EXPERIMENTAL
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PREPARATION OF ISATINS

Isatin was readily available and its derivatives were prepared from the respective anilines.

Aniline \[\rightarrow\] Isonitrosoacetanilide \[\rightarrow\] Isatin.

Isatins were prepared by the Sandmeyer procedure involving the formation of an isonitrosoacetanilide from an aniline, chloral hydrate and hydroxylamine hydrochloride. The isonitrosoacetanilide was converted into isatin by treatment with conc. sulphuric acid or polyphosphoric acid.

General Procedure:

a) Isonitrosoacetanilides

To a solution of 90 g (0.54 mole) of chloral hydrate in 1200 ml of water in a 5 l. round-bottomed flask, 1300 g of hydrated sodium sulphate was added, followed by a solution of aniline hydrochloride [prepared from 0.5 mole of aniline and 0.52 mole of conc. hydrochloric acid (43 ml. sp. gr. 1.19) in 300 ml of water] and finally a solution of 110 g (1.58 mole) of hydroxylamine hydrochloride in 500 ml of water. The contents of the flask were heated to vigorous boiling (this process required about 40 min.) and cooled under a water tap. The isonitrosoacetanilide
that separated was collected by filtration and purified by recrystallisation from aqueous alcohol.

**p-Chloroisonitrosoacetanilide**

p-Chloroaniline : 63.78 g; chloral hydrate: 90 g; hydrated sodium sulphate : 1300 g; conc. HCl. : 43 ml; hydroxylamine hydrochloride : 110 g; Yield: 75 g (75.5%); m.p. 171 - 172° (aqueous alcohol) (Lit. m.p. 165°).

**b) ISATINS**

Using conc. H₂SO₄ as the cyclising agent

163 ml. of conc. sulphuric acid (p. gr. 1.84) was warmed to 50° in a 1 lit. round bottomed flask fitted with a mechanical stirrer and to this 0.23 mole of dry isonitrosoacetanilide was added at such a rate as to keep the temperature between 60° and 70°. External cooling was applied at this stage to carry out the reaction more rapidly. After the addition was over, the solution was heated to 80° and kept at this temperature for about 10 min. to complete the reaction. The reaction mixture was then cooled to room temperature and poured into 10 times its volume of crushed ice. After standing for about one-half hour, the isatin was filtered, washed with cold water and then air dried. It was purified as described by Marvel and Heirs and recrystallised from alcohol.
5-chloroisatin

p-Chloroisonitrosoacetanilide : 68.5 g; concentrated sulphuric acid : 245 ml. The temperature was maintained at 90-95°C and then heated to 105°C for completion. Yield: 43 g (69%); m.p.249°C (Lit.69 m.p. 246°C).

5-bromoisoatin

To 93 g. isatin suspended in 2000 ml. of water, 30 ml. of bromine was slowly added with stirring. After the addition was over, stirring was continued for 3 h. and the reaction mixture was set aside overnight. The solid was collected, washed with water and recrystallised from alcohol. 5-bromoisoatin was obtained as orange yellow crystals. Yield : 124 g (87%); m.p. 250-252°C (Lit.71 m.p.251-253°C).

5,7-Dibromoisoatin

90 g. of isatin in 1200 ml of 95% alcohol was heated on a steam bath until the isatin was completely dissolved. While the solution was hot, 75 ml of bromine was added dropwise with slow stirring of the mixture. After complete addition of bromine, the mixture was cooled slowly at first and later in ice. The product was washed with water and then with alcohol. Recrystallisation from alcohol furnished long orange-red needles of 5,7-dibromoisoatin. Yield : 149.4 g. (80%); m.p. 250°C (Lit.72 m.p.248-250°C).
PREPARATION OF 3-BUTENOYL CHLORIDE

a) Allyl cyanide

A mixture of allyl alcohol (350 ml) cuprous cyanide (422 g) and conc. hydrochloric acid (500 ml) was stirred well in a three-necked round bottomed flask fitted with a stirrer and a condenser. After 30 min. the reaction mixture turned into a dark pasty mass. Immediately it was set-up for distillation and the distillate coming at 90-95° was collected. The organic layer was separated, dried and redistilled. The fraction distilling between 116-121° was collected. Yield: 250 g.

b) 3-Butenoic acid

A mixture of allyl cyanide (67 g) and conc. hydrochloric acid (d 1.18, 100 ml) was heated with a small flame in a 2 lit round bottomed flask fitted with a lengthy condenser and shaken frequently. After 10 min. voluminous precipitate of ammonium chloride separated and the temperature rose rapidly. The mixture was refluxed for 15 min, allowed to cool and then treated with minimum amount of water (100 ml) to dissolve the ammonium chloride. The upper layer of the acid was separated and the aqueous layer was extracted with ether. The acid and the ether extracts were combined, dried and distilled to remove most of the ether at atmospheric pressure and then remaining
at diminished pressure. The residual liquid was distilled under vacuum. The fraction distilling at 70-72°/9 mm. was collected. Yield: 50 g.

**Purification**

The acid was purified further by dropping the acid (45 g) slowly into a well cooled solution of sodium hydroxide (24 g) in water (80 ml) and removing the non acidic components by extraction with chloroform and adding the alkaline solution solution into well cooled dilute sulphuric acid (300 ml) with stirring. The acid liberated was recovered by extraction with chloroform. It was dried with anhydrous sodium sulphate and distilled. The acid distilling at 69-70°/12 mm. was collected. Yield: 30 g.

C) 3-Butenoyl chloride

Thionyl chloride (24 ml) was taken in a 100 ml Claisen flask fitted with a reflux condenser and a dropping funnel. 3-butenoic acid (22 ml) was slowly added through the dropping funnel into thionyl chloride. After the addition was over, it was refluxed gently for 30 min. on a steam bath. It was then set-up for distillation and the acid chloride distilling at 98-100° was collected. Yield: 20.8 g.

The thionyl chloride used for preparing 3-butenoic chloride was specially purified. Thionyl chloride (500 ml)
was mixed with quinoline (20 ml) and distilled under anhydrous condition. It was redistilled after mixing with triphenylphosphite (15 ml). The colourless thionyl chloride distilling at 76°C was collected.

PREPARATION OF 4-CARBOXY-3-VINYLUQUINOLIN-2-(1H)-ONES (120a-d)

Isatin \(\rightarrow\) Sodioisatin \(\rightarrow\) N-(3-butenoyl)isatin \(\rightarrow\) 4-carboxy-3-vinylquinolin-2-(1H)-one.

The vinylquinolone acids were prepared by condensing sodioisatins with 3-butenoyl chloride and subjecting the resulting N(3-butenoyl)isatins to a Pfitzinger reaction with aqueous alkali.

SODIOISATINS

1) Sodioisatin

0.37 mole (54.6 g) of well powdered and dry isatin was suspended in absolute ethanol (75 ml) in a three-necked R.B. Flask fitted with a mercury sealed stirrer. Sodium ethoxide prepared from 7.2 g of sodium and 150 ml of absolute ethanol, was added with stirring. After 10 min. the sodioisatin was filtered in dry condition, washed successively with absolute ethanol and dry benzene and dried in vacuo. Yield: 52 g.
2) 5-Chlorosodioisatin

5-Chloroisatin: 67.16 g (in 100 ml absolute ethanol):
sodium: 7.2 g; Absolute ethanol: 150 ml; Yield: 68 g.

3) 5-Bromosodioisatin

5-Bromoisatin: 83.58 g (in 100 ml absolute ethanol):
sodium: 7.2 g; Absolute ethanol: 150 ml; Yield: 85 g.

4) 5,7-Dibromosodioisatin

5,7-Dibromoisatin: 112.8 g (in 200 ml absolute ethanol);
sodium: 7.2 g; Absolute ethanol: 150 ml; Yield: 102 g.

4-CARBOXY-3-VINYLQUINOLIN-2(1H)-ONES

1) 4-Carboxy-3-vinyl-2-quinolone (120a) (Modified Procedure)

0.2 mole (35 g) of sodioisatin was suspended in 200 ml of dry benzene in a three necked R.B. Flask fitted with a mercury sealed stirred and an addition funnel 0.2 mole (20.8 g) of 3-butenoyl chloride in 50 ml dry benzene was slowly added with stirring. Perfect anhydrous conditions were maintained during the addition. After the addition, the reaction mixture was heated under reflux for 15 min. cooled and filtered. The clear filtrate was slowly dropped into a boiling solution of KOH (11.2 g in 100 ml H₂O) taken in a three-necked flask provided with
a condenser and a stirrer. After the addition, vigorous stirring was continued for 20 min. and allowed to cool. The aqueous layer was separated and acidified, when the vinylquinolone acid separated as yellow granular powder. It was purified by dissolving in aqueous bicarbonate solution and acidifying the clear solution. Yield: 24 g, m.p. >340° (alcohol).

The procedure adopted is a modified one of the earlier procedure reported from this laboratory and the yield of the acid has been improved from 65% to 80% based on isatin not recovered.

The vinylquinolone acids120b to 120d were similarly prepared, following the above newly designed technique.

2) 6-Chloro-4-carboxy-3-vinylquinolin-2(1H)-one(120b)

5-Chlorosodiumisatin : 40.70 g (in 200 ml dry benzene);
3-butenoyl chloride: 20.8 g. (in 50 ml dry benzene);
potassium hydroxide : 11.2 g (in 100 ml water); Yield: 19.8 g (82% based on 5-chloroisatin not recovered)
m.p. 237-239° (alcohol).

I.R.(KBr) : \( \nu_{\text{max}} = 3025(\text{NH}), 1710-1600 \ \text{cm}^{-1} \) (br-COOH and -NHCQ)
3) 6-Bromo-4-carboxy-3-vinylquinolin-2(1H)-one (I20c)

5-Bromosodioisatin: 49.60 g; in 200 ml dry benzene; 3-butenoyl chloride: 20.8 g (in 50 ml dry benzene); potassium hydroxide: 11.2 g (in 100 ml water); Yield: 23 g (79.5% based on 5-bromoisatin not recovered) m.p. 250° (alcohol).
I.R. (KBr): $\nu_{\text{max}} = 3020 \text{ (NH)}, 1700-1600 \text{ cm}^{-1} \text{ (br.-COOH and NHCO)}$.

4) 6,8-Dibromo-4-carboxy-3-vinylquinolin-2(1H)-one (I20d)

5,7-Dibromosodioisatin: 65.36 g (in 200 ml dry benzene); 3-butenoyl chloride: 20.8 g (in 50 ml dry benzene); potassium hydroxide: 11.2 g (in 100 ml water); Yield: 3.6 g (31% based on 5,7-dibromoisatin not recovered) m.p. 210-215° (alcohol).
I.R. (KBr): $\nu_{\text{max}} = 3010 \text{ (NH)}, 1710-1600 \text{ cm}^{-1} \text{ (br.-COOH and -NHCO)}$

**PREPARATION OF 2-CHLORO-4-CYANO-3-VINYLUINOLINES**

4-Carboxy-3-vinylquinolin-2(1H)-one $\rightarrow$
4-carboxamido-3-vinylquinolin-2(1H)-one $\rightarrow$
2-chloro-4-cyano-3-vinylquinoline.
4-CARBOXYAMIDO-3-VINYLUQUINOLINE-2(1H)-ONES

4-Carboxamido-3-vinylquinoline-2(lH)-one (121a)

To 0.02 mole (4.30 g) of 4-carboxy-3-vinylquinolin-2 (1H)-one suspended in dry benzene (20 ml), was added 5 ml of thionyl chloride (in excess) and refluxed for 45 min. The excess thionyl chloride was removed by co-distillation with benzene and the residue was dissolved in dry chloroform. The chloroform solution was dropped slowly into 200 ml of ammonia solution (25%) with stirring and cooling the flask in an ice bath. Ammonia gas was also passed during the addition. After the addition, stirring was continued for 4-5 hr. and the solid amide that separated was collected. The chloroform layer of the filtrate was separated, washed with water, dried and evaporated to get a further yield of the amide. It was recrystallised from aqueous alcohol. Yield: 3.95 g (92.3%) m.p. > 330°C.

6-Chloro-4-carboxamido-3-vinylquinolin-2(1H)-one (121b)

6-Chloro-4-carboxy-3-vinylquinolin-2(1H)-one: 4.99 g; dry benzene: 20 ml; thionyl chloride: 5 ml (excess); ammonia solution: 200 ml; Yield: 4.5 g (90.5%); m.p. 220° dec. (aq. alcohol).

6-Bromo-4-carboxamido-3-vinylquinolin-2(1H)-one (121c)

6-Bromo-4-carboxy-3-vinylquinoline-2(1H)-one: 5.2 g; dry benzene: 20 ml, Thionyl chloride 5 ml, Ammonia 200 ml, Yield: 4.5 g (78% m.p. > 300°C) (aq.alcohol)
6,8-Dibromo-4-carboxamido-3-vinylquinolin-2(1H)-one (121d)

6,8-Dibromo-4-carboxy-3-vinylquinolin-2(1H)-one; 3.5 g.
dry benzene: 20 ml; thionyl chloride: 5 ml (excess);
ammonia solution: 200 ml; Yield: 1.9 g (53%);
m.p. > 300° (aq. alcohol).

2-CHLORO-4-CYANO-3-VINYLQUINOLINES

2-Chloro-4-cyano-3-vinylquinoline (122a)

0.01 mole (2.14 g) of 4-carboxamido-3-vinylquinolin-2(1H)-one was heated with 10 ml of phosphorus oxychloride on a steam bath for 5 h. The excess phosphorus oxychloride was removed under vacuum and the residue treated with ice water to give a brown solid. It was extracted with benzene, dried (anhydrous Na₂SO₄) and the solvent distilled off. The residue was chromatographed over alumina in benzene. The colourless solid that obtained was recrystallised from benzene-pet. ether to furnish the cyanoquinoine (122a) as colourless needles. Yield: 1.85 g (86%); m.p. 125-126°.

I.R.(KBr): \( \nu_{\text{max}} = 2230\text{(CN)}, 950,970,990 \text{ cm}^{-1}(\text{-CH=CH}_2) \)

Analysis: \( \text{C}_{12}\text{H}_7\text{N}_2\text{Cl} \)

- Found: C 67.33 H 3.38
- Calcd: C 67.13 H 3.26

2,6-Dichloro-4-cyano-3-vinylquinoline (122b)

6-Chloro-4-carboxamido-3-vinylquinolin-2(1H)-one:
2.48 g; phosphorus oxychloride: 10 ml (excess); Yield: 2.0 g (82%); m.p. 156-157°; colourless needles (pet. ether-benzene).
I.R.(KBr):

$\nu_{\text{max}} = 2200 (\text{CN}), 920, 960, 980 \text{ cm}^{-1} \ (\text{-CH=CH}_2)$

**Analysis:**

$\text{C}_{12}\text{H}_6\text{N}_2\text{Cl}_2$ Found: C 57.90 H 2.67

(249) Calcd: C 57.83 H 2.41

6-Bromo-2-chloro-4-cyano-3-vinylquinoline (122c)

6-Bromo-4-carboxamido-3-vinylquinolon-2(-H)-one:

2.93 g; phosphorus oxychloride: 10 ml (excess);
Yield: 2.6 g (89.6%); m.p.: 157-158°; colourless silky needles (pet. ether-benzene).

I.R.(KBr):

$\nu_{\text{max}} = 2210 (\text{CN}), 940, 950, 965 \text{ cm}^{-1} \ (\text{-CH=CH}_2)$

**Analysis:**

$\text{C}_{12}\text{H}_6\text{N}_2\text{Cl}_2\text{Br}$ Found: C 48.88 H 1.88

(293.5) Calcd: C 49.06 H 2.04

6,8-Dibromo-2-chloro-4-cyano-3-vinylquinoline (122d)

6,8-Dibromo-4-carboximido-3-vinylquinolon-2(1H)-one: 1.9 g; phosphorous oxychloride 10 ml (excess)
Yield: 500 mg mpt. 180°.

I.R.(KBr):

$\nu_{\text{max}} = 2210 (\text{CN}), 940, 965 \text{ cm}^{-1} (\text{CH=CH}_2)$
4-Cyano-2,3-dihydropyrrolo(2,3-b)quinolines.

Reaction of 2-chloro-4-cyano-3-vinylquinoline with ammonia in Methanol.

To 0.002 mole (0.428 g) of 2-chloro-4-cyano-vinylquinoline in 50 ml methanol kept at 5° dry ammonia gas bubbled through for 3-4 hrs. The mixture was stirred at room temperature for over night. The methanol was concentrated and the crude material was poured into a column of Neutral alumina. Elution with Benzene:Ethyl acetate (10:1) afforded the dihydro pyrroloquinolines(129a) as an yellow powder. m.p.252° (Recrystalized from chloroform) Yield: 210 mg (53%)

Mass : 195

IR(KBr) :
\[ \nu_{\text{max}} = 2950(\text{NH}), 2250(\text{CN}), 1620, 1500 \text{ cm}^{-1}. \]

Analysis:

\[ \text{C}_{12}\text{H}_{9}\text{N}_3 \quad \text{Found C} \ 73.69 \ H \ : \ 4.29 \]
(195.22)\text{Calcd C} \ 73.84 \ H \ : \ 4.61

N.M.R : \( \delta \) values

<table>
<thead>
<tr>
<th>Value</th>
<th>Description</th>
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<tbody>
<tr>
<td>3.8 ( t,2H,C_3H_2 )</td>
<td>ppm.</td>
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<tr>
<td>3.3 ( t,2H,C_2CH_2 )</td>
<td>ppm.</td>
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<tr>
<td>7.2 ( \text{b.r.s,}1H,\text{NH} )</td>
<td>ppm.</td>
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<tr>
<td>7.3-7.8 ( m,4H,C_3,C_5,C_7 ) and ( C_6-H )</td>
<td>ppm.</td>
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6-Chloro-4-cyano-2,3-dihydropyrrole(2,3-b)quinoline(129b)

2,6-Dichloro-4-cyano-3-vinylquinoline : 120 mg; ammonia gas 2-3 h. mp. >270; methanol 150 ml. Yield : 20 mg (16%).

I.R.(KBr): \( \nu_{\text{max}} = 2950\, (\text{NH}), 2250\, (\text{CN}), 1620\, (\text{C=C}) \, \text{cm}^{-1}. \)

'H N.M.R : Product insoluble in CDCl\(_3\)

6-Bromo-4-cyano-2,3-dihydropyrrole(2,3-b)quinoline (129c)

6-Bromo-4-cyano-3-vinylquinoline : 300 mg; ammonia gas 3-4 h m.p. 262°. Methanol 150 ml; Yield : 180 mg (61%).

I.R(KBr): \( \nu_{\text{max}} = 2960\, (\text{NH}), 2250\, (\text{CN}), 1620 \, \text{and} \, 1580 \, \text{cm}^{-1}. \)

N.M.R : Product insoluble in CDCl\(_3\)

Analysis :

<table>
<thead>
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<th>Found</th>
<th>Calcd</th>
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<tr>
<td>C(_{12})H(_7)N(_3)Br</td>
<td>C 52.36</td>
<td>H 2.83</td>
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6,8-Dibromo-4-cyano-2,3-dihydropyrrole(2,3-b)quinoline(129d)

6,8-Dibromo-2-chloro-4-cyano-3-vinylquinoline : 30 mg; ammonia gas 3-4 h; mp. > 270; methanol 150 ml. Yield: 10mg (32%).

I.R (KBr) : \( \nu_{\text{max}} = 2990\, (\text{NH}), 2250\, (\text{CN}) \, \text{cm}^{-1}. \)

N.M.R : Product insoluble in CDCl\(_3\)
N-Methyl-4-cyano-2,3-dihydropyrrolo[2,3-b]quinoline (131a)

To (430 mg) 0.002 mole of 2-chloro-4-cyano-3-vinyl-quinoline taken in 100 ml methanol, 1.36 gm of Methylamine hydrochloride (0.02 mole) was added. To generate methylamine gas sodiummethoxide prepared from 0.50 g of Na and Methanol was added dropwise. The temperature was maintained between 0-5° during 3 h and was left at room temperature overnight. The methanol solution was evaporated and poured into water. It was then extracted with chloroform, dried and concentrated. The concentrated solution was put into a column of Neutral alumina. The yellow crystals was obtained in Petrol:Benzene eluate m.p.158°; Yield : 76% (320 mg).

Mass: 209.

I.R. (KBr): \( \nu_{\text{max}} = 2990, 2280, 1620, 1580 \text{ cm}^{-1} \).

N.M.R : \( \delta \) values

- 3.03 (s, 3H, N-CH\(_3\)) ppm.
- 3.2 (t, 2H, C\(_3\)-CH\(_2\)) ppm.
- 3.5 (t, 2H, C\(_2\)-CH\(_2\)) ppm.
- 7.1 to 7.8 (m, 4H, C\(_5\)-C\(_8\) Ar-H) ppm.

Analysis:

\( \text{C}_{13}\text{H}_{11}\text{N}_3 \) Found: C 68.68 H 5.45

(209.25) Calcd: C 68.89 H 5.26
6-Bromo-N-Methyl-4-cyano-2,3-dihydropyrrol/0(2-3b)-quinoline(131c)

6-Bromo-4-cyano-3-vinyl-2-chloro quinoline: 400 mg; sodium methoxide 1.06 g in 50 ml methanol methylamine hydrochloride 1.36 gm; mp. 180°; Yield: 280 mg (72%).

I.R(KBr): \( \nu_{\text{max}} = 2250(\text{CN}), 1620, 1580 \text{ cm}^{-1} \).

N.M.R.: values

\[ \begin{align*}
3.09 & \text{ (s, 3H, N-CH}_3\text{) ppm.} \\
3.33 & \text{ (t, 2H (C}_3\text{-CH}_2\text{) ppm.} \\
3.72 & \text{ (t, 2H C}_2\text{-CH}_2\text{) ppm.} \\
7.22-3.41 & \text{ (m, 3H C}_5\text{-C}_7\text{, C}_8\text{ Ar-H) ppm.} 
\end{align*} \]

Analysis:

\[ \begin{align*}
\text{C}_{13}\text{H}_{10}\text{N}_3\text{Br} & \quad \text{Found: C 53.93 H 3.52} \\
(288.14) & \quad \text{Calcd: C 54.16 H 3.47}
\end{align*} \]

N-Ethyl-4-cyano-2,3-dihydropyrrol/0(2,3-b)quinoline(133a)

To prepare the 133a the same procedure like previous one was adapted.

4-Cyano-3-vinyl-2-chloro quinoline: 420 mg; Ethylamine hydrochloride 1.62 g sodium methoxide 1.36 g in 50 ml methanol m.p. 138°. Yield: 470 mg (80.4%).

I.R (KBr) \( \nu_{\text{max}} = 2990, 2250(\text{C=N}), 1640, 1580, 760, 700, 640 \text{ cm}^{-1} \).
N.M.R: 

\[ \delta \text{ values} \]

1.23 (s, 3H N-CH\(_2\)-CH\(_3\)) ppm.
3.70 (q, 2H N CH\(_2\)-CH\(_3\)) ppm.
3.80 (t, 2H C\(_3\) - CH\(_2\)) ppm.
3.48 (t, 2H C\(_2\) CH\(_2\)) ppm.
7.1-7.81 (m, 4H C C\(_5\)-C\(_6\), C\(_7\) and C\(_8\)-1Ar-H) ppm.

Analysis:

\[ \text{C}_{14}\text{H}_{12}\text{N}_3 \text{Br} \quad \text{Found C } 55.36 \ \text{H } 3.83 \]  
\[ (303.17) \quad \text{Calcd C } 55.41 \ \text{H } 3.95 \]

6-Bromo-N-ethyl-4-cyano-2,3-dihydropyrrolo[2,3-b]quinoline(133c)

6-Bromo-4-cyano-3-vinyl-2-chloroquinoline: 400 mg; ethylamine hydrochloride 1.62 g. Sodium methoxide 1.36 g in 50 ml methanol. m.p. 145; Yield: 305 mg (76%).

I.R(K\text{Br}) \ \nu_{\text{max}}=2990,2250,\text{COC=N}) 1640,1580,760,700,640 \ \text{cm}^{-1}.

N.M.R: 

\[ \delta \text{ values} \]

1.26 (s, 3H, N-CH\(_2\)-CH\(_3\)) ppm.
3.72 (q, 3H,2H,N-CH\(_2\)_2 CH\(_3\)) ppm.
3.33 (6,2H,C\(_3\)-CH\(_2\)) ppm.
3.51 (t, 2H,C\(_2\)-CH\(_2\)) ppm.
7.12-7.84 (m, 3H,C\(_5\),C\(_7\),C\(_8\) Ar-H) ppm.

Analysis:

\[ \text{C}_{14}\text{H}_{12}\text{N}_3\text{Br} \quad \text{Found C } 55.36 \ \text{H } 3.83 \]  
\[ (303.17) \quad \text{Calcd C } 55.41 \ \text{H } 3.95 \]
N-Isopropyl-4-cyano-2,3-dihydropyrrolo(2,3-b)quinoline (135a)

To the starting compound 135a in methanol (0.002 mole) Isopropylamine (0.02 mole) 1.18 g was added and stirred with the temperature between 0-5° and at room temperature for overnight 118°C.; Yield: 320 mg (68%).

I.R (KBr): $\nu_{\text{max}} = 2210 (\text{CN})$, 1620 cm$^{-1}$.

$^1$H N.M.R (CDC$_3$): $\delta$ values

- 1.25 (2s, 6H) N-CH$_3$
- 1.35 ppm.
- 3.3 (t, 2H, C$_3$-CH$_2$) ppm.
- 3.7 (t, 2H C$_2$-CH$_2$) ppm.

Analysis:

C$_{15}$H$_{15}$N$_3$ Found C 75.85 H 6.15
(237.30) Calcd C 75.94 H 6.32

6-Bromo-4-cyano-N-Isopropyl-2,3-dihydropyrrolo(2,3-b)-quinoline (135c)

6-Bromo-4-cyano-3-vinyl-2-chloro quinoline: 400 mg Isopropylamine 1.2 g; m.p. 125°C; Yield: 370 mg (70%)

I.R(KBr): $\nu_{\text{max}} = 2240, 1620, 1600, 1410$ cm$^{-1}$.

N.M.R(CDC$_3$): $\delta$ values

- 1.3, 1.4 (2s, 6H N-CH$_3$, ppm.)
N.M.R:  
6.9 (d, 1H, ) ppm  
7.42-8.53 (C_2-C_5, C_6, C_7 and C_8 H') ppm  
8.8 (brs 1H, NH) ppm.

Dehydrogenation of 2,3-dihydropyrroloquinolines

The corresponding dihydropyrroloquinolines (0.001 mole) and 2,3-dichloro-4,5-dicyano dihydroquinone (DDQ) (0.001 mole) was taken in benzene (100 ml) and was refluxed for two days. The solid material was filtered off and the filtered solution was evaporated. The gummy residue was put into a column of Neutral alumina and the compound was recrystallized from the suitable solvents as the case may be.

4-Cyano(2,3-b)pyrrolo(2,3-b)quinoline: 195 mg DDQ: 226 mg m.p. 160° (Benzene); Yield: 26 mg (13.47%).

I.R. (KBr):  
\( \nu_{\text{max}} = 2290, 2250 (\text{CN}), \text{ cm}^{-1} \).
6-Bromo-4-cyanopyrrolo(2,3-b)quinolines (130C)

6-Bromo-4-cyano-2,3-dihydropyrrolo(2,3-b)quinoline:
274 mg; DDQ: 226 mg; m.p. 210°C (Benzene); Yield: 30 mg (11%).

I.R. (KBr):
\[ \nu_{\text{max}} = 2980, 2250, (CN) 1620 \text{ cm}^{-1}. \]

N.M.R. (CDCl₃):
- \(\delta\) values.
- 6.9 (d, 1H) ppm.
- 7.7-8.4 (m, 3H, C₅, C₇ and C₈ -H) ppm
- 8.6 (brs, 1H, NH) ppm.

N-Methyl-4-cyanopyrrolo(2,3-b)quinolines (132a)

N-Methyl-4-cyano-2,3-dihydropyrrolo(2,3-b)quinolines:
210 mg.

DDQ: 226 mg; m.p. 151°C; Yield: 120 mg (57%).

I.R. (KBr):
\[ \nu_{\text{max}} = 2980, 2250, 1610, 1580 \text{ cm}^{-1}. \]

N.M.R.:
- \(\delta\) values.
- 6.77 (d, 1H, C₃ -H) ppm.
- 7.46-8.51 (m, 5H, C₂, C₅, C₆, C₇ and C₈ -H) ppm.
- 3.93 (s, 3H N-Me) ppm.

Analysis:
- \(C_{13}H_{19}N_3\) Found: 75.52 H 4.46
- (207.23) Calcd: 75.34 H 4.37
6-Bromo-N-methyl-4-cyanopyrrolo(2,3-b)quinolines

6-Bromo-N-methyl-4-cyano-2,3-dihydropyrrolo(2,3-b)-quinoline 286 mg; m.p. 167°C; DDQ 226 mg; Yield 145 mg (51%).

I.R. (KBr): \( \nu_{\text{max}} = 2980, 2250, 1610, 1580 \text{ cm}^{-1} \).

N.M.R (CDCl₃): \( \delta \) VALUES

6.0 (d, 1H, C₃-H) ppm.
7.32-8.38 (m, 4H, C₂, C₅, C₇ and C₈-H) ppm.
3.86 (s, 3H, N-Me) ppm.

Analysis:

C₁₃H₈N₃Br Found C 54.78 H 2.72
(286.12) Calcd C 54.53 H 2.81

N-Ethyl-4-cyanopyrrolo(2,3-b)quinoline(134a)

N-Ethyl-4-cyano-2,3-dihydropyrrolo(2,3-b)quinoline
225 mg; DDQ = 225 mg; m.p. 132°C; Yield: 50%.

I.R. (KBr): \( \nu_{\text{max}} = 2990, 2250(\text{CN}), 1620 \text{ cm}^{-1} \).

\( ^1H \) N.M.R: \( \delta \) VALUES

1.4 (s, 3H, N-CH₂-CH₃) ppm.
3.9 (q, 2H, N-CH₂CH₃) ppm.
6.8 (d, 1H, C₃-H) ppm.
7.7 to 8.8 (m, 5H, C₂, C₃, C₅ and C₈-H) ppm.
Analysis:

\[ C_{14}H_{11}N_3 \] Found C 76.36 H 4.86
(221.25) Calcd C 76.01 H 4.97

6-Bromo-N-ethylpyrrolo(2,3-b)quinoline (134c)

6-Bromo-N-ethyl-2,3-dihydropyrrolo(2,3-b)quinoline:

300 mg; DDQ 225 mg; m.p. 142°C; Yield:

I.R. (KBr): \( \nu_{\text{max}} = 2250(\text{CN}), 1620, 1580 \text{ cm}^{-1} \).

N.M.R.: \( \delta \) values

1.4 (s, 3H, N-CH\( _2 \)-CH\( _3 \)) ppm.
3.7 (q, 2H, N CH\( _2 \)-CH\( _3 \)) ppm.
6.9 (d, 1H, C\( _3 \)-H) ppm.
7.9 to 8.7 (m, 4H C\( _2 \), C\( _3 \), C\( _5 \) and C\( _8 \)-H) ppm.

Analysis:

\[ C_{14}H_{10}N_3Br \] Found C 56.26 H 3.53
(300.15) Calcd C 56.00 H 3.33

N-Isopropyl-4-cyanopyrrolo(2,3-b)quinoline (136a)

N-Isopropyl-4-cyano-2,3-dihydropyrrolo(2,3-b)-quinoline: 240 mg; DDQ = 230 mg; m.p. 106°C. Yield: 80 mg (34%).

I.R. (KBr): \( \nu_{\text{max}} = 2980, 2250(\text{CN}), 1620, 1580 \text{ cm}^{-1} \).
N.M.R (CDCl₃) values

1.51 and 1.63 (2s, each 3H $\text{CH}_3$) ppm
5.33 (q, 1H, CH $\text{CH}_3$) ppm.
6.8 (d, 1H, C₃-H) ppm.
7.6-8.6 (m, 4H, C₅-C₈-H) ppm.

Analysis:

$C_{15}H_{13}N_3$ Found C 76.65 H 5.78
(235.28) Calcd C 76.59 H 5.53

6-Bromo-N-Isopropyl-4-cyanopyrrollo(2,3-b)quinoline (136c)

6-Bromo-N-isopropyl-4-cyano-2,3-dihydropyrrollo(2,3-b)-quinoline : 250 mg.; DDQ = 180 mg; m.p. 115°C; Yield : 60 mg (23.9%)  

I.R. (KBr) $\nu_{\text{max}}$ = 2290, 2250(CN) 1620 cm⁻¹.

N.M.R (CDCl₃) values

1.5 and 1.6 (2s, each N-H $\text{CH}_3$) ppm
5.4 (1H, q, N-CH $\text{CH}_3$) ppm.
7.9 to 8.8 (4H, m, C₂, C₅, C₆ and C₈-H) ppm.

Analysis:

$C_{15}H_{12}N_3\text{Br}$ Found C 57.48 H 3.68
(314.17) Calcd C 57.32 H 3.82