly added with stirring to a cooled mixture of 2-propyl-3,1,4-benzoxazone (0.5 gms, 0.002 mole) and ethanol 20 ml. The reaction mixture was refluxed for 2 hours on a water bath. On completion, filtered hot which furnished colourless needles. Melting point 125°C, yield 24%.

Found : C : 65.0%, H : 6.42% and N : 20.69%

C_{11}H_{13}N_{3}O requires : C : 65.02%, H : 6.40% and N : 20.68%

18 3-Anilino-2-propyl-4-ketoquinazoline

A mixture of 2-propyl-3,1,4-benzoxazone (0.5 gms, 0.002 mole) and slight excess of phenylhydrazine (0.5 gms, 0.005 mole) was refluxed on a water bath for 4 hours using methanol as a solvent. On completion, the reaction mixture was filtered hot. On cooling, the yellow filtrate gave pale yellow needles. Melting Point 120°C, yield 31%.

Found : C : 73.12%, H : 8.30% and N : 14.30%

C_{17}H_{17}N_{3}O requires : C : 73.11%, H : 8.33% and N : 14.37%
19  Ethoxalylanthranilic acid
A mixture of anthranilic acid (10 gms, 0.07 mole) and diethyloxalate (11 ml, 0.075 mole) was refluxed on a water bath for 6 hours. Initially a dark brown melt is formed and finally on completion a brown mass was obtained. When cold, the mass was pulverised and extracted from boiling water. From the hot aqueous extract colourless needles of ethoxalylanthranilic acid separate on cooling. Melting point 184°C, yield 14.35 gms. 1.4 gms of oxalyl dianthranilic acid is obtained. (Bogert reported m.p. 184°C)³

Found : N : 5.8%
C₁₁H₁₁O₅N requires : N : 5.9%

20  2-Ethoxycarbonyl-3,1,4-benzoxazone
A mixture of ethoxalylanthranilic acid (5 gms, 0.02 mole) and acetic anhydride (15 ml) almost three times its weight of ethoxalylanthranilic acid was boiled for few minutes and filtered hot through a cotton plug. Colourless needles separate on cooling. Melting point 130°C yield 99%
(Bogert reported m.p. 129°C)³

Found : N : 6.41%
C₁₁H₉NO₄ requires : N : 6.39%
21 2-Ethoxycarbonyl-3(H)-4-ketoquinazoline
A mixture of anthranilamide (6.8 gms, 0.05 mole) and ethyl oxalate (14.6 gms, 0.1 mole) was heated on a oil bath at 170°C for 6 hours. The melt solidifies on cooling. The solid was dissolved in 300 ml of hot absolute alcohol and the solution was filtered hot to remove the insoluble bisubstituted oxamide 0.12 gms, then cooled. The product obtained was cooled and washed with cold ethanol and recrystallised from absolute ethanol to furnish white needles. Melting point 180°C , Yield 57%.
(Baker reported m.p. 179°C) 4

Found : C : 60.51%, H : 4.4% and N : 12.77%
C_{11}H_{10}N_2O requires : C : 60.55%, H : 4.5% and N : 12.78%

22 3-Phenyl-2-ethoxycarbonyl-4-ketoquinazoline
A mixture of 2-ethoxycarbonyl-3,1,4-benzoxazone (2 gms, 0.009 mole) and slight excess of freshly distilled aniline (1 ml) was heated for a few minutes, till the mixture boils and a clear solution is formed. On cooling, it gave a reddish brown glassy mass, which was extracted with 90% ethanol. From the alcoholic extract pale yellow needles separate. Melting Point 163°C, yield 44%.
(Bogert reported m.p. 160°C) 3

Found : C:69.40%, H:4.95% & N:9.50%
C_{17}H_{14}N_2O_3 requires : C:69.38%, H:4.76% & N:9.52%
3-Amino-2-hydrazinocarbonyl-4-ketoquinazoline

Hydrazine hydrate (50%, 3 ml) was added dropwise with stirring to a cooled mixture of 2-ethoxycarbonyl-3,1,4-benzoxazone (1 gm, 0.009 mole) and ethanol (20 ml). The reaction mixture was refluxed for 2 hours on a water bath and on completion, filtered hot. Instantly colourless needles separated, recrystallised from ethanol to give colourless needles. Melting Point 205°C, yield 58%.

Found: C: 49.30%, H: 4.0 % and N: 25.50%

C$_9$H$_9$N$_3$O$_2$ requires: C: 49.31%, H: 4.1% and N: 25.57%

3-Amino-2-ethoxycarbonyl-4-Ketoquinazoline

Equimolar amount of 2-ethoxycarbonyl-3,1,4-benzoxazone (2 gms, 0.09 mole) and (1 ml, 0.09 mole) of phenylhydrazine was heated till a clear solution was formed. Water was evolved and no evidence of any alcohol being given off. On cooling a clear amber glass resulted. This was crystallised from ethanol and crystals washed with dilute ethanol. Recrystallised from ethanol to furnish long lemon yellow needles. Melting Point 145°C, yield 44% (Bogert reported m.p. 142°C).

Found: C:66.0%, H:4.5% and N:9.01%

C$_{17}$H$_{15}$N$_3$O$_3$ requires: C:66.01%, H:4.81% and N:9.06%
II  SYNTHESIS OF SUBSTITUTED OXOQUINAZOLINES WITH SUBSTITUTION IN BENZENE RING

1  5-Bromoanthranilic acid

Anthranilic acid (14 gms, 0.1 mole) was dissolved in glacial acetic acid (almost three times the weight of anthranilic acid) (42 ml) in a beaker. Running in slowly from a tap funnel, while the solution is constantly stirred with a mechanical stirrer, the theoretical amount (16 gms) of bromide dissolved in twice its volume of glacial acetic acid. The beaker was cooled in ice during the addition, as the reaction is exothermic. Allow it to stand for an hour in ice and then add cold water and keep it overnight and filter off. Crystallised from acetic acid to give brown coloured needles. Melting Point 235°C, yield 100%. (Wheeler reported m.p. 235°C)

Found :  N : 10.3% and Br : 36.90%
C$_7$H$_6$NO$_2$Br requires :  N : 10.2% and Br : 36.95%

2  N-Acetyl-5-bromoanthranilic acid

A mixture of 5-bromoanthranilic acid (21.7 gms, 0.1 mole) and acetic anhydride (three times its weight of 5-bromoanthranilic acid) (60 ml) is refluxed on a water bath for 8 hours and worked up as described before. The product obtained was crystallised from acetic acid to give cream coloured needles. Melting Point 220°C, yield 50% (Errede et al reported m.p. 220°C)

Found :  N : 5.52% and Br 30.90%
C$_9$H$_8$NO$_3$Br requires :  N : 5.4% and Br 30.88%
6-Bromo-2-methyl-3,1,4-benzoxazone

It was obtained by boiling the mixture of N-acetyl-5-bromoanthranilic acid (5 gms, 0.01 mole) and acetic anhydride (three times its weight of N-acetyl-5-bromoanthranilic acid) (15 ml). It was worked up as described before. The product obtained was crystallised from acetic acid to give colourless needles. Melting point 134°C yield 56% (Wheeler reported m.p. 134.5°C)5

Found: N: 5.80% and Br: 33.33%
C\textsubscript{15}H\textsubscript{11}NO\textsubscript{2}Br requires: N: 5.83% and Br: 33.33%

6-Bromo-2-methyl-3-(H)-4-ketoquinazoline

6-Br-3,1,4-benzoxazone (0.5 gm. 0.002 mole) is dissolved in ethanol and boiled with excess of ammonium carbonate and heating was continued till the ammonia was driven off. The mass was then boiled with water and made alkaline with NaOH and filtered. The quinazoline is precipitated from the filterate by addition of solid ammonium carbonate. The ppts are washed and treated with bone-black and recrystallised from alcohol giving colourless needles. Melting point 300°C, yield 34% (Bogert and Hand reported m.p. 298-300°C)7

Found: N: 11.70% and Br: 33.40%
C\textsubscript{9}H\textsubscript{7}N\textsubscript{2}OBr requires: N: 11.71% and Br: 33.47%
6-Bromo-2-methyl-3-phenyl-4-ketoquinazoline

A mixture of 6-bromo-2-methyl-3,1,4-benzoxazone (0.5 gms 0.02 mole) and freshly distilled aniline (2 ml) was taken in dry hard glass tube and heated till 150°C for one hour. It was then worked up as described earlier. The product obtained was recrystallised from ethanol furnishing colourless needles. Melting point 213°C, yield 13%

Found: C: 75.30%, H: 4.5% and N: 8.32% and Br: 25.35%

C\textsubscript{15}H\textsubscript{11}N\textsubscript{2}OBr requires: C:75.31%, H: 4.6%, N: 8.3% and Br: 25.39%

6-Bromo-3-amino-2-methyl-4-ketoquinazoline

Hydrazine hydrate (50%, 2 ml) was added dropwise with stirring to a cooled mixture of 6-Br-2-Me-3,1,4-Benzoxazone (0.5 gm, 0.002 mole) and methanol 20 ml. The reaction mixture was refluxed for 2 hours. On completion, the reaction mixture was filtered hot, which on cooling, gave white needles. Melting Point 230°C, yield 33%

Found: C:34.25%, H:2.54% N:15.89% and Br: 30.33%

C\textsubscript{9}H\textsubscript{8}N\textsubscript{3}OBr requires: C:34.28%, H:2.53%, N:15.90% and Br: 30.30%
6-Bromo-2-methyl-3-anilino-4-ketoquinazoline

A mixture of 6-bromo-2-methyl-3,1,4-benzoxazone (0.5 mgs, 0.002 mole) in methanol and slightly more than equimolar amount of phenylhydrazine was refluxed for 2 hours and worked up as described before. The product obtained was crystallised from ethanol to give pale yellow needles. Melting point 235°C, yield 43%.

Found: C:54.50%, H:3.65%, N:12.73% and Br : 24.23%

C_{15}H_{12}N_{3}OBr requires: C:54.54%, H:3.63%, N:12.73% and Br : 24.24%

5-Bromo-N-Propionylanthranilic acid

A mixture of 5-bromoanthranilic acid (10.85 gms, 0.05 mole) and excess of propionic anhydride (33 ml) was refluxed 10 hrs on a water bath and worked up as described earlier. The product observed was crystallised from boiling water to furnish white needles. Melting Point 190°C, yield 45%

Found: N:5.15% and Br : 29.30%

C_{10}H_{10}NO_{3}Br requires: N : 5.14%, and Br : 29.41%
9 6-Bromo-2-ethyl-3,1,4-benzoxazone

A mixture of 5-bromo-N-propionylantranilic acid (5.0 gms, 0.01 mole) and acetic anhydride (15 ml) was boiled for a few minutes and filtered hot. On cooling, colourless needles obtained, are washed with ether.
Melting point 172°C, yield 80%.

Found : N: 5.5% and Br 31.5%

C_{10}H_{9}N_{2}Br requires : N: 5.51% and Br: 31.49%

10 6-Bromo-2-ethyl-3(1H)-4-ketoquinazoline

It was obtained by boiling together a mixture of 6-bromo-2-ethyl-3,1,4-benzoxazone (0.5 gms 0.002 mole) in ethanol with excess of ammonium carbonate. It was worked up as described earlier.
The product obtained was crystallised from ethanol to give white needles.
Melting Point 255°C, yield 25%.

(Bogert reported m.p. 267°C)

Found : C: 47.40%, H: 3.53% N: 11.05% and Br: 31.52%

C_{10}H_{9}N_{2}OBr requires : C: 47.43%, H: 3.55%, N: 11.06% and Br: 31.62%
6-Bromo-2-ethyl-3-phenyl-4-ketoquinazoline

Equimolar mixture of 6-bromo-2-propyl-3,1,4-benzoxazone (0.5 gm, 0.002 mole) and freshly prepared aniline (0.002 mole) was taken in a dry hard glass tube and heated to 150°C for one hour. The mass was treated with dilute hydrochloric acid and then extracted with ethanol to give pale yellow needles.

Melting Point 247°C, yield 34%

Found: C: 58.30%, H: 3.97%

N: 8.53% and Br: 24.32%

C_{16}H_{13}N_{2}OBr requires: C: 58.35%, H: 3.95%

N: 8.51% and Br: 24.31%

6-Bromo-3-amino-2-ethyl-4-ketoquinazoline

It was also obtained by direct condensation of 6-bromo-2-ethyl-3,1,4-benzoxazone 90.5 gm, 0.002 mole) and slight excess of hydrazine hydrate (50% 2 ml), as described earlier. The product obtained was crystallised from methanol to give colourless needles.

Melting Point 185°C, yield 36%

Found: C: 44.75%, H: 3.72%

N: 15.69% and Br: 29.90%

C_{10}H_{10}N_{3}OBr requires: C: 44.77%, H: 3.73%

N: 15.67% and Br: 29.9%
13 6-Bromo-3-anilino-2-ethyl-4-ketoquinazoline

It was also obtained by direct condensation of
6-bromo-2-ethyl-3,1,4-benzoxazine (0.5 gms, 0.002 mole)
and slight excess of phenylhydrazine (2.1 gms 0.002
mole) and proceeded as described before to furnish pale
yellow needles.
Melting Point 251°C, yield 66%
Found :  N:12.19%, and Br:23.26%
C16H14N3OBr requires :  N:12.10%, and Br:23.25%

14 5-Bromo-N-butyrylanthranilic acid

A mixture of 5-bromoanthranilic acid (10.85 gms, 0.05
mole and excess of butyric anhydride (30 ml) was
refluxed for 12 hours. on a water bath and proceeded as
described earlier. The product obtained was
crystallised from boiling water to furnish cream
coloured cottony needles.
Melting Point 184°C, yield 78%.
Found :  N:4.88% and Br : 27.85%
C9H12NO2Br requires :  N:4.87% and Br : 27.87%

15 6-Bromo-2-propyl-3,1,4-benzoxazone

It is obtained by boiling together a mixture of
5-bromo-N-butylanthranilic acid (5 gm, 0.01 mole)
with excess of acetic anhydride (15 ml) and worked up
as described earlier to give colourles needles.
Melting Point 171°C, yield 90%
6-Bromo-2-propyl-3(\(\text{H}\))-4-ketoquinazoline

It was obtained by boiling (0.5 gm, 0.001 mole) of 6-bromo-2-propyl-3,1,4-benzoxazine with excess of ammonia dissolved in 95% alcohol and worked up as described earlier to give white needles.
Melting point 215°C, yield 62%.

Found : C : 49.45%, H:4.0%, N:10.50% and Br : 29.89%

\(\text{C}_{11}\text{H}_{11}\text{N}_{2}\text{OBr}\) requires: C : 49.43%, H:4.1%, N:10.4% and Br : 29.95%

6-Bromo-3-phenyl-2-propyl-4-ketoquinazoline

An equimolar mixture of 6-bromo-2-propyl-3,1,4-benzoxazine (0.5 gms, 0.001 mole) and freshly distilled aniline (0.001 mole) was taken in dry hard glass tube and heated for 1 hr. at 150°C and worked up as described earlier to give white needles.
Melting Point 220°C, yield 35%.

Found : C : 59.49%, H:4.35%, N:8.17% and Br : 23.30%

\(\text{C}_{17}\text{H}_{15}\text{N}_{2}\text{OBr}\) requires: C : 59.47%, H:4.37%, N:8.16% and Br : 23.32%
6-Bromo-3-amino-2-propyl-4-ketoguinazoline

It was obtained by direct condensation of 6-bromo-2-propyl-3,1,4-benzoxazole (0.5 gms, 0.001 mole) and hydrazine hydrate (50%, 2ml) and proceeded as described before to give colourless needles. Melting point 175°C yield 54%

Found : C:46.79%, H:4.25%, N:14.80% and Br:28.37%

C_{11}H_{12}N_{3}OBr requires: C:46.80%, H:4.25%, N:14.89% and Br: 28.36%

6-Bromo-3-anilino-2-propyl-4-ketoguinazoline

It was also obtained by direct condensation of 6-bromo-2-propyl-3,1,4-benzoxazole (0.5gms, 0.001 mole) and slightly excess of phenyl hydrazine (2.1gm, 0.02mole) and proceeds as described earlier to furnish pale yellow needles. Melting point 193°C, yield 61%

Found : C:56.95%, H:4.43%, N:11.72% and Br: 22.36%

C_{17}H_{16}N_{3}OBr requires: C:56.98%, H:4.46%, N:11.73% and Br: 22.34%

5-Bromoethoxalylanthranilic acid

A mixture of 5-bromoanthranilic acid (5.0gms, 0.02 mole) and deithyl oxalate (5ml, 0.03 mole) is refluxed on a oil bath at 140°C for 2 hours and further heated at 160°C for 10 minutes. A dark brown mass obtained was cooled and pulverised and extracted from boiling water to furnish white cottony needles.
Melting Point 185°C, yield 34%
Found : N:6.46% and Br : 25.27%
C_{11}H_{10}NO_{5}Br requires: N:6.45% and Br : 25.23%

21 6-Bromo-2-ethoxycarbonyl-3,1,4-benzoxazone
A mixture of 5-bromoethoxalylanthranilic acid (5.0 gms, 0.01 mole) and excess of acetic anhydride (15 ml, 0.1 mole) was boiled for few minutes. The reaction mixture was filtered hot, through a cotton plug which on cooling, furnished yellow coloured needles.
Melting Point 150°C, yield 63%
Found : N:4.39%, and Br:25.35%
C_{11}H_{9}NO_{4}Br requires: N:4.41% and Br : 25.31%

22 6-Bromo-2-ethoxycarbonyl-3(H)-4-ketoquinazoline
(2.98 gms, 0.01 mole) of 6-bromo-2-ethoxycarbonyl-3,1,4-benzoxazone is treated with 25 ml of 90% alcoholic ammonia and kept at 100°C for 30 minutes. till it forms a clear solution and all excess of ammonia was driven off. On completion the reaction mixture was filtered hot, which on cooling, gave white shiny flakes.
Melting Point 310°C, yield 22%
Found : C:44.4%, H:3.05%
N:9.40% and Br:25.93%
C_{11}H_{9}N_{9}O_{3}Br requires C:44.44%, H:3.03%,
N:9.42% and Br:25.9%
23 6-Bromo-3-phenyl-2-ethoxycarbonyl-4-ketoquinazoline

A mixture of 6-bromo-2-ethoxycarbonyl-3,1,4-benzoxazone (2.9 gms 0.01 mole) and freshly distilled aniline (2 ml) was heated for a few minutes till a clear solution is formed. On cooling, it gave a reddish brown glassy mass which was extracted with 90% ethanol. From the alcoholic extract pale yellow needles are obtained.

Melting Point 227°C, yield 23%.

Found : C:54.95%, H:4.0%, N:7.54% and Br:25.23%  
C\textsubscript{17}H\textsubscript{13}N\textsubscript{2}O\textsubscript{3}Br requires: C:54.98%, H:4.1%  
N:7.55% and Br:25.25%

24 6-Bromo-3-amino-2-hydrazinocarbonyl-4-ketoquinazoline

Hydrazine hydrate (50%, 5 ml) was added dropwise with stirring to a cooled mixture of 6-bromo-2-ethoxycarbonyl-3,1,4-benzoxazone (2.98 gms 0.01 mole) and 50%, 25 ml ethanol. Instantly yellowish white ppt separate. The reaction mixture was refluxed for 2 hours. On completion, filtered hot, and on cooling furnished yellow coloured needles,

Melting Point 210°C, yield 25%.

Found : C:36.02%, H:2.5%  
N:22.43% and Br:26.62%  
C\textsubscript{18}H\textsubscript{18}N\textsubscript{3}O\textsubscript{3}Br requires : C:36%, H:2.6%  
N:22.43% and Br:26.06%
Equimolar amount of 6-bromo-2-ethoxycarbonyl-3,1,4-benzoxazone (2.98gm, 0.01mole) and freshly prepared phenylhydrazine (1.5ml, 0.01mole) was heated together for few minutes till a clear solution was formed. Water was evolved and there was no evidence of any alcohol being given off. On cooling a clear amber glass like material resulted, which was extracted with ethanol and from the alcoholic extract yellow needles separate.

Melting point 265°C, yield 47%

\[ \text{Found: } C:52.55\%, \ H:3.5\%, \ N:10.84\% \]

\[ \text{requires: } \text{C}_17\text{H}_{14}\text{N}_3\text{O}_3\text{Br} \text{: } C:52.57\%, \ H:3.6\% \]

\[ \text{and Br:20.63\%} \]

\[ \text{N: 10.82\% and Br:20.61\%} \]
III SYNTHESIS OF 2-HYDROXICARBAMOYL-4-KETOQUINAZOLINE WITH SUBSTITUENTS IN POSITION 3 and 6

1 2-Hydroxycarbamoyl-3(H)-4-ketoquinazoline

It was obtained by the action of hydroxylamine hydrochloride (0.70 gms, 0.01 mole) on 2-ethoxycarbonyl-3(H)-4-ketoquinazoline (2.18 gms, 0.01 mole) in the presence of sodium metal (0.23 gm, 0.01 mole) in methanol. The mixture is stirred well and kept aside at room temperature for 10 hours. It was neutralized (pH=7) with dilute hydrochloric acid and filtered. The filtrate was evaporated under vacuum and the residue was crystallized from ethanol to give white needles.

Melting Point 222°C, yield 55%

Found: C:52.69%, H:3.40%
and N:20.50%

C₁₉H₁₇NO₃ requires: C:52.68%, H:3.41%
and N:20.48%

2 2-Hydroxycarbamoyl-3-phenyl-4-ketoquinazoline

It was also obtained by the action of hydroxylamine hydrochloride (0.7 gm, 0.01 mole) on 2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (2 gms 0.01 mole) in presence of sodium metal (0.23 gm 0.01 M) in methanol. It was proceeded as described earlier. The product obtained was crystallized from ethanol to give white fluffy needles.

Melting Point 157°C, yield 87%
3 2-Hydroxycarbamoyl-3-anilino-4-ketoquinazoline

It was also obtained by the action of hydroxylamine hydrochloride (0.7 gms, 0.01 mole) on 2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.0 gms 0.01 mole) in the presence of sodium metal (0.23 gms, 0.01 mole) in methanol. It was proceeded as described earlier. The product obtained was crystallised from ethanol which gave white coloured needles.

Melting Point 147°C, yield 76%

Found : C:60.84%, H:4.09% and N:18.89%

C_{15}H_{11}N_{13}O_{3} requires : C:60.81%, H:4.05% and N:18.91%

4 6-Bromo-2-hydroxycarbamoyl-3(H)-4-ketoquinazoline

It was obtained by the action of hydroxylamine hydrochloride (0.7 gm, 0.01 mole) on 2-ethoxycarbonyl-3(H)-4-ketoquinazoline (2.97 gms, 0.01 mole) in presence of sodium metal (0.23 gms, 0.01 mole) in methanol. It was proceeded and cooled up as described earlier. The product obtained was recrystallised from ethanol which gave white needles.

Melting Point 200°C, yield 90%
6-Bromo-2-hydroxycarbamoyl-3-phenyl-4-ketoquinazoline

It was also obtained by the action of hydroxylamine hydrochloride (0.7 gm 0.01 mole) on 6-bromo 2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (3.71 gms 0.01 mole) in presence of sodium metal (0.23 gms 0.01 mole) in methanol. It was proceeded and worked up as described earlier. The product obtained was recrystallised from ethanol to give white needles.

Melting Point 218°C, yield 72°C.

Found : C:50.07%, H:2.9%
        N:1.54% and Br:22.20%

C_{15}H_{10}N_{3}O_{3}Br requires : C:50%, H:2.7%
                             N:11.55% and Br:22.22%

6-Bromo-2-hydroxycarbamoyl-3-anilino-4-ketoquinazoline

It was also obtained by the action of hydroxylamine hydrochloride (0.7 gm, 0.01 mole) 6-bromo-2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.3 gms 0.01 mole) in presence of sodium metal (0.23 gm. 0.01 mole) in methanol. It was proceeded and worked up as described earlier. The product obtained was recrystallised from ethanol to give cream coloured needles.
Melting Point 210°C, yield 40%

Found: C: 48.10%, H: 2.75%, N: 14.35%, and Br: 21.31%.

C₁₅H₁₁N₄O₃Br requires: C: 48.0%, H: 2.9%, N: 14.33% and Br: 21.33%.
IV SYNTHESIS OF 2-N-(SUBSTITUTED BENZENESULFONYL) - HYDROZINOCARBONYL-4-KETOQUINAZOLINES WITH SUBSTITUENTS IN POSITION 3 AND 6

1 p-Bromobenzenesulphonyl chloride
A mixture of bromobenzene (50 gms, 0.3 mole) in chloroform (250 ml) was cooled to 0 to 5°C. Add (250 ml) of chlorosulphonic acid dropwise, with constant stirring. When initial evolution of hydrogen chloride subsides, remove the reaction mixture from the ice and stir it for 30 minutes at room temperature. Then pour it on to one kilo of crushed ice. Separate the chloroform layer, wash it well with water and evaporate the solvent. Recrystallise it from light petroleum, benzene of chloroform to give white needles.
Melting Point 76°C, yield 71%
(Meerwein reported m.p. 76°C)

2 p-Bromobenzenesulphonamide
Boil 5 gm of p-bromobenzenesulphonyl chloride with 50 ml of concentrated ammonia solution, sp. gravity for 10 minutes, cool to room temperature, add 100 ml of cold water, filter with suction, wash well and recrystallise from dilute alcohol to give long white needles.
Melting Point 163°C, yield 26%
3  **p-Bromobenzenesulphonylhydrazine**

p-Bromobenzenesulphonyl chloride (2.5 gms 0.01 mole) was dissolved in dry benzene in a flask, provided with a mechanical stirrer. Hydrazine hydrate (50% 5 ml) was added dropwise, keeping the mixture stirred at 35-40°C, for an hour. The mixture was kept overnight at room temperature and benzene was distilled off. The residue was crystallized from dilute alcohol to give white needles.

Melting Point 116°C Yield 49%

4  **p-Chlorobenzenesulphonyl chloride**

It was also obtained by the action of chlorosulphonic acid on p-chlorobenzene. Dissolve (50 gms) of chlorobenzene in 250 ml of chloroform and cooled in a freezing mixture of ice and salt to 0 - 5°C. Add (250 ml) chlorosulphonic acid dropwise with constant stirring and proceed as described earlier. The product obtained was recrystallised from chloroform to give white needles.

Melting Point 52°C, yield 63%

(Meerwein reported m.p. 53°C)

5  **p-Chlorobenzenesulphonamide**

Boil 5 gms of p-Chlorobenzenesulphonyl chloride with 50 ml of concentrated ammonia solution, sp.gr. 0.88, for 10 minutes, cool to room temperature, add 100 ml of cold water, filter and recrystallise from dilute alcohol to give white needles.
Melting point 145°C, yield 75%.

6 p-Chlorobenzenesulphonylhydrazine

It was obtained by the action of hydrazine hydrate on p-chlorobenzenesulphonyl chloride. p-Chlorobenzenesulphonyl chloride (2.11gm, 0.01mole) was dissolved in dry benzene and hydrazine hydrate 50% (5ml) was added dropwise with constant stirring and proceeded as described earlier. The product obtained was crystallised from dilute alcohol to give white needles.
Melting point 105°C, yield 60%.

7 p-Toluenesulphonyl chloride

Toluene (58 ml) was slowly added over 1 hour to cooled chlorosulphonic acid (200 gms) maintaining the reaction temperature between 0 to 5°C. After complete addition, it was stirred for 2 hours at room temperature and then it was poured into crushed ice. The oily layer was separated from the aqueous solution and washed with cold water. The oil was cooled to -10° to -20°C, almost pure p-toluenesulphonyl chloride crystallised out. It was filtered and recrystallised from petroleum ether.
Melting point 68°C, yield 31%.
(Friemann reported m.p. 69°C)
p-Toluenesulphonamide
A mixture of p-toluenesulphonyl chloride (5gms) and (50ml) of concentrated ammonia solution sp. gr.0.88. was boiled for 10 minutes. The reaction mixture was cooled to room temperature and (100ml) of cold water was added and filtered. The product obtained was recrystallised from dilute alcohol to give white needles.
Melting point 139°C, yield 22%.

p-Toluenesulphonylhydrazine
It was also obtained by the action of hydrazine hydrate on p-toluenesulphonyl chloride. Hydrazine hydrate (50%, 0.02 mole) was added dropwise with constant stirring to a mixture of p-toluenesulphonyl chloride (1.9gms 0.01mole) in dry benzene. It was proceed as described earlier. The product obtained was crystallised from dilute alcohol to give white plates.
Melting point 110°C, yield 53%.

2-N-(p-Bromobenzenesulphonyl)-hydrazinocarbonyl-3(H)-4-ketoquinazoline.
A mixture of p-bromosulphonylhydrazine (2.51gm, 0.01 mole) and 2-ethoxycarbonyl-4-ketoquinazoline (2.18 gms, 0.01mole) was taken in a three neck flask fitted with a water condensor and a mechanical stirrer. The mixture was refluxed on a water bath for 5 hours using dry methonal as a solvent. On completion, the reaction mixture was filtered hot. Excess of solvent was evaporated and the remaining solid was crystallised
and the remaining solid was crystallised from ethanol to furnish white needles.

Melting Point 215°C, yield 73%

**Found** : C:42.50%, H:2.62% and N:13.22%

C_{15}H_{11}O_{4}N_{4}S Br requires: C:42.55%, H:2.6% and N:13.25%

11 2-N-(p-Toluenesulphonyl)-hydrazinocarbonyl-3(H)-4-ketoquinazoline

An equimolar amount of p-toluenesulphonylhydrazine (2.07 gm, 0.01 mole) and 2-ethoxy-carbonyl-3(H)-4-ketoquinazoline (2.18 gm, 0.01 mole) was taken in a three neck flask fitted with a water condensor and a mechanical stirrer. The reaction mixture was refluxed for 5 hours using dry benzene (50 ml) as a solvent, with constant stirring. On completion, it was filtered hot and excess of solvent was evaporated The solid obtained was crystallised from methanol which gave white needles.

Melting Point 221°C, yield 40%

**Found** : C:59.65%, H:4.35% and N:17.4%

C_{16}H_{14}O_{4}N_{4}S requires: C:59.62%, H:4.34% and N:17.39%

12 2-N-(p-Chlorobenzenesulphonyl)-hydrazinocarbonyl-3(H)-4-ketoquinazoline

It was also obtained by direct condensation of an equimolar amount of p-chlorobenzenesulphonylhydrazine (2.07 gm, 0.01 mole) and 2-ethoxycarbonyl-3(H)-4-
ketoquinazoline (2.17 gms, 0.01 mole). The mixture is taken in the three neck flask fitted with a water condenser and a mechanical stirrer. The reaction mixture was refluxed for 5 hours, with constant stirring and using dry benzene (50 ml) as a solvent, and worked up as described earlier. The product obtained was crystallised from ethanol to give colourless needles.

Melting Point 198°C, yield 77%

Found : C:47.44%, H:2.87% and N: 14.75%

C_{15}H_{11}O_{4}N_{4}S_{4}K requires : C:47.43%, H:2.89% and N:14.75%

It was also obtained by direct condensation of an equimolar amount of p-bromobenzenesulphonylhydrazine (2.51 gm 0.01 mole) and 2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (2.94 gms, 0.01 mole).

The mixture was taken in a three neck flask fitted with a water condenser and a mechanical stirrer and refluxed for 5 hours, with constant stirring and using dry benzene (50 ml) as solvent. It was worked up as described earlier. The product obtained was crystallised from methanol to give white fluffy needles.

Melting point 130°C, yield 62%

Found : C:52.62% H:3.15% N:11.70%

C_{15}H_{11}O_{4}N_{4}S_{4}Br requires : C:52.60% H:3.13% N:11.69%
2-N-(p-Bromobenzenesulphonyl)-hydrazino carbonyl-3-phenyl-4-ketoquinazoline

It was also obtained by direct condensation of an equimolar amount of p-bromobenzenesulphonylhydrazine (2.51 gm, 0.01 mole) and 2-ethoxycarbonyl-3-phenyl-4-keto-quinazoline (2.94 gms, 0.01 mole). The mixture was taken in a three neck flask fitted with a water condensor and a mechanical stirrer and refluxed for 5 hours with constant stirring and using dry benzene (50 ml) as solvent. It was worked up as described earlier. The product obtained was crystallised from methanol to give white fluffy needles. Melting Point 130°C yield 62%

Found : C:52.62%, H:3.15% and N:11.70%

C_{21}H_{15}O_4 N_4 SBr requires: C:52.60%, H:3.13% and N:11.69%

2-N-(p-Chlorobenzenesulphonyl)-hydrazinocarbonyl-3-phenyl-4-ketoquinazoline

A mixture of p-chlorobenzenesulphonylhydrazine (2.07 gms 0.01 mole) and 2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (2.94 gms 0.01 mole) was taken in a three neck flask fitted with a water condensor and a stirrer. The reaction mixture was refluxed for 5 hours, with constant stirring and using dry benzene (50 ml) as solvent. On completion, benzene was distilled off and the residue was crystallised from ethanol to give white needles.
Melting Point 126°C, Yield 70%

Found : C: 55.40%, H: 3.33% and 
N: 12.33%

C_{21}H_{15}O_{4}N_{4}SCl : C: 55.44%, H: 3.3% and 
requires N: 12.32%

15 2-N-(p-Toluenesulphonyl)-hydrazinocarbonyl-3-phenyl-4-ketoquinazoline

A mixture of p-toluenesulphonylhydrazine (1.80 gms, 0.01 mole) and 
2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (2.94 gms, 0.01 mole) was taken in a three neck flask 
fitted with a water condensor and a stirrer. The 
reaction mixture was refluxed for 5 hours, with 
constant stirring and using dry benzene (50ml) as 
a solvent. On completion, benzene was distilled 
off and the residue was crystallised from ethanol 
to give white needles.

Melting Point 95°C, Yield 88%

Found : C: 60.78%, H: 4.15% and 
N: 12.89%

C_{22}H_{18}O_{4}N_{4}S requires: C: 60.82%, H: 4.14% and 
N: 12.90%

16 2-N'(p-Bromobenzenesulphonyl)-hydrazino carbonyl- 
3-anilino-4-ketoquinazoline

A mixture of p-bromobenzenesulphonylhydrazine 
(2.51 gms 0.01 mole) and 2-ethoxycarbonyl-3-anilino- 
4-ketoquinazoline (3.09 gms, 0.01 mole) was taken 
in a three neck flask fitted with a water
condensor and a mechanical stirrer. The reaction mixture was refluxed for 5 hours with constant stirring and using dry benzene as solvent. On completion benzene was distilled off and the residue was crystallised from ethanol which gave white needles.

Melting Point 140°C Yield 94%
Found : C:49.0%, H:3.09% and N:13.59%

C_{21}H_{16}O_{4}N_{5}Br requires: C:49.02%, H:3.11% and N:13.60%

2-N-(p-Toluenesulphonyl)-hydrazinocarbonyl-3-anilino-4-ketoquinazoline

Equimolar mixture of p-toluenesulphonylhydrazine (1.50 gms, 0.01 mole) and 2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.09 gms, 0.01 mole) was taken in the three neck flask fitted with a water condensor and a mechanical stirrer. The reaction mixture was refluxed for 5 hours, with constant stirring and using dry benzene as a solvent. On completion, benzene was distilled off and the residue was crystallised from ethanol to gave pale yellow needles.

Melting Point 110°C, Yield 98%
Found : C:57.19%, H:3.65% and N:15.19%

C_{22}H_{17}O_{4}N_{5} requires : C:57.26%, H:3.68% and N:15.18%
18 2-N-(p-Chlorobenzensulphonyl)-hydrazinocarbonyl-3-anilino-4-ketoquinazoline

An equimolar mixture of p-chlorobenzensulphonyl-hydrazine (2.07 gms, 0.01 mole) and 2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.09 gms, 0.01 mole) was taken in a three neck flask, fitted with a water condensor and a mechanical stirrer. The reaction mixture was refluxed for 5 hours, with constant stirring and using dry benzene as a solvent. On completion, benzene was distilled off and the residue was crystallised from ethanol, which gave cream coloured needles.

Melting Point 115°C, Yield 92%

Found : C:56.12%, H:3.60% and N:14.88%

C\textsubscript{22}H\textsubscript{17}O\textsubscript{4}N\textsubscript{5}Cl requires C:56.11%, H:3.61% and N:14.87%

19 6-Bromo-2-N-(p-bromobenzensulphonyl)-hydrazinocarbonyl-3(H)-4-ketoquinazoline

Equimolar amount of p-bromobenzensulphonylhydrazine (2.51 gms, 0.01 mole) and 6-bromo-2-ethoxy carbonyl-3(H)-4-ketoquinazoline (2.97 gms, 0.01 mole) was taken in dry benzene (50 ml) and proceeded as described earlier. The product obtained was crystallised from ethanol to give yellow coloured needles.

Melting Point : 265°C, Yield 90%

Found : C:35.80%, H:1.90%

N:11.0% and Br:31.80%
20 6-Bromo-2-N-(p-toluenesulphonyl)-hydrazinocarbonyl-3(H)-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of p-toluenesulphonylhydrazine (1.8 gms, 0.01 mole) and 6-bromo-2-ethoxycarbonyl-3(H)-4-ketoquinazoline (2.97 gms 0.01 mole) using dry benzene as a solvent. It was proceeded as described earlier. The product obtained was crystallised from ethanol to give yellow needles.

Melting Point 285°C, yield 63%

Found: C:47.88%, H.3.22%

N:13.89% and Br:19.94%

C_{15}H_{10}O_4N_4SBr_2 requires C:55.85%, H:1.99%

N:11.0% and Br:31.80%

21 6-Bromo-2-N-(p-chlorobenzenesulphonyl)-hydrazinocarbonyl-3(H)-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of p-chlorobenzenesulphonylhydrazine (2.07 gms, 0.01 mole) and 6-bromo-2-ethoxycarbonyl-3(H)-4-ketoquinazoline (2.97 gms, 0.01 mole) using dry benzene as a solvent. It was proceeded as described earlier. The product obtained was crystallised from ethanol to give white needles.

Melting Point 260°C, Yield 98%
Found: C: 39.30%, H: 2.20%, N: 12.20% and Br: 17.45%

C\textsubscript{15}H\textsubscript{10}O\textsubscript{4}N\textsubscript{4}SClBr: C: 39.25%, H: 2.18%

22 6-Bromo-2-N-(p-bromobenzenesulphonyl-hydrazino-carbonyl-3-phenyl-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of p-bromobenzenesulphonylhydrazine (2.5 gms, 0.01 mole) and 6-bromo-2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (3.71 gm 0.01 mole) using dry benzene as a solvent. It was proceeded as described earlier. The product obtained was crystallised from methanol to give white needles.

Melting Point 165°C, Yield 79%

Found: C: 45.10%, H: 2.51%, N: 10.0% and Br: 28.56%

C\textsubscript{21}H\textsubscript{14}O\textsubscript{4}N\textsubscript{4}SBr\textsubscript{2}: C: 45.16%, H: 2.50%

23 6-Bromo-2-N-(p-toluenesulphonyl)-hydrazinocarbonyl-3-phenyl-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of p-toluenesulphonylhydrazine (1.8 gms, 0.01 M) and 6-bromo-2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (3.71 gm, 0.01 M) using dry benzene as a solvent. It was proceeded as prescribed earlier. The product obtained was crystallised from methanol to give white needles.
Melting Point 120°C Yield 74%

Found : C:51.49% H:3.33%
        N:10.90% and Br:15.51%

\[ \text{C}_{22}\text{H}_{17}\text{O}_{4}\text{N}_{4}\text{SBr} \] : C:51.46%, H:3.31%
requires N:10.91% and Br:15.59%

24 6-Bromo-2-N'(p-chlorobenzenesulphonyl)-hydrazino-carbonyl-3-phenyl-4-ketoquinazoline

It was obtained by direct condensation of equimolar amount of p-chlorobenzenesulphonylhydra-
zine (2.07 gm, 0.01 mole) and 6-bromo-2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline
(3.71 gm, 0.01 mole) using dry benzene as a solvent. It was proceeded as described earlier.
The product obtained was crystallised from ethanol to give white needles. Melting Point 205°C, yield 61%

Found : C:41.65% H:2.68%
        N:8.84% and Br:12.50%

\[ \text{C}_{22}\text{H}_{17}\text{O}_{4}\text{N}_{4}\text{SClBr} \] : C:41.67% H:2.68%
requires N:8.83% and Br:12.52%

25 6-Bromo-2-N'(p-Bromobenzenesulphonyl)-hydrazino-carbonyl-3-anilino-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of p-bromobenzenesulphonylhydra-
zine (2.5 gms 0.01 mole and 6-bromo-2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.88 gms, 0.01 M)
using dry benzene as a solvent. It was proceeded as described earlier. The product obtained was crys-
tallised from ethanol to give white needles.

Melting Point 200°C, yield 23%
2-N"-(p-chlorobenzenesulphonyl)-hydrazinocarboyln-3-anilino-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of p-toluenesulphonylhydrazine (1.8 gms 0.01 mole) and 6-bromo-2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.88 gms, 0.01 mole) using dry benzene as a solvent. It was proceeded as described earlier. The product obtained was crystallised from ethanol to give white needles.

Melting Point 177°C Yield 32%

Found : C:48.88%, H:2.95%
        N:12.95% and Br:14.80%

C_{21}H_{15}O_{4}N_{5}Br requires

26

C_{22}H_{16}O_{4}N_{5}Br requires

2-N"-(p-chlorobenzenesulphonyl)-hydrazino carbonyl-3-anilino-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of p-chlorobenzenesulphonylhydrazine (2.07 gms, 0.01 mole) and 6-bromo-2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.88 gms 0.01 mole) using dry benzene as a solvent. It was proceeded as described earlier. The product obtained was crystallised from ethanol to give white needles.

Melting Point 200°C, yield 36%
\[
\text{Found: C:45.92\%, H:2.90\%
N:12.74\% and Br:14.56\%}
\]
\[
\text{C}_{21}\text{H}_{16}\text{O}_6\text{N}_4\text{ClBr: C:45.9\%, H:2.91\%}
\]
\[
\text{requires: N:12.73\% and Br:14.55\%}
\]
SYNTHESIS OF 2-N-(SUBSTITUTED BENZENESULPHONYL)-OXAMOYL-HYDRAZINOCARBONYL-4-KETOQUINAZOLINE WITH SUBSTITUENTS IN POSITION 3 AND 4

1 Ethoxalyl chloride from Diethyl Oxalate

Method I

Anhydrous potassium acetate ((84 gms 1.0 M) was added with stirring to the solution of freshly diluted diethyl oxalate (146 gms, 1.0 mole) in absolute alcohol (300 ml) and the mixture was refluxed for 4 hours on a steam bath. It is then distilled to remove ethanol and ethylacetate. The residual monocr potassiu m ethyl oxalate was mixed with thionyl chloride (120 gms 1.0 mole) and heated for 6 hours under reflux on a steam bath. The reaction mixture is cooled, decanted and distilled when ethoxalyl chloride distills over at 130-134°C. It was purified by redistillation B.P. 131°C, colourless transparent liquid, with strong odour of HCl. Yield 50%

Method II

The mixture of phosphorous pentachloride (20 gms) and freshly distilled diethyloxalate (14.2 gms) was refluxed on a oil bath for 10 hours, accurately at 129° to 130°C. POCl₃ and other higher boiling fractions were removed by distillation under vacuum as 1st and 3rd factors. The intermediate fraction was collected and repeatedly distilled to get pure ethoxalyl chloride. Melting Point 130-132°C, Yield 40%
2-Hydrazinocarbonyl-3(H)-4-ketoquinazoline

Hydrazine hydrate (50% 5 ml) was added dropwise to a cooled mixture of 2-ethoxycarbonyl-3(H)-4-ketoquinazoline (2.18 gms, 0.01 mole) and methanol (50 ml). It reacts spontaneously and a yellow mass was formed. The reaction mixture was refluxed for 4 hours on a water bath. On completion, filtered hot. The filtrate was allowed to stand overnight at room temperature, which gave pale yellow needles.

Melting Point 247°C, Yield 86%

Found : C: 52.45%, H: 3.89%
        N: 27.19%

C₉H₈O₂N₂ requires : C: 52.42%, H: 3.88%,
                     and N: 27.18%

2-Ethoxalylhydrazinocarbonyl-3(H)-4-ketoquinazoline

Ethoxalyl chloride (1.37 gms, 0.01 mole) triethylamine (1.01 gm, 0.01 mole) and 2-hydrazinocarbonyl-3(H)-4-Ketoquinazoline (2.06 gms, 0.01 mole) was mixed in dry benzene 20 ml) in a three neck flask fitted with a water condenser and a mechanical stirrer. The reaction mixture was refluxed for 8 hours. On completion, the reaction mixture was filtered hot and the filtrate was made free from benzene by distillation. The product was crystallised from the mixture of ethanol and ethylacetate (1:1) to furnish white needles.

Melting Point 241°C, yield 52%
Found : C:50.90%, H:4.52% & N:18.33%

C₁₃H₁₄O₅N₄ : C:50.98%, H:4.5% and N:18.30%

4 2-N-(p-bromobenzenesulphonyl)- oxamoylhydrazinocarbonyl-3(H)-4-ketoquinazoline

An equimolar amount of 2-ethoxalylhydrazinocarbonyl-3(H)-4-ketoquinazoline (3.06 gms 0.01 mole) and p-bromobenzenesulphonamide (2.22 gms 0.01 mole) was dissolved in methanol (25 ml) and refluxed for 2 hours on a water bath. On completion, filtered hot, which on cooling, gave yellowish white needles.

Melting Point 180°C. Yield 40%

Found : C:45.94%, H.3.40% and N:14.10%

C₁₉H₁₇O₇N₅BrS : C:45.96%, H:3.42% and N:14.11%

5 2-N-(p-toluenesulphonyl)- oxamoylhydrazinocarbonyl-3(H)-4-ketoquinazoline

It was also obtained by direct condensation of 2-ethoxalylhydrazinocarbonyl-3(H)-4-ketoquinazoline (3.06 gms 0.01 mole) and p-toluenesulphonamide (1.71 gms 0.01 mole) using methanol (25 ml) as a solvent. It was proceeded as described earlier.

The product obtained was recrystallised from methanol to furnish white needles.

Melting Point 172°C, Yield 42%
6 2-N'-(p-chlorobenzenesulphonyl)-oxamoyl-hydrazino-carbonyl-3(H)-4-ketoquinazoline

It was also obtained by direct condensation of equimolar amount of 2-ethoxalylhydrazinocarbonyl-3(H)-4-ketoquinazoline (3.06 gm 0.01 mole) and p-chlorobenzene-sulphonamide (1.91 gm 0.01 mole) using methanol as a solvent. It was proceeded as described earlier. The product obtained was recrystallized from methanol to give gelatinous white needles.

Melting Point 227°C, yield 38%

Found : C:50.50%, H:3.77%
        N:15.52%

\[ \text{C}_{19}\text{H}_{17}\text{O}_{7}\text{N}_{5}\text{Cl}_5 \]
requires : C:50.4%, H:3.76%
           N:15.50%

7 2-(N-hydroxy)-oxamidemhydrazinocarbonyl-3(H)-4-ketoquinazoline

It was obtained by the action of hydroxylamine hydrichloride (1 gm, 0.03 mole) on 2-ethoxalylhydrazinocarbonyl-3(H)-4-ketoquinazoline (3.06 gm, 0.01 mole) in the presence of sodium metal (0.03 mole) in methanol (25 ml). The mixture was stirred well and kept at room temperature overnight. Then neutralized (pH=7) with dilute hydrochloric acid and filtered and
concentrated, to furnish fluffy cotton like needles.

Melting Point 315°C, yield 55%

<table>
<thead>
<tr>
<th>Found</th>
<th>C:45.0%, H:3.77% and N:23.88%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11}H_{11}O_5N_5 requires</td>
<td>C:45.05%, H:3.75% and N:23.89%</td>
</tr>
</tbody>
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8 2-Hydrazinocarbonyl-3-phenyl-4-ketoquinazoline

Hydrazine hydrate (50% 5 ml) was added slowly to a cooled mixture of 2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (2.94 gm 0.01 mole) in (25 ml) methanol. Immediately white needles separate ultimately forming a white mass. The reaction mixture was refluxed on a water bath for 2 hours. On completion, filtered hot. The product obtained was recrystallised from a mixture of ethanol and ethyl acetate (1:1) to furnish white needles.

Melting point 267°C yield 42%

<table>
<thead>
<tr>
<th>Found</th>
<th>C:64.30%, H:4.3% and N:20.02%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{15}H_{12}N_4O_2 requires</td>
<td>C:64.28%, H:4.28% and N:20.0%</td>
</tr>
</tbody>
</table>

9 2-Ethoxyalylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline

Ethoxalyl chloride (1.37 gms, 0.01 mole) triethylamine (1.01 gms 0.01 mole) and 2-hydrazino carbonyl-3-phenyl-4-ketoquinazoline (2.8 gm, 0.01 mole) was mixed in dry benzene (20 ml) in a three neck flask, fitted with a water condenser and a
stirrer. The mixture was refluxed for 8 hours and worked up as described earlier. The product obtained was recrystallised from a mixture of ethanol and ethyl acetate (1:1) to furnish white cotton like needles.

Melting Point 300°C Yield 40%
Found: C:60.05%, H:2.90%
and N:14.6%

C₁₉H₁₁N₄O₅ requires C:60.0% H:2.89% and N:14.7%

10 2-N(p-Bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline

A mixture of p-bromobenzenesulphonamide (2.36 gms, 0.01 mole) and 2-ethoxalylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline (3.8 gms 0.01 mole) was taken in hard dry glass tube and heated at 150°C for 1 hour till a homogenous mass was formed. The mass was cooled to room temperature and extracted with methanol, which gave pale yellow granules.

Melting point 160°C yield 72%

Found: C:52.65% H:2.30, and N:12.1%

C₂₅H₁₃O₆N₅SBr requires C:52.63% H:2.28% and N:12.2%
2-N-(p-toluenesulphonyl)- oxamoylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline.

It was also obtained by direct fusion of p-toluenesulphonamide (1.71 gm, 0.01 mole) and 2-ethoxalylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline (3.8 gms, 0.01 mole). The mixture was taken in a hard glass tube and heated at 150°C for 1 hour, till a homogenous mass was formed. The mass was cooled and extracted with methanol, which gave pale yellow needles. Melting Point 127°C, yield 60%

Found : C:61.75%, H:3.09% and N:13.87%

C_{26}H_{16}O_{6}N_{5}S : C:61.78% H:3.16% and requires N:13.86

2-N-(p-chlorobenzenesulphonyl)- oxamoyl hydrazinocarbonyl-3-phenyl-4-ketoquinazoline

A mixture of p-chlorobenzenesulphonamide (1.9 gms, 0.01 mole) and 2-ethoxalylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline (3.8 gm, 0.01 mole) was taken in a hard glass tube and heated together a 150°C for an hour. The mass obtained was extracted with methanol to furnish yellow needles. Melting Point 145°C, Yield 58%

Found : C:57.04%, H:2.5% N:13.4%

C_{25}H_{13}O_{6}N_{5}SCl : C:57%, H:2.47% N:13.32% requires
13 2-(N-hydroxy)-oxamidehydrazinocarbonyl-3-phenyl-4-ketoquinazoline

It was obtained by the action of hydroxylamine hydrochloride (1 gm 0.03 mole) on 2-ethoxalylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline (3.8 gm, 0.01 mole) in the presence of sodium metal (0.03 mole) in methanol (25 ml). The mixture was stirred well and kept at room temperature overnight. It was worked up as described earlier. The product obtained was crystallised from ethanol to furnish fluffy cotton like needles.

Melting Point 143°C, yield 42%

Found : C:55.55%, H:2.20% N:19.05%
C₁₇H₈N₅O₅  : C:55.5%, H:2.17% N:19.07% requires

14 2-Ethoxalylhydrazinocarbonyl-3-amino-4-ketoquinazoline

Ethoxalyl chloride (1.37 gm, 0.01 mole) triethylamine (1.01 gm 0.01 mole) and 2-hydrazinocarbonyl-3-amino-4-ketoquinazoline (2.1 gms 0.01 mole) was mixed in dry benzene (20 ml) in a three neck flask, fitted with a water condensor and a stirrer. The reaction mixture was refluxed for 8 hours with constant stirring and worked up as described earlier. The product obtained was crystallised from methanol to give pale yellow needles.

Melting Point 100°C Yield 90%
15 2-(N'-hydroxy)-oxamidehydrazinocarbonyl-3-amino-4-ketoquinazoline

It is obtained by the action of hydroxylamine hydrochloride (1 gm, 0.03 mole) on 2-ethoxalylhydrazinocarbonyl-3-amino-4-ketoquinazoline (3.19 gms 0.01 mole) in the presence of sodium metal (0.03 mole) in methanol (25 ml) The mixture is stirred well and kept at room temperature overnight. It is worked up as described earlier. The product obtained is crystallised from ethanol to give white needles. Melting Point 145°C, yield 37%

Found
\[C_{13}H_{13}O_5N_5\] : C:43.15%, H:3.30% N:27.49%

requires

16 2-N'-(p-bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline.

A mixture of p-bromobenzenesulphonamide (2.5 gm, 0.01 mole) and 2-ethoxalylhydrazinocarbonyl-3-amino-ketoquinazoline (3.19 gm 0.01 mole) is dissolved benzene (25 ml) and taken in a three neck flask, fitted with a condensor and a stirrer. The mixture is refluxed for 2 hours , on completion, benzene is distilled off and the residue is crystallised from ethanol and ethylacetate mixture (1:1) to give white needles. Melting Point 150°C, yield 49%
17 Acetyl derivative of 2-N'-(p-bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline.

2-N'-(p-Bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline (0.5gm), is dissolved in 2N hydrochloric acid and a little crushed ice was added. A solution of 5gm of hydrated sodium acetate in 25ml water was introduced, followed by 5ml of acetic anhydride. The reaction mixture is stirred well until the odour of acetic anhydride disappears. The solid acetyl derivative was collected and recrystallised from dilute alcohol to give white needles. Melting point 172°C, yield 58%.

Found : C:41.30%, H:2.75%, N:15.25% and Br:14.50%

C₁₉H₁₅O₂N₆SBr requires : C:41.37%, H:2.72%, N:15.24% and Br:14.51%.

18 p-Toluenesulphonyl derivative of 2-N'-(p-bromobenzene-sulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline.
2-N'-(p-Bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline (lgm), is treated with 4mols of 10 percent, sodium or potassium hydroxide solution (20ml), 1.5moles of p-toluenesulphonyl chloride is added in small portions with constant stirring. The reaction mixture is gently warmed to remove the excess acid chloride. Then acidified with dilute hydrochloric acid and the sulphonamide is filtered off. Recrystallised from alcohol to give white needles. Melting point 150°C, yield 63%.

Found : C: 41.94%, H: 2.90%, N: 12.25%

and Br: 11.65%

\[ C_{24}H_{20}O_8N_6S_2Br \]

requires : C: 41.92%, H: 2.91%, N: 12.22%

and Br: 11.64%

It is also obtained by direct condensation of p-toluenesulphonamide (2.5gms, 0.01mole) and 2-ethoxalyl-hydrazinocarbonyl-3-amino-4-ketoquinazoline (3.19gm, 0.01mole). The mixture is taken in three neck flask provided with a water condensor and a stirrer and refluxed for 2 hours with constant stirring, using benzene (25ml) as solvent. On completion, benzene is
distilled off and the residue is crystallised from ethanol and ethylacetate mixture (1:1) to furnish cream coloured needles.

Melting Point 110°C, yield 80%
Found : C:48.65% H:3.65% N:18.89%
\[ C_{18}H_{16}O_6N_6S \] : C:48.64% H:3.6% N:18.91%
requires

20 Acetyl derivative of 2-N'-(p-toluenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline

It is obtained by the action of excess of acetic anhydride and sodium acetate on 2-N'-(p-toluenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline in aqueous solution, as described earlier. The acetyl derivative is recrystallised from dilute alcohol to give colourless shining plates.
Melting point 100°C, yield 44%.

Found : C:47.81%, H:3.60% and N:16.76%.
\[ C_{20}H_{18}O_{7}N_6S \] requires: C:47.80%, H:3.58% and N:16.70%
21 p-Toluenesulphonyl derivative of 2-N'-(p-toluenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline.

It is obtained by the action of excess of p-toluenesulphonyl chloride on 2-N'-(p-toluenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-ketoquinazoline. It is proceeded as described earlier and the product obtained is recrystallised from dilute alcohol to give colourless needles.

Melting point 120°C, yield 55%.

Found: C: 52.07%, H: 4.05% and N: 13.50%.

C₂₇H₂₅O₉N₆S₂ requires: C: 52.0%, H: 4.01% and N: 13.48%.

22 2-N'-(p-chlorobenzenesulphonyl)oxamoyl-hydrazino-carbonyl-3-amino-4-ketoquinazoline

It is also obtained by direct condensation of p-chlorobenzenesulphonamide (2.5 gms, 0.01 mole) and 2-ethoxalylhydrazineocarbonyl-3-amino-4-ketoquinazoline (3.19 gms 0.01 mole). It is proceeded as described earlier. The product obtained is crystallised from a mixture of ethanol and ethylacetate (1:1) to give cream coloured needles.

Melting Point 125°C yield 33.13%
Found :  C:43.92%, H:2.8%, N:18.05%

C_{17}H_{13}O_{6}N_{6}S_{1}Cl :  C:43.9%, H:2.79%, N:18.08%

requires

23 Acetyl derivative of 2-N'-(p-chlorobenzensulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline.

It is obtained by the action of excess of acetic anhydride and sodium acetate on 2-N'-(p-chlorobenzensulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline in aqueous solution, as described earlier. The acetyl derivative is recrystallised from dilute alcohol to give white needles. Melting point 145°C, yield 62%.

Found :  C:43.65%, H:2.55% and N:16.09%.

C_{19}H_{14}O_{7}N_{6}S_{1}Cl :  C:43.63%, H:2.67% and N:16.07%

requires

24 p-Toluenesulphonyl derivative of 2-N'-(p-chlorobenzensulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline.

It is obtained by the action of excess of p-toluenesulphonyl chloride on 2-N'-(p-chlorobenzensulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline. It is proceeded as described earlier and the product is recrystallised from dilute alcohol to give colourless needles. Melting point 137°C, yield 60%. 

2-Hydrazinocarbonyl-3-anilino-4-ketoquinazoline

Hydrazine hydrate (50%, 5ml) was added slowly to a cooled mixture of 2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.09 gms, 0.01 mole) and methonal (25 ml) instantly white needles separate. The mixture is refluxed on a water bath for 3 hours. On completion, it is filtered hot. The hot filtrate on cooling furnished white needles. Melting point 90°C, yield 69%.

Found : C:61.0%, H:4.5%, N:28.5%
C_{15}H_{13}N_5O_2 requires : C:61.01%, H:4.4%, N:28.47%

19 2-Ethoxalylhydrazinocarbonyl-3-anilino-4-ketoquinazoline

Ethoxalylchloride (1.37 gms, 0.01 mole), triethylamine (1.01 gms, 0.01 mole) and 2-hyrazino-carbonyl-3-anilino-4-ketoquinazoline (2.95 gms, 0.01 mole) was mixed in dry benzene (20ml) in a three neck flask, provided with a water condensor and a stirrer. The mixture is refluxed for 8 hours and worked up as described earlier. The product obtained is recrystallised from a mixture of ethanol and ethylalacetate (1:1) to furnish yellow coloured needles. Melting point 100°C, yield 65%.
27 2-Hydrazinocarbonyl-3-anilino-4-ketoquinazoline.

Hydrazine hydrate (50%, 5 ml) was added slowly to a cooled mixture of 2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.09 gms, 0.01 mole) and methanol (25 ml), instantly, white needles separate. The mixture is refluxed on a water bath for 3 hours. On completion, it is filtered hot. The hot filtrate on cooling, furnishes white needles.

Melting point 90°C, yield 69%.

Found : C:61.0%, H:4.5%, N:28.5%.
C15H13N5O2 requires : C:61.01%, H:4.4%, N:28.47%.

28 Ethoxalylhydrazinocarbonyl-3-anilino-4-ketoquinazoline

Ethoxalyl chloride (1.37 gms, 0.01 mole), triethylamine (1.01 gms, 0.01 mole) and 2-hydrazinocarbonyl-3-anilino-4-ketoquinazoline (2.95 gms, 0.01 mole) was mixed in dry benzene (20 ml) in a three neck flask, provided with a water condensor and a stirrer. The mixture is refluxed for 8 hours and worked up as described earlier. The product obtained is recrystallised from a mixture of ethanol and ethylacetate (1:1) to furnish yellow coloured needles.

Melting point 100°C, yield 65%.
29 2-N'(p-bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-anilino-4-ketoquinazoline

Equimolar amount of p-bromobenzenesulphonamide (2.36 gm, 0.01 mole) and 2-ethoxalylhydrazinocarbonyl-3-anilino-4-ketoquinazoline (3.95 gms, 0.01 mole) is taken in dry benzene (25 ml) in a three neck flask. The mixture is refluxed, with constant stirring for 2 hours. It is worked up as described earlier. The product obtained is crystallised from ethanol and ethylacetate mixture (1:1) to provide yellow needles.

Melting Point 140°C yield 20%

Found : C:75.90% H:5.0% N:11.95%
C₂₅H₂₀N₅O₇SBr requires : C:75.94% H:5.06% N:11.96%

30 2-N'(p-toluenesulphonyl)-oxamoylhydrazinocarbonyl-3-anilino-4-ketoquinazoline

Equimolar amount of p-toluenesulphonamide (1.71gm, 0.01 mole) and 2-ethoxalylhydrazinocarbonyl-3-anilino-4-ketoquinazoline (3.95 gms, 0.01 mole) is taken in dry benzene (25 ml) in a three neck flask. The mixture is refluxed for 2 hours, with constant stirring and worked up as described earlier. The product obtained is crystallised from ethanol and ethylacetate mixture (1:1) to give pale yellow needles.

Melting Point 123°C yield 45%
Equivol amount of p-chlorobenzenesulphonamide (1.91 gm 0.01 mole) and 2-ethoxalylhydrazino-carbonyl-3-anilino-4-ketoquinazoline (3.95 gms 0.01 mole is taken in dry benzene (25 ml) in a three neck flask. The mixture is refluxed for 2 hours with constant stirring and worked up as described earlier. The product obtained is crystallised from ethanol and ethylacetate mixture to give pale yellow needles.

Melting Point 115°C, yield 43%

It is obtained by the action of hydroxylaniline - hydrochloride (1 gm, 0.03 mole) on 2-ethoxalylhydrazinocarbonyl-3-anilino-4-ketoquinazoline (3.95 gms, 0.01 mole) in presence of sodium metal (0.03 mole) in methanol. (25 ml). The reaction mixture is stirred well and kept at room temperature overnight. It is worked up as described earlier. The product obtained is crystallised from ethanol to give pale yellow needles.
33 6-Bromo-2-hydrazinocarbonyl-3(H)-4-ketoquinazoline
Hydrazine hydrate (50%, 5 ml) is added slowly to a
cooled mixture of 6-bromo-2-ethoxycarbonyl-3(H)-
4-ketoquinazoline (2.97 gms, 0.01 mole) and
methanol (25 ml). The reaction mixture was
refluxed for 6 hours and on completion, filtered
hot. From the hot filtrate white coloured fluffy
needles separate instantly. Recrystallised from
ethanol.
Melting Point 305°C, yield 83%
Found : C:37.90%, H:2.5% N:9.83%
and Br:20.01%
C_{9}H_{7}O_{2}N_{2}Br requires : C:37.89%, H:2.45% N:9.8%
and Br:20.07%

34 6-Bromo-2-ethoxalylhydrazinocarbonyl-3(H)-4-keto-
quinazoline
Ethoxalyl chloride (1.37 gm, 0.01 mole)
triethylamine (1.01 gms, 0.01 mole) and 6-bromo-2-
hydrazinocarbonyl-3(H)-4-ketoquinazoline (2.85 gms
0.01 mole) was mixed in dry benzene (25 ml) in a
three neck flask, provided with a water condensor
and a stirrer. The mixture was refluxed on a steam
bath for 8 hours, with constant stirring. On
completion, benzene is distilled off and the
residual solid was crystallised from ethanol to give white fluffy needles.
Melting Point 300°C yield 50%
Found: C:40.52% H:3.08% N:14.51%
and Br:20.79%

\[ C_{13}H_{12}O_5N_4Br \] requires C:40.5%, H:3.18% N:14.54%

35 6-Bromo-2-N\(^{1}\)(p-bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3(H)-4-ketoquinazoline
Equimolar amount of p-bromosulphonamide (2.22 gm, 0.01 mole) and 6-bromo-2-ethoxalylhydrazinocarbonyl-3(H)-ketoquinazoline (3.85 gms 0.01 mole) is refluxed for 2 hours on a water bath, using methanol (25 ml) as a solvent. On completion, filtered hot and the filterate is allowed to stand overnight, which gave white needles.
Melting Point 178°C, yield 52%
Found: C:39.7% H:2.94% N:12.18%
and Br:27.87%

\[ C_{19}H_{16}O_7N_5Br_2S \] : C:39.65% H:2.95% N:12.17%
requires and Br:27.82%

36 6-Bromo-2-N\(^{1}\)(p-toluenesulphonyl)-oxamoylhydrazinocarbonyl-3(H)-4-ketoquinazoline
Equimolar amount of p-toluenesulphonamide (1.71 gm 0.01 mole) and 6-bromo-2-ethoxalylhydrazinocarbonyl-3(H)-ketoquinazoline (3.85 gm, 0.01 mole) is refluxed for 6 hours, on a water bath, using methanol (50 ml) as a solvent. On completion, filtered hot
and the filtrate is allowed to stand overnight which gave pale yellow needles.

Melting Point 130°C, yield 48%

Found : C:46.55% H:3.90% N:13.49%
and Br:15.55%

$C_{20}H_{19}O_7N_7BrS$ : C:46.6% H:3.88% N:13.59%
requires and Br:15.53%

37 6-Bromo-2-N-(p-chlorobenzensulphonyl)-oxamoylhydrazinocarbonyl-3(H)-4-ketoquinazoline

Equimolar amount of p-chlorobenzenesulphonamide (1.91 gm 0.01 mole) and 6-bromo-2-ethoxalylhydrazinocarbonyl-3(H)-4-ketoquinazoline (3.85 gm, 0.01 mole) is refluxed for 6 hours on a water bath, using methanol (50 ml) as a solvent. On completion, filtered hot, which on cooling gave pale yellow granules.

Melting Point 290°C yield 47%

Found : C:42.99% H:3.0% N:13.2%
and Br:14.94%

$C_{19}H_{16}O_7N_7ClSB$ : C:42.97% H:3.01% N:13.9%
requires and Br:14.93%

38 6-Bromo-2-N-(hydroxy)-oxamidehydrazinocarbonyl-3(H)-4-ketoquinazoline

It is obtained by the action of hydroxylamine hydrochloride (0.69 gm 0.01 mole) on 6-bromo-2-ethoxalylhydrazinocarbonyl-3(H)-4-ketoquinazoline
(3.85 gms, 0.01 mole) in presence of sodium metal (0.01 mole) in methanol. The mixture is stirred well and kept at room temperature for 10 hours, and neutralized (pH = 7) with dilute hydrochloric acid and filtered. The filtrate is concentrated to give white fluffy needles.

Melting Point 280°C, yield 40%

Found : C:35.5% H:2.6% N:13.34%
  and Br:21.48%

C_{11}H_{10}O_{5}N_{5}Br requires and Br:21.5%

39  6-Bromo-2-hydrazinocarbonyl-3-phenyl-4-ketoquinazoline

Hydrazine hydrate (50% 5 ml) was added dropwise to a cooled mixture of 6-bromo-2-ethoxycarbonyl-3-phenyl-4-ketoquinazoline (3.71 gms, 0.01 mole) and methanol (50% 25 ml). The mixture is refluxed for 2 hours on a water bath. On completion, filtered hot, which on cooling, furnished white needles. It is crystallised from ethanol.

Melting Point 170°C yield 55%

Found : C:50.15% H:3.10% N:15.60%
  and Br:22.22%

C_{15}H_{11}N_{4}O_{2}Br requires and Br:22.28%

40  6-Bromo-2-ethoxalylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline

It is obtained by the action of ethoxalyl chloride
(1.37 gm 0.01 mole) on 6-bromo-2-hydrazinocarbonyl-3-phenyl-4-ketoquinazoline in presence of triethylamine (1.01 gm 0.01 mole). It is proceeded as described earlier. The product obtained is recrystallised from ethanol to give white needles.

Melting Point 200°C, yield 42%

Found: C:49.65% H:2.4% N:12.22%
and Br:17.45%

C_{19}H_{11}N_{4}O_{5}Br requires: C:49.67% H:2.39% N:12.20%
and Br:17.42%

Equimolar amount of 6-bromo-2-ethoxalylhydrazino-carbonyl-5-phenyl-4-ketoquinazoline (4.5 gms 0.01 mole) and p-bromobenzenesulphonamide (2.36 gm 0.01 mole) mixture is taken in dry methanol (50 ml) and refluxed on a water bath for 5 hours. On completion, filtered hot, which gave white needles on cooling.

Melting Point 150°C yield 19%

Found: C:46.22% H:1.6% N:10.77%
and Br:24.59%

C_{25}H_{12}N_{5}O_{6}Br_{2}S requires: C:46.2% H:1.8% N:10.78%
and Br:24.55%

It is also obtained by direct condensation of 6-bromo-2-ethoxalylhydrazinocarbonyl-3-phenyl-4-
ketoquinazoline 94.59 gms 0.01 mole) add p-toluene-sulphonamide (1.71 gms 0.01 mole) and proceeded as described earlier. The product obtained is recrystallised from ethanol to give white needles.

Melting Point 130°C Yield 77%

Found : C:53.42% H:2.54% N:11.35%
and Br:13.6%

requires : C₂₆H₁₅O₆N₅SBr : C:53.42% H:2.56% N:11.33%
and Br:13.59%

6-Bromo-2-N-(p-chlorobenzenesulphonyl)-oxamoylhydrazino-carbonyl-3-phenyl-4-ketoquinazoline

It is also obtained by direct condensation of 6-bromo-2-ethoxalylhydrazinocarbonyl-3-phenyl-4-ketoquinazoline (4.59 gms 0.01 mole) and p-chlorobenzene-sulphonamide (1.915 gms, 0.01 mole). It is proceeded as described earlier. The product obtained is recrystallised from ethanol to give white needles.

Melting Point 140°C yield 74%

Found : C:49.59% H:1.98% N:11.58%
and Br:13.23%

requires : C₂₅H₁₂O₆N₅SClBr : C:49.5% H:1.9% N:11.57%
and Br:13.23%

6-Bromo-2-N-(hydroxy)-oxamidehydrazino-carbonyl-3-phenyl-4-ketoquinazoline

It is obtained by the action of hydroxyalamine
hydrochloride (0.69 gm 0.01 mole) on 6-bromo-2-
ethoxalylhydrazinocarbonyl-3-phenyl-4-ketoquinaz-
oline (4.59 gms, 0.01 mole) in presence of sodium
metal (0.01 mole) in methanol. The reaction
mixture is stirred well and kept at room
temperature for 10 hours and neutralised (pH = 7)
with dilute hydrochloric acid and filtered. The
filtrate is concentrated to give white needles.
Melting Point 170°C yield 39%
Found : C:45.7% H:1.56% N:15.70%
and Br:17.35%
C_{17}H_{10}N_{5}O_{5}Br requires: C:45.7% H:1.56% N:15.69%
and Br:17.33%

6-Bromo-2-ethoxalylhydrazinocarbonyl-3-amino-4-
ketoquinazoline
It is obtained by the action of ethoxalyl chloride
(1.37gms 0.01 mole) on 6-bromo-2-hydrazinocarbonyl
3-amino-4-ketoquinazoline (3.0 gm 0.01 mole) in
presence of triethylamine (1.01 gm, 0.01 mole). It
is proceeded as described earlier. The product
obtained is recrystallised from ethanol to give
white needles.
Melting Point 243°C yield 39%
Found : C:39.2% H:3.05% N:17.52%
and Br:20.12%
C_{13}H_{12}N_{5}O_{5}Br requires : C:39.19% H:3.08% N:17.53%
and Br:20.12%
6-Bromo-2-N-(hydroxy)-oxamido hydrazinocarbonyl-3-amino-4-ketoquinazoline

It is obtained by the action of hydroxyalmine hydrochloride on monoethylester of 6-bromo-2-ethoxalylhydrazinocarbonyl-3-amino-4-ketoquinazoline (3.98 gms 0.01 mole) in the presence of sodium metal (0.01 mole) in methanol. It is proceeded as described earlier. The product obtained is recrystallised from ethanol to give white needles.

Melting Point 241°C yield 64%

Found : C:34.30% H:2.35% N:21.8% and Br:20.79%

\[ \text{C}_{11}\text{H}_{9}\text{O}_{5}\text{N}_{6}\text{Br} \text{ requires} \]

\[ \text{C}:34.28\% \text{ H}:2.33\% \text{ N}:21.81\% \text{ Br}:20.77\% \]

6-Bromo-2-N-(p-bromobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline

Equimolar amount of 6-bromo-2-ethoxalylhydrazinocarbonyl-3-amino-4-ketoquinazoline (3.98 gms 0.01 mole) and p-bromobenzenesulphonamide (2.36 gms 0.01 mole) is taken in dry methanol (50 ml) in a three neck flask and refluxed on a water bath for 5 hours. On completion, filtered hot, which gave white needles on cooling.

Melting Point 195°C yield 42%

Found : C:34.70% H:2.20% N:14.29% and Br:27.20%

\[ \text{C}_{17}\text{H}_{12}\text{O}_{6}\text{SBr}_{2} \text{ requires} \]

\[ \text{C}:34.69\% \text{ H}:2.21\% \text{ N}:14.28\% \text{ Br}:27.21\% \]
6-Bromo-2-N-(p-toluenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline

It is obtained by direct condensation of 6-bromo-2-ethoxalylhydrazinocarbonyl-3-amino-4-ketoquinazoline (3.98 gms 0.01 mole) and p-toluenesulphamide (1.71 gms, 0.01 mole). The mixture is taken in dry benzene (50 ml) in a three neck flask and refluxed for 5 hours on a water bath and proceeded as described earlier. The product obtained is recrystallised from ethanol to give white needles.

Melting Point 176°C yield 47%

Found: C:41.30% H:3.05% N:15.06%
and Br:15.30%

C_{18}H_{15}O_{6}N_{6}SBr requires:
C:41.30% H:3.05% N:16.05%
and Br:15.29%

6-Bromo-2-N-(p-chlorobenzenesulphonyl)-oxamoylhydrazinocarbonyl-3-amino-4-ketoquinazoline

Equimolar mixture of 6-bromo-2-ethoxalylhydrazinocarbonyl-3-amino-4-ketoquinazoline (3.98 gms 0.01 mole) and p-chlorobenzenesulphonamide (1.915 gms, 0.01 mole) is taken in dry benzene in a three neck flask. The reaction mixture is refluxed for 5 hours with constant stirring. It is proceeded as described earlier. The product obtained is recrystallised from ethanol to give white needles.

Melting Point 261°C yield 46%
Hydrazine hydrate (50% 5 ml) is added dropwise to a cooled mixture of 6-bromo-2-ethoxycarbonyl-3-anilino-4-ketoquinazoline (3.88 gms, 0.01 mole) and methanol (50 ml). The reaction mixture is refluxed for 2 hours on a water bath. On completion, filtered hot which on cooling furnished pale yellow needles.

Melting Point 274°C yield 50%

Found : C:48.01% H:3.22% N:18.72%
and Br:21.40%

C_{15}H_{12}N_{5}O_{2}Br : C:48.12% H:3.20% N:18.17%
requires and Br:21.39%

6-Bromo-2-ethoxalylhydrazinocarbonyl-3-anilino-4-ketoquinazoline

It is obtained by the action of ethoxalylchloride. (1.37 gms 0.01 mole) on 6-bromo-2-hydrazinocarbonyl-3-anilino-4-ketoquinazoline (3.74 gms, 0.01 mole) in presence of triethylamine (1.01 gm 0.01 mole). It is proceeded as described earlier. The product obtained is crystallised from ethanol to give pale yellow needles.

Melting point 95°C yield 52%
Equimolar amount of 6-bromo-2-ethoxalyl-hydrazino carbonyl-3-anilino-4-ketoquinazoline (4.74 gms, 0.01 mole) and p-bromobenzenesulphonamide (2.36 gms 0.01 mole) is taken in dry benzene (50 ml) in a three neck flask and proceeded as described earlier. The product obtained is crystallised from ethanol to give pale yellow needles.

Melting Point 123°C yield 50%

Equimolar amount of 6-bromo-2-ethoxalyl-hydrazino carbonyl-3-anilino-4-ketoquinazoline (4.74 gms, 0.01 mole) and p-toluenesulphonamide (1.71 gm 0.01 mole) is taken in dry benzene (50 ml) is taken in a three neck flask and proceeded as described earlier. The product obtained is crystallised from ethanol to give pale yellow needles.

Melting Point 77°C yield 50%
Equimolar amount of 6-bromo-2-ethoxalyl-hydrazino-carbonyl-3-anilino-4-ketoquinazoline (4.74 gms, 0.01 mole) is taken in dry benzene (50 ml) in a three neck flask. It is proceeded as described earlier. The product obtained is crystallised from ethanol to give pale yellow needles.

Melting point 115°C yield 32%

54 6-Bromo-2-N-(p-chlorobenzenesulphonyl)-oxamoyl-hydrazinocarbonyl-3-anilino-4-ketoquinazoline

It is obtained by the action of hydroxylamine hydrochloride on 6-bromo-2-ethoxalylhydrazino-carbonyl-3-anilino-4-ketoquinazoline (4.74 gm, 0.01 mole) in the presence of sodium metal in methanol (0.23gm, 0.01 mole). It is proceeded as described earlier. The product obtained is crystallised from ethanol to give pale yellow needles.

Melting point 155°C yield 54%
REFERENCES:


