Synthetic utility of 1-hydroxycarbazoles

It is well established that the pyridocarbazole ring is an appropriate skeleton to design DNA intercalating drug. Some compounds such as ellipticine, olivacine and pyridazino[4,5-b]carbazoles, representing 3-aza analogs of pyrido[4,3-b]carbazoles elicit high antitumour properties. Since the discovery of the potent activity of 11H-pyrido[2,3-a]carbazoles and 6H-pyrido[4,3-b]carbazoles, numerous syntheses have been reported. These methods, often have low yields either due to the large number of steps or due to the presence of several isomers. However, based on the discovery of enhanced anticancer activity in 9-hydroxy ellipticine compared to ellipticine, many compounds have been synthesized to study the effect of different substituents at different positions or replacement of the pyridine ring by other heterocyclic rings. Hence, we were interested to obtain new derivatives or analogues of pyridocarbazoles for pharmacological evaluation. In this connection, we made an attempt to prepare some new furo carbazoles, thiazepino carbazoles, pyrano carbazoles and quinolino carbazoles utilizing 1-hydroxycarbazole as a potential precursor in our synthetic strategy.

4.1. Synthesis and synthetic utility of 1-hydroxycarbazole-2-carbaldehydes (3a-3d)

In this context, 1-oxo-1,2,3,4-tetrahydrocarbazoles (1a-1d) were first reduced to the corresponding 1-hydroxycarbazoles (2a-2d) by heating with Pd/C in diphenyl ether. 1-Hydroxycarbazole-2-carbaldehydes (3a-3d) were prepared from 1-hydroxycarbazoles (2a-2d) with excellent yield according to our reported procedure. The product (3a) was characterized by analytical (C_{14}H_{11}NO_{2}) and spectral data. Its IR spectrum displayed a strong band at 1662 cm\(^{-1}\) which may be due to the formyl group, hydrogen bonded with adjacent hydroxyl group. Additional evidence regarding the position of formyl group was derived from the appearance of signal corresponding to the phenolic proton at δ 11.75 in its \(^1\)H NMR spectrum (Fig 4.1) which is significantly downfield indicating a fairly strong intramolecular interaction with the adjacent formyl group. The spectrum showed a three proton singlet at δ 2.54 ascribed to the methyl group. The aromatic protons resonated as an unresolved multiplet in the region δ 7.05 – 7.87.
whereas carbazole-NH and formyl proton resonated as two broad singlets at δ 8.47 and δ 9.99 respectively. The generality of the reaction was justified by preparing a series of substituted compounds 3b-3d from 2b-2d.

**Scheme 4.1**

1. Zn(CN)₂, dry HCl
2. H⁺, H₂O

\[ 1 \rightarrow 3 \]

1-3 a: \( R_1 = \text{CH}_3, R_2 = R_3 = H \)
b: \( R_2 = \text{CH}_3, R_1 = R_3 = H \)
c: \( R_3 = \text{CH}_3, R_1 = R_2 = H \)
d: \( R_1 = R_2 = R_3 = H \)

### 4.1.1. Synthesis of 2-acetylfuro[2,3-a]carbazoles (4a-4d)

The benzofuran nucleus is a common one in natural products. These products are usually complicated, and the furan ring especially may present in a somewhat modified form. For example, morphine, lignite and some alkaloids were derived from isobenzofuran but not from benzofuran. Benzofuran can be found in certain fractions of coal tar, lignite tar and in the tar from beechwood.

The required precursor 1-hydroxycarbazole-2-carbaldehydes (3) were prepared according to our reported procedure. Reaction of 3a with chloroacetone in presence of potassium carbonate in dry acetone afforded the product 2-acetyl-7-methylfuro[2,3-a]-carbazole (4a) in 80% yield. The structure of 4a was confirmed on the basis of its spectral and analytical studies as follows. Its IR spectrum (Fig 4.3) of this compound showed two strong absorptions at 3363 cm⁻¹ and at 1660 cm⁻¹ corresponding to -NH and carbonyl stretching frequencies respectively. The ¹H NMR spectrum (Fig 4.4) of 4a displayed two singlets at δ 2.49 and at δ 2.61 due to C₇-CH₃ and C₂-COCH₃ protons respectively. Three doublets each for one proton centered at δ 7.27 \( (J=8.08 \text{ Hz}) \), δ 7.46 \( (J=8.08 \text{ Hz}) \) and δ 7.51 \( (J=8.24 \text{ Hz}) \) corresponding to C₉-H, C₉-H and C₄-H protons respectively. A multiplet resonated in the range of δ 8.06-8.08 corresponding to C₅-H and
Fig 4.1  IR spectrum of 1-hydroxy-6-methylcarbazole-2-carbaldehyde (3a)

Fig 4.2  $^1$H NMR spectrum of 1-hydroxy-6-methylcarbazole-2-carbaldehyde (3a)
C_3-H proton. In addition to this, a singlet at δ 7.97 and a broad singlet at δ 12.11, were ascribable to C_6-H and carbazole-NH respectively. This was also supported by the electron impact mass spectrum of the compound which displayed the molecular ion peak at m/z 263, and also elemental analysis agreed well with the molecular formula C_{17}H_{13}NO_2. From the spectral and analytical data, the structure of the compound was confirmed as 4a. A series of similar compounds 4b-4d were obtained from 3b-3d.

Scheme 4.2

![Scheme 4.2](image)

4.1.2. Reaction of 1-hydroxycarbazole-2-carbaldehyde (3a-3d)

Pyrano[3,2-a]carbazoles such as grinimbine, mahanimbine, murrayanol and mahanine were isolated from the plant species of rutaceae family. In particular, the alkaloids mahanimbine, murrayanol and mahanine were reported to posses mosquitocidal antimicrobial, anti-inflammatory and antioxidant activities. To our knowledge there is no report on the synthesis of 2-alkyl- or 2-aryl-4-oxopyrano[2,3-a]carbazoles. From biogenetic point of view, there exists a possibility for the formation of these compounds in plant body. Based on these above facts, it was felt to device a simple synthetic method for the preparation of 2-aryl-4-oxopyrano[2,3-a]carbazoles. With this in mind, we attempt to prepare pyrano carbazoles.

Further, we carried out the reaction of 1-hydroxycarbazole-2-carbaldehyde (3a) with phenyl acetic acid in acetic anhydride at 160°C with an interest that the reaction would proceed as shown in Scheme 4.3. At the end, this attempt yielded a single product, with mp. 175°C. The IR spectrum (Fig 4.5) of this compound showed strong absorptions at 3247 cm⁻¹, 1759 cm⁻¹ and 1666 cm⁻¹ which are accountable for -NH, estercarbonyl and aldehydic carbonyl groups respectively. The ¹H NMR spectrum (Fig 4.6) exhibited the
Fig 4.3  IR spectrum of 2-acetyl-7-methylfuro[2,3-a]carbazole (4a)

Fig 4.4  $^1$H NMR spectrum of 2-acetyl-7-methylfuro[2,3-a]carbazole (4a)
following resonances. Two singlets, each for three protons at $\delta$ 2.50 and $\delta$ 2.51, a multiplet at $\delta$ 7.31-8.01 for five protons and two singlets, each for one proton at $\delta$ 8.16 and $\delta$ 10.19. A set of singlets each for three protons at $\delta$ 2.50 and $\delta$ 2.51 due to C$_6$-CH$_3$ and C$_1$-OCOCH$_3$ protons respectively. The aromatic cluster appeared at $\delta$ 7.31-8.01 with five proton integration was due to C$_3$, C$_4$, C$_5$, C$_7$ and C$_8$ protons accordingly. The signals due to indole-NH and C$_2$-CHO resonated as broad singlet and a singlet at $\delta$ 8.16 and $\delta$ 10.19 respectively. The non-existence of any signals in the olefinic region revealed that the product formed was not the expected one. This was also supported by the electron impact mass spectrum of the compound displayed the molecular ion peak at m/z 267, whereas the expected product requires the molecular ion at m/z 325. The elemental analysis C 71.75%, H 04.79, N 05.36% was in good agreement with the molecular formula C$_{16}$H$_{13}$NO$_3$. Hence, both spectral and analytical data indicated that the reaction did not afford the expected 2-oxo-3-phenylpyrano[2,3-$a$]carbazole 5a as given in the Scheme 4.3.

Scheme 4.3

Based on the above discussion and spectral characters, the structure of the product was confirmed to be 1-acetyloxycarbazole-2-carbaldehyde (6a). Since same
Fig. 4.5 IR spectrum of 1-acetyloxy-6-methylcarbazole-2-carbaldehyde (6a)

Fig. 4.6 $^1$H NMR spectrum of 1-acetyloxy-6-methylcarbazole-2-carbaldehyde (6a)
acylated products were observed in the absence of phenylacetic acid, which is a simple o-acylated reaction. A series of similar compounds 6b-6d were obtained from 3b-3d.

4.1.3. Synthesis of benzo[1,2-b]-1,4-thiazepino[7,6-a]carbazoles (7a-7d)

The pyrrolo[2,1-c][1,4]benzodiazepines were a well-known class of sequence-selective DNA-binding agents. Among the PDB family, anthracine has shown significant in vitro cytotoxicity but has not progressed in clinical trials due to side effects. Improvements have been done to enhance antitumour potency and to surmount, this drawback.

The product 7a was obtained by the treatment of 3a with o-aminothiophenol in glacial acetic acid, and well characterized using its spectral and analytical data. Its IR spectrum (Fig 4.7) revealed the presence of >C=N group by exhibiting a strong absorption at 1616 cm⁻¹. The ¹H NMR spectrum (Fig 4.8) of 7a in CDCl₃ showed a singlet at δ 2.54 assignable for C₁₀-CH₃. The complex multiplet at δ 7.25-7.98 was assigned for nine aromatic protons. The signals corresponding to indole –NH and C₅-H were observed at δ 13.00 and δ 8.48 as a broad singlet and a singlet respectively. The elemental analysis of the compound 7a was in good agreement with the proposed molecular formula C₂₀H₁₄N₂S. This was supported by the electron impact mass spectrum of the compound which displayed the molecular ion peak at m/z 314. A series of similar compounds 7b-7d were obtained from 3b-3d.

![Scheme 4.4](image)

Scheme 4.4

3.7 a: R₂ = R₃ = H, R₁ = CH₃
b: R₁ = R₃ = H, R₂ = CH₃
c: R₁ = R₂ = H, R₃ = CH₃
d: R₁ = R₂ = R₃ = H
Fig 4.7 IR spectrum of 9-methylbenzo[1,2-b]-1,4-thiazepino[7,6-a]carbazole (7a)

Fig 4.8 $^1$H NMR spectrum of 9-methylbenzo[1,2-b]-1,4-thiazepino[7,6-a]carbazole (7a)
Fig 4.23 $^1$H NMR spectrum of 10-methylbenzo[1,2-6]-1,4-thiazepino[7,6-a]carbazole (7b)

Fig 4.24 $^1$H NMR spectrum of 11-methylbenzo[1,2-6]-1,4-thiazepino[7,6-a]carbazole (7c)
4.2. Attempt towards the synthesis of dimerised product of carbazole and quinoline alkaloids

On the basis of the vinylacetate reaction of quinoline alkaloid232a,b from our laboratory we want to extend the same reaction with 1-hydroxycarbazole with an expectation to get the dimerised product of carbazole and quinoline moieties. This dimerised product may have enhanced medicinal properties like bactericidal, analgesic, antibiotic, insecticidal and neuroleptic, since the dimerised one contains both carbazole and quinoline alkaloids.

4.2.1. Synthesis of pyrano[2,3-α]carbazoles (8a-8d)

Coumarins were reported to possess biological activity233a, and are used in the treatment of vitiligo psoriasis and other dermal diseases233b. In recent times 1benzopyran-2[H]-ones have been extensively used as laser materials234, photosensitizers235, brighteners236, intermediates for dyes, pesticides and pharmaceuticals237, in perfume formulations238, 239 and in enzymology as biological probes240. Coumarins show activities such as antifungal241, anticoagulant242, antibacterial243, and insecticidal244.

The reaction of 1-hydroxy-6-methyl-carbazole (2a) with malonic acid in presence of fused zinc chloride and phosphorous oxychloride at room temperature afforded a single product, which was purified by column chromatography using petroleum ether – ethyl acetate mixture as an eluant. It yielded a single product which was found to be 3,11-dihydro-2,4-dioxo-8-methylpyrano[2,3-α]carbazole (8a).

![Scheme 4.5](image)
Fig 4.9 IR spectrum of 3,11-dihydro-2,4-dioxo-8-methylpyrano[2,3-α]carbazole (8a)

Fig 4.10 $^1$H NMR spectrum of 3,11-dihydro-2,4-dioxo-8-methylpyrano[2,3-α]carbazole (8a)
The IR spectrum (Fig 4.9) of newly arrived one 8a showed a strong >C=O stretching vibration at 1722 cm⁻¹ along with the shoulder at 1643 cm⁻¹. When we scrutinized the ¹H NMR spectrum (Fig 4.10) of 8a, it showed the appearance of two singlets at δ 2.50 and δ 2.91 for C₈-CH₃ and C₃-H₂ protons respectively. A multiplet for six aromatic protons appeared at δ 7.02-7.70 for C₃-H, C₅-H, C₆-H, C₇-H, C₉-H and C₁₀-H protons, and a broad singlet at δ 7.74 for -NH proton. A sharp singlet appeared at δ 11.04 for C₄-OH proton. From the proton integration of C₃-H₂ of 4-oxo form 8 and that of C₃-H and C₄-OH of 4-hydroxy form 9, the ratio of keto and enol forms was found to be 3:1. The elemental analysis agreed well with the proposed molecular formula C₁₆H₁₁NO₃. Based on the above spectral and analytical data the product was attested as 3,11-dihydro-2,4-dioxo-8-methylpyrano[2,3-a]carbazole (8a). A series of similar compounds 8b-8d were obtained from respective 2b-2d under identical conditions (Scheme 4.5).

4.2.1. Reaction of 3,11-dihydro-2,4-dioxo-pyrano[2,3-a]carbazole (8a-8d) with vinyl acetate

When, 3,11-dihydro-2,4-dioxo-8-methylpyrano[2,3-a]carbazole (8a) obtained from the above step was treated with vinyl acetate in presence of 4% alc. KOH with an expectation to obtain 11 or 12 or both (Scheme 4.6).
The reaction mixture after work up showed single spot on TLC which was purified by column chromatography. Its IR spectrum (Fig 4.11) showed two strong bands at 3413 cm\(^{-1}\) and 3274 cm\(^{-1}\) for \(-\text{NH}\) and \(-\text{OH}\) stretching vibrations respectively and a band at 1643 cm\(^{-1}\) due to >C=O stretching vibrations. Its \(^1\text{H}\) NMR spectrum (Fig 4.12) showed the following signals: a singlet for three protons at \(\delta 2.58\), a broad singlet \(\delta 5.70\), a multiplet at \(\delta 7.56-7.62\) for nine aromatic protons, a broad singlet \(\delta 8.61\) and a singlet \(\delta 11.01\) respectively. A singlet for three protons at \(\delta 2.58\) was due to C\(_{12}\)-CH\(_3\), broad singlet \(\delta 5.70\) due to N\(_2\)-H proton. A multiplet at \(\delta 7.56-7.62\) was due to the eight aromatic protons. A singlet at \(\delta 8.12\) was due to C\(_{11}\)-H proton. A broad singlet and singlet at \(\delta 8.61\) and \(\delta 11.01\) were due to carbazole-NH and C\(_7\)-OH respectively. The mass spectrum showed the molecular ion peak at m/z 366 where as the expected product requires the molecular ion peak at m/z 434. Elemental analysis agreed well with the proposed molecular formula C\(_{23}\)H\(_{14}\)N\(_2\)O\(_3\). A series of similar compounds 14b-14d were obtained under identical conditions (Scheme 4.7).
Synthetic Studies on Cyclopent[b]indoles and Carbazoles

Scheme 4.7

When the reaction was carried out under similar conditions in the absence of vinyl acetate to give a similar product in all the cases. On this basis, the following mechanism has been proposed. In the plausible mechanism (Scheme 4.8) it seems that the reaction gets initiated by the degradation of 3,11-dihydro-2,4-dioxopyrano[2,3-\(a\)]carbazole (8) under basic conditions to 1-hydroxycarbazole-2-carboxylic acid (13). Then the carboxylic carbon of 13 gets attacked by the carbanion generated from 2,4-dihydroxyquinoline under basic conditions to give the intermediate II, which subsequently loses water molecule during cyclisation to yield the final product 14.

Scheme 4.8
**Fig 4.11** IR spectrum of 12-methylquinoline[2,3-b]carbazole[6,5-e]pyran-7,8-dione (14a)

**Fig 4.12** $^1$H NMR spectrum of 12-methylquinoline[2,3-b]carbazole[6,5-e]pyran-7,8-dione (14a)
4.3. Synthesis of 12,13-dihydro-5-oxoquinolinoc[2,3-a]carbazoles (17a-17d)

Pyrido[4,3-a]carbazoles were well known for their anticancerous properties. Quinocarbazoles can be considered as substituted pyridocarbazoles, which can be expected to exhibit anticancerous properties. As a part of our continuous interest in the synthesis of novel heterocyclic systems, we report herein the synthesis of hitherto unknown 12,13-dihydro-5-oxoquinolinoc[2,3-a]carbazoles.

In our attempt to derive 12,13-dihydro-5-oxo-9-methylquinolinocarbazole (17a), 1-hydroxy-6-methylcarbazole (2a) was treated with anthranilic acid in the presence of fused zinc chloride and phosphorous oxychloride at room temp. It showed two spots on TLC, which were separated by performing column chromatography using petroleum ether – ethyl acetate mixture as an eluant. The two products obtained from petroleum ether – ethyl acetate fractions, 99:1 and 97:3 were found to be 1,7-dibenzoazocin-6,12-dione (16) and 12,13-dihydro-5-oxo-9-methylquinolinocarbazole (17a) respectively.
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Scheme 4.9

The IR spectrum (fig 4.13) of 16 showed two strong absorption bands at 3450 cm\(^{-1}\) and 1625 cm\(^{-1}\) for -NH and >C=O stretchings respectively. Its \(^1\)H NMR (fig 4.14) spectrum showed a multiplet at \(\delta 6.49-7.79\) for eight aromatic protons and two broad singlets each for one proton at \(\delta 8.10\) and \(\delta 8.20\) for N1 and N7-H. The elemental analysis agreed well with the molecular formula C\(_{14}\)H\(_{10}\)N\(_2\)O\(_2\). Based on the above mentioned spectral data the structure was proposed as 1,7-dibenzoazocin-6,12-dione (16).

The IR spectrum (fig 4.15) of 17a showed two strong absorptions at 1681 cm\(^{-1}\) and 3327 cm\(^{-1}\) for >C=O and -NH stretching vibrations respectively. The \(^1\)H NMR spectrum (Fig 4.16) of 17a registered the signals as a singlet at \(\delta 2.53\) for C9-CH\(_3\) and a broad singlet at \(\delta 5.81\) for quinolino -NH. A multiplet appeared at \(\delta 6.74-8.23\) corresponding to nine aromatic protons and indole -NH proton. The elemental analysis data of compound 17a was also in good agreement with molecular formula C\(_{20}\)H\(_{14}\)N\(_2\)O. The same out come leading to 17b-17d was realized when 2b-2d were treated with anthranilic acid under identical conditions along with 1,7-dibenzoazocin-6,12-dione (14) in all the cases. Due to the formation of similar product 16 in all the cases, it was concluded that anthranilic acid gets dimerised to 1,7-dibenzoazocin-6,12-dione (16).
Fig 4.13  IR spectrum of 1,7-dibenzoazocin-6-12-dione (16)

Fig 4.14  $^1$H NMR spectrum of 1,7-dibenzoazocin-6-12-dione (16)
Fig 4.15 IR spectrum of 12,13-dihydro-9-methyl-5-oxoquinolino[2,3-a]carbazole (17a)

Fig 4.16 $^1$H NMR spectrum of 12,13-dihydro-9-methyl-5-oxoquinolino[2,3-a]carbazole (17a)
4.4. Conclusion

In this chapter, 1-hydroxycarbazole-2-carbaldehydes (3) were successfully employed as synthon to derive the following hetero-annelated carbazoles.

* Reaction of 1-hydroxycarbazole-2-carbaldehydes (3) with chloroacetone yielded 2-acetylfuro[2,3-a]carbazoles (4)
* Our attempt to synthesis 3-phenyl-2-oxo-pyran[2,3-a]carbazoles (5) from 1-hydroxycarbazole-2-carbaldehydes (3) and phenylacetic acid yielded only simple α-acylated products 1-acetyloxycarbazole-2-carbaldehydes (6).
* Reaction of 1-hydroxycarbazole-2-carbaldehydes (3) with o-amino thiophenol yielded novel benzo[1,2-b]-1,4-thiazepino[7,6-a]carbazoles (7).

In addition, we paid our attention towards the synthesis of some novel annelated carbazoles by employing 1-hydroxycarbazoles (2) as synthons.

* Reaction of 1-hydroxycarbazoles (2) with malonic acid yielded 3,11-dihydro-2,4-dioxopyran[2,3-a]carbazoles (8). Further our attempt towards the synthesis of dimerised product from 3,11-dihydro-2,4-dioxopyran[2,3-a]carbazoles (8) and 2,4-dihydroxyquinoline alkaloids using vinyl acetate resulted in the formation of novel hetero annelated (pyrido-pyrano) carbazoles (14).
* Reaction of 1-hydroxycarbazoles (2) with anthranilic acid in presence of zinc chloride and phosphorus oxychloride afforded a mixture of 12,13-dihydro-5-oxoquinolino[2,3-a]carbazoles (17) along with 1,7-dibenzoazocin-6,12-dione (16), as a common entity in all the cases.

4.5. Experimental

Starting materials: The required precursors 1-hydroxycarbazoles\textsuperscript{112,153} (2a-2d) and 1-hydroxycarbazole-2-carbaldehydes (3a-3d) have been prepared according to our published procedures\textsuperscript{153,219}. 

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Preparation of 1-hydroxycarbazole-2-carbaldehydes (3a-3d)

**General procedure**: A mixture of the respective 1-hydroxycarbazole (2, 8 mmol) was dissolved in dry ether (75 mL) and freshly prepared zinc cyanide (0.944 g, 8 mmol) was added to the reaction mixture. This heterogeneous mixture was maintained at 0 to -5°C for 3 - 4 h with constant stirring and dry HCl gas was passed. After saturating the ether with HCl, the HCl gas was passed more slowly and stirring was continued for another 0.5 h to ensure the completion of the reaction. The reaction mixture was then placed in a refrigerator for 48 h and the resulting precipitated imine hydrochloride was filtered, dissolved in water and heated under reflux for 1 h. Cooling, filtration, extraction with ethyl acetate, drying over anhydrous sodium sulphate followed by solvent removal afforded a crude product which was purified by column chromatography (petroleum ether /ethyl acetate mixture, 95/5). The product thus obtained was recrystallised from the same solvent system.

**1-Hydroxy-6-methylcarbazole-2-carbaldehyde (3a)**

<table>
<thead>
<tr>
<th>1-Hydroxy-6-methylcarbazole (2a)</th>
<th>Yield</th>
<th>Mp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.576 g (0.008 mol)</td>
<td>1.530 g (85%)</td>
<td>200°C</td>
</tr>
<tr>
<td>IR (KBr) [v&lt;sub&gt;max&lt;/sub&gt; cm&lt;sup&gt;-1&lt;/sup&gt;]</td>
<td>1662, 1610, 1593, 1461, 1415, 1388, 1344, 1307, 1276, 1251</td>
<td></td>
</tr>
<tr>
<td>(Fig 4.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;sup&gt;1&lt;/sup&gt;H NMR (CDCl&lt;sub&gt;3&lt;/sub&gt;) [δ ppm]</td>
<td>2.54 (s, 3H, CH&lt;sub&gt;3&lt;/sub&gt;), 7.05-7.87 (m, 5H, H&lt;sub&gt;3,5,7,8&lt;/sub&gt;) 8.47 (b s, 1H, NH, D&lt;sub&gt;2&lt;/sub&gt;O exchangeable), 9.99 (s, 1H, CHO), 11.75 (b s, 1H, OH, D&lt;sub&gt;2&lt;/sub&gt;O exchangeable)</td>
<td></td>
</tr>
<tr>
<td>(Fig 4.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis (C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;NO&lt;sub&gt;2&lt;/sub&gt;) Calcd</td>
<td>C, 74.65 %; H, 04.92 %; N, 06.22 %</td>
<td></td>
</tr>
<tr>
<td>Found (263.294)</td>
<td>C, 74.78 %; H, 04.82 %; N, 06.37 %</td>
<td></td>
</tr>
</tbody>
</table>

**1-Hydroxy-7-methylcarbazole-2-carbaldehyde (3b)**

<table>
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<th>1-Hydroxy-7-methylcarbazole (2b)</th>
<th>Yield</th>
<th>Mp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.576 g (0.008 mol)</td>
<td>1.620 g (90%)</td>
<td>190°C</td>
</tr>
</tbody>
</table>

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IR (KBr) \([\nu_{\text{max}} \text{ cm}^{-1}]\) 1666, 1610, 1595, 1666, 1610, 1595, 1485, 1461, 1456, 1398, 1350, 1288

\(^1\)H NMR (CDCl\(_3\)) [\(\delta \text{ ppm}\)] : 2.57 (s, 3H, CH\(_3\)), 6.99-8.72 (m, 6H, H\(_{3-8}\), NH), 9.37 (s, 1H, CHO), 10.78 (br s, 1H, OH, D\(_2\)O exchangeable)

Analysis (C\(_{14}H_{11}NO_2\)) Calcd (263.294) Found: C, 74.65 %; H, 04.92 %; N, 06.22 %

1-Hydroxy-8-methylcarbazole-2-carbaldehyde (3c)

1-Hydroxy-8-methylcarbazole (2c) : 1.576 g (0.008 mol)
Yield : 1.530 g (85%)
Mp : 198°C

IR (KBr) [\(\nu_{\text{max}} \text{ cm}^{-1}\)] : 1666, 1610, 1593, 1541, 1508, 1460, 1417, 1386, 1334, 1313

\(^1\)H NMR (CDCl\(_3\)) [\(\delta \text{ ppm}\)] : 2.61 (s, 3H, CH\(_3\)), 7.17-7.96 (m, 5H, H\(_3-7\)), 8.48 (b s, 1H, NH, D\(_2\)O exchangeable), 10.01 (s, 1H, CHO), 11.82 (s, 1H, OH, D\(_2\)O exchangeable)

Analysis (C\(_{14}H_{11}NO_2\)) Calcd (263.294) Found: C, 74.65 %; H, 04.92 %; N, 06.22 %

1-Hydroxycarbazole-2-carbaldehyde (3d)

1-Hydroxywcarbazole (2d) : 1.464 g (0.008 mol)
Yield : 1.348 g (85%)
Mp : 147°C

IR (KBr) [\(\nu_{\text{max}} \text{ cm}^{-1}\)] : 1662, 1610, 1593, 1541, 1508, 1460, 1417, 1386, 1334, 1313

\(^1\)H NMR (CDCl\(_3\)) [\(\delta \text{ ppm}\)] : 7.08-8.11 (m, 6H, H\(_{3-8}\)), 8.57 (b s, 1H, NH, D\(_2\)O exchangeable), 10.01 (s, 1H, CHO), 11.75 (b s, 1H, OH, D\(_2\)O exchangeable)

Analysis (C\(_{13}H_9NO_2\)) Calcd (263.294) Found: C, 77.55 %; H, 04.97 %; N, 05.31 %
Synthesis of 2-acetylfuro[2,3-a]carbazoles (4a-4d)

General procedure: A mixture containing 1-hydroxycarbazole-2-carbaldehyde (2, 0.001 mol), chloroacetone (0.001 mol), ignited K$_2$CO$_3$ (1g) in dry acetone (10mL) was refluxed on a water-bath for 1 h. After that the reaction mixture was filtered and washed with excess acetone. Then the filtrate was concentrated and poured into ice. The solid thus separated was extracted with solvent, the combined organic layers were washed with water successively and dried over anhydrous sodium sulphate. Solvent removed on evaporation gave the crude product, which was purified by passing through a silica gel column and eluting with petroleum ether-ethyl acetate mixture (95:5) yielded the title compounds (4).

2-Acetyl-7-methylfuro[2,3-o]carbazole (4a)

1-Hydroxy-6-methylcarbazole-2-carbaldehyde (3a)

Yield: 0.210 g (80%)

Mp: 240°C

IR (KBr) [$\nu_{max}$ cm$^{-1}$] (Fig 4.3): 3363, 1660, 1577, 1450, 1369, 1294, 1168, 964, 844, 796, 590

$^1$H NMR (CDCl$_3$) [$\delta$ ppm] (Fig 4.4): 2.49 (s, 3H, C$_7$-CH$_3$), 2.61 (s, 3H, C$_2$-COCH$_3$), 7.27 (d, 1H, C$_8$-H, $\delta$=8.08 Hz), 7.46 (d, 1H, C$_9$-H, $\delta$=8.08 Hz), 7.51 (d, 1H, C$_4$-H, $\delta$=8.24 Hz), 7.97 (s, 1H, C$_6$-H), 8.06-8.08 (m, 2H, C$_3$-H, C$_5$-H), 12.11 (b s, 1H, NH)

Analysis (C$_{17}$H$_{13}$NO$_2$) Calcd: C, 77.55%; H, 4.97%; N, 5.31%  Found: C, 77.79%; H, 4.80%; N, 5.45%

2-Acetyl-8-methylfuro[2,3-a]carbazole (4b)

1-Hydroxy-7-methylcarbazole-2-carbaldehyde (3b)

Yield: 0.215 g (82%)

Mp: 230°C
Synthetic Studies on Cyclopent[b]indoles and Carbazoles

IR (KBr) \( [\nu_{\text{max}} \text{ cm}^{-1}] \) : 3346, 1658, 1577, 1542, 1463, 1369, 1325, 1172, 968, 790, 738

\(^1\)H NMR (CDCl\(_3\)) [\( \delta \text{ ppm} \)]:
(Fig 4.17)
2.51 (s, 3H, C\(_8\)-CH\(_3\)), 2.62 (s, 3H, C\(_2\)-COCH\(_3\)), 7.07 (d, 1H, C\(_7\)-H, \( J = 8.38 \text{ Hz} \)), 7.36 (s, 1H, C\(_9\)-H), 7.52 (d, 1H, C\(_6\)-H, \( J = 8.38 \text{ Hz} \)), 8.05-8.13 (m, 3H, C\(_3\)-H, C\(_4\)-H, C\(_5\)-H), 12.15 (b s, 1H, NH)

Analysis (C\(_{17}\)H\(_{13}\)NO\(_2\)) Calcd
(263.294) Found
C, 77.55 %; H, 04.97 %; N, 05.31 %

2-Acetyl-9-methylfuro[2,3-a]carbazole (4c)

1-Hydroxy-8-methylcarbazole-2-carbaldehyde (3c)

Yield : 0.225 g (0.001 mol)

Mp : 260°C

IR (KBr) \( [\nu_{\text{max}} \text{ cm}^{-1}] \) : 3415, 1662, 1618, 1577, 1502, 1458, 1328, 1232, 1174, 1068, 964, 927

\(^1\)H NMR (CDCl\(_3\)) [\( \delta \text{ ppm} \)]:
(Fig 4.18)
2.50 (s, 3H, C\(_9\)-CH\(_3\)), 2.63 (s, 3H, C\(_2\)-COCH\(_3\)), 7.14-7.16 (m, 1H, C\(_7\)-H), 7.25 (d, 1H, C\(_8\)-H, \( J = 8.14 \text{ Hz} \)), 7.55 (d, 1H, C\(_6\)-H, \( J = 8.14 \text{ Hz} \)), 8.02 (d, 1H, C\(_4\)-H, \( J = 7.72 \text{ Hz} \)), 8.11-8.13 (m, 2H, C\(_3\)-H, C\(_5\)-H), 12.14 (b s, 1H, NH)

Analysis (C\(_{17}\)H\(_{13}\)NO\(_2\)) Calcd
(263.294) Found
C, 77.65 %; H, 04.82 %; N, 05.33 %

2-Acetyl[2,3-a]carbazole (4d)

1-Hydroxycarbazole-2-carbaldehyde (3d)

Yield : 0.211 g (0.001 mol)

Mp : 235°C

IR (KBr) \( [\nu_{\text{max}} \text{ cm}^{-1}] \) : 3359, 1662, 1620, 1577, 1325, 1296, 1700, 1064, 964, 848, 732, 590

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$^1$H NMR (CDCl$_3$) [$\delta$ ppm] (Fig 4.19) : 2.62 (s, 3H, C$_2$-COCH$_3$), 7.23-7.59 (m, 4H, C$_6$-H, C$_7$-H, C$_8$-H, C$_9$-H), 8.11-8.14 (m, 3H, C$_3$-H, C$_4$-H, C$_5$-H), 12.27 (b s, 1H, NH)

Analysis (C$_{16}$H$_{11}$NO$_2$) Calcd : C, 77.09 %; H, 04.44 %; N, 05.61 %
(249.267) Found : C, 77.29 %; H, 04.50 %; N, 05.55 %

Preparation of 1-acetyloxy carbazole-2-carbaldehydes (6a-6d)

General procedure : A mixture of the respective 1-hydroxycarbazole-2-carbaldehyde (2, 0.001 mol) was treated with phenylacetic acid (0.001 mol) in acetic anhydride (5 mL) at 120°C for 5 h. The reaction mixture was poured into crushed ice, and the solid separated was extracted with chloroform (3 x 10 mL) and washed with water. The combined organic layers were dried over anhydrous sodium sulphate. Removal of the solvent by evaporation afforded the crude product which was purified by column chromatography over silica gel using petroleum ether-ethyl acetate mixture (99 : 1) as an eluant.

1-Acetyloxy-6-methylcarbazole-2-carbaldehyde (6a)

1-Hydroxy-6-methyl-carbazole-2-carbaldehyde (3a) : 0.225 g (0.001 mol)
Yield : 0.240 g (90%)
Mp : 175°C
IR (KBr) [v$_{max}$ cm$^{-1}$] (Fig 4.5) : 3247, 1759, 1666, 1560, 1371, 1292, 1205, 1186, 1132, 1014, 893, 808, 599
$^1$H NMR (CDCl$_3$) [$\delta$ ppm] (Fig 4.6) : 2.50 (m, 3H, C$_6$-CH$_3$), 2.51 (m, 3H, C$_1$-OCOCH$_3$), 7.31-8.01 (m, 5H, aromatic-H), 8.16 (b s, 1H, NH), 10.19 (s, 1H, C$_2$-CHO)
Analysis (C$_{16}$H$_{13}$NO$_2$) Calcd : C, 71.89 %; H, 04.90 %; N, 05.24 %
(267.282) Found : C, 71.75 %; H, 04.79 %; N, 05.36 %
1-Acetyloxy-7-methylcarbazole-2-carbaldehyde (6b)

1-Hydroxy-7-methylcarbazole-2-carbaldehyde (3b) : 0.225 g (0.001 mol)

Yield : 0.229 g (86%)

Mp : 156°C

IR (KBr) [v max cm\(^{-1}\)] : 3325, 1749, 1699, 1633, 1506, 1191, 1016, 935, 866, 763

\(^1\)H NMR (CDCl\(_3\)) [\(\delta\) ppm] : 2.54 (s, 3H, C\(_7\)-CH\(_3\)), 2.59 (s, 3H, -OCOCH\(_3\)), 7.08 – 8.16 (m, 6H, aromatic-5H, NH), 10.20 (s, 1H, C\(_2\)-CHO)

(Fig 4.20) Analysis (C\(_{16}\)H\(_{13}\)NO\(_3\)) Calcd : C, 71.89 %; H, 04.90 %; N, 05.24 %
Found : C, 71.77 %; H, 04.81 %; N, 05.40 %

1-Acetyloxy-8-methylcarbazole-2-carbaldehyde (6c)

1-Hydroxy-8-methylcarbazole-2-carbaldehyde (3c) : 0.225 g (0.001 mol)

Yield : 0.245 g (92%)

Mp : 190°C

IR (KBr) [v max cm\(^{-1}\)] : 3371, 1745, 1681, 1633, 1566, 1325, 1201, 1166, 1124, 1031, 777, 711, 478

\(^1\)H NMR (CDCl\(_3\)) [\(\delta\) ppm] : 2.57 (s, 3H, C\(_8\)-CH\(_3\)), 2.59 (s, 3H, -OCOCH\(_3\)), 7.10 – 8.04 (m, 6H, aromatic-5H, NH), 10.21 (s, 1H, C\(_2\)-CHO)

(Fig 4.21) Analysis (C\(_{16}\)H\(_{13}\)NO\(_3\)) Calcd : C, 71.89 %; H, 04.90 %; N, 05.24 %
Found : C, 71.70 %; H, 04.84 %; N, 05.29 %

1-Acetyloxycarbazole-2-carbaldehyde (6d)

1-Hydroxycarbazole-2-carbaldehyde (3d) : 0.211 g (0.001 mol)

Yield : 0.240 g (95%)

Mp : 165°C

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IR (KBr) [v max cm⁻¹] : 3309, 1751, 1637, 1504, 1436, 1325, 1191, 1008, 943, 744, 405

¹H NMR (CDCl₃) [δ ppm] : 2.51 (s, 3H, -OCOCH₃), 7.22 – 8.17 (m, 7H, aromatic-6H, NH), 10.19 (s, 1H, C₂-CHO)
(Fig 4.22)

Preparation of benzo[1,2-b]-1,4-thiazepino[7,6-a]carbazoles (7a-7d)

General procedure: The appropriate 1-hydroxycarbazole-2-carbaldehyde (2, 0.001 mol) was refluxed with α-amino thiophenol (0.001 mol) in acetic acid (10 mL) at 130°C for 5 h. The resulting reaction mixture was then poured into crushed ice. The product separated as a yellow solid was extracted with ethylacetate, washed with water and dried over anhydrous sodium sulphate. Excess solvent was removed by evaporation to obtain the crude product which was then purified by passing through a silica gel column and eluting with petroleum ether-ethyl acetate mixture (99:1) to furnish the respective compound (7).

10-Methylbenzo[1,2-b]-1,4-thiazepino[7,6-a]carbazole (7a)

Yield : 0.094 g (30%)
Mp : 290°C
IR (KBr) [v max cm⁻¹] : 3415, 1922, 1616, 1473, 1447, 1402, 968, 752, 597, 445
(Fig 4.7)
¹H NMR (CDCl₃) [δ ppm] : 2.54 (s, 3H, C₁₀-CH₃), 7.25-7.98 (m, 9H, aromatic-H), 8.48 ( s, 1H, C₆-H), 13.00 (b s, 1H, NH)
(Fig 4.8)
Analysis (C₂₀H₁₄N₂S) Calcd (314.212) Found : C, 76.36 %; H, 04.49 %; N, 08.91 %
11-Methylbenzo[1,2-b]-1,4-thiazepino[7,6-a]carbazole (7b)

1-Hydroxy-7-methylcarbazole-2-carbaldehyde (3b) : 0.225 g (0.001 mol)

Yield : 0.110 g (35%)

Mp : 287°C

IR (KBr) [v max cm⁻¹] : 3261, 2970, 1635, 1571, 1537, 1469, 1336, 1251, 1143, 1043, 898, 744, 597

¹H NMR (CDCl₃) [δ ppm] (Fig 4.23) : 2.54 (s, 3H, C₃CH₃), 7.03-8.01 (m, 9H, aromatic-H), 8.58 (s, 1H, C₆-H), 13.02 (b s, 1H, NH)

Analysis (C₂₀H₁₄N₂S) Calcd (314.212) Found: C, 76.36 %; H, 04.49 %; N, 08.91 %

12-Methylbenzo[1,2-b]-1,4-thiazepino[7,6-a]carbazole (7c)

1-Hydroxy-8-methylcarbazole-2-carbaldehyde (3c) : 0.225 g (0.001 mol)

Yield : 0.094 g (30%)

Mp : 270°C

IR (KBr) [v max cm⁻¹] : 3413, 2923, 1618, 1560, 1544, 1483, 1305, 1235, 1020, 758

¹H NMR (CDCl₃) [δ ppm] (Fig 4.24) : 2.62 (s, 3H, C₁₂CH₃), 7.16-8.08 (m, 9H, aromatic-H), 8.45 (s, 1H, C₆-H), 13.11 (b s, 1H, NH)

Analysis (C₂₀H₁₄N₂S) Calcd (314.212) Found: C, 76.29 %; H, 04.39 %; N, 08.66 %

Benzo[1,2-b]-1,4-thiazepino[7,6-a]carbazole (7d)

1-Hydroxycarbazole-2-carbaldehyde (3d) : 0.211 g (0.001 mol)

Yield : 0.117 g (39%)

Mp : 273°C

IR (KBr) [v max cm⁻¹] : 3411, 3273, 2927, 1641, 1539, 1469, 1328, 1249, 1137, 1018, 736
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\[ ^1 \text{H NMR (CDCl}_3 [\delta \text{ ppm}] \right \}

(Fig 4.25)

\[ 7.40-8.09 (\text{m, 10H, aromatic-H}), \quad 8.55 (\text{s, 1H, C}_6\text{-H}), \quad 13.10 (\text{b s, 1H, NH}) \]

Analysis (C\textsubscript{19}H\textsubscript{12}N\textsubscript{2}S) Calcd

(300.383) Found

C, 75.97 %; H, 04.02 %; N, 09.32 %
C, 75.85 %; H, 04.17 %; N, 05.36 %

Preparation of 3,11-dihydro-2,4-dioxopyrano[2,3-a]carbazoles (8a-8d)

General procedure: A mixture of the respective 1-hydroxycarbazole (2, 0.005 mol), malonic acid (0.005 mol), freshly fused powdered zinc chloride (3 g) and phosphorous oxychloride (4 mL) was kept at room temperature for 24 h, with occasional shaking. The reaction mixture was then poured into crushed ice and the precipitate obtained was filtered, washed with water, dried and purified by column chromatography over silica gel eluting with petroleum ether - ethyl acetate mixture (98 : 2) to get yellow crystals of 3,11-dihydro-2,4-dioxopyrano[2,3-a]carbazoles (8).

3,11-Dihydro-2,4-dioxo-8-methylpyrano[2,3-a]carbazole (8a)

1-Hydroxy-6-methylcarbazole (2a)

Yield : 0.106 g (40%)

Mp : 102\degree C

IR (KBr) [\nu \text{ max cm}^{-1}] (Fig 4.9)

3350, 2858, 1722, 1643, 1583, 1400, 1315, 1218, 1170, 918, 767, 653

\[ ^1 \text{H NMR (CDCl}_3 [\delta \text{ ppm}] \right \}

(Fig 4.10)

\[ 2.50 (\text{s, 3H, C}_8\text{-CH}_3), \quad 2.91 (\text{s, 2H, C}_3\text{-H}_2), \quad 7.02-7.70 (\text{m, 6H, C}_7\text{-H}, \quad \text{C}_5\text{-H}, \quad \text{C}_6\text{-H}, \quad \text{C}_7\text{-H}, \quad \text{C}_6\text{-H}, \quad \text{C}_7\text{-H}, \quad \text{C}_9\text{-H}, \quad \text{C}_{10}\text{-H}), \quad 7.74 (\text{b s, 1H, NH}), \quad 11.04 (\text{s, 1H, OH}) \]

Analysis (C\textsubscript{16}H\textsubscript{11}NO\textsubscript{3}) Calcd

(265.266) Found

C, 72.44 %; H, 04.17 %; N, 05.28 %
C, 72.54 %; H, 04.16 %; N, 05.37 %

3,11-Dihydro-2,4-dioxo-9-methyl-pyrano[2,3-a]carbazole (8b)

1-Hydroxy-7-methylcarbazole (2b)

Yield : 0.098 g (37%)
Synthetic Studies on Cyclopen[b]indoles and Carbazoles

Mp : 110°C
IR (KBr) [ν max cm⁻¹] : 3365, 2848, 1710, 1634, 1573, 1420, 1335, 1228, 1180, 928, 777, 643

¹H NMR (CDCl₃) [δ ppm] (Fig 4.26) : 2.55 (s, 3H, C₉-CH₃), 2.83 (s, 2H, C₃-H₂), 7.02-7.74 (m, 6H, C₃-H, C₅-H, C₆-H, C₇-H, C₈-H, C₁₀-H), 8.39 (b s, 1H, NH), 10.10 (s, 1H, OH), (The ratio of 4-oxo- and 4-hydroxy forms, 3:1)

Analysis (C₁₆H₁₁NO₃) Calcd : C, 72.44 %; H, 04.17 %; N, 05.28 %
(265.266) Found : C, 72.53 %; H, 04.20 %; N, 05.40 %

3,11-Dihydro-2,4-dioxo-10-methylpyrano[2,3-a]carbazole (8c)

1-Hydroxy-8-methylcarbazole (2c) : 0.197 g (0.001 mol)
Yield : 0.109 g (41%)
Mp : 115°C
IR (KBr) [ν max cm⁻¹] : 3446, 2925, 1731, 1653, 1583, 1457, 1303, 1253, 1209, 1123, 1067, 783

¹H NMR (CDCl₃) [δ ppm] (Fig 4.27) : 2.75 (s, 3H, C₁₀-CH₃), 2.93 (s, 2H, C₃-H₂), 7.04-7.95 (m, 6H, C₃-H, C₅-H, C₆-H, C₇-H, C₈-H, C₉-H), 7.97 (s, 1H, NH), 10.95 (s, 1H, OH), (The ratio of 4-oxo- and 4-hydroxy forms, 3:1)

Analysis (C₁₆H₁₁NO₃) Calcd : C, 72.97 %; H, 04.17 %; N, 05.28 %
(265.266) Found : C, 72.90 %; H, 04.10 %; N, 05.19 %

3,11-Dihydro-2,4-dioxopyrano[2,3-a]carbazole (8d)

1-Hydroxycarbazole (2d) : 0.183 g (0.001 mol)
Yield : 0.119 g (45%)
Mp : 120°C
IR (KBr) [ν max cm⁻¹] : 3415, 2925, 1728. 1652, 1434, 1388, 1336, 1299, 1244, 1205, 1163. 1028
Synthetic Studies on Cyclopent[b]indoles and Carbazoles

$^1$H NMR (CDCl$_3$) [δ ppm] (Fig 4.28) : 2.94 (s, 2H, C$_3$-H$_2$), 7.00-7.90 (m, 7H, C$_3$-H, C$_5$-H, C$_6$-H, C$_7$-H, C$_8$-H, C$_9$-H, C$_{10}$-H), 7.95 (b s, 1H, NH), 11.04 (s, 1H, OH), (The ratio of 4-oxo and 4-hydroxy forms, 3:1)

Analysis (C$_{15}$H$_9$NO$_3$) Calcd : C, 71.71 %; H, 03.61 %; N, 05.57 %
(251.240) Found : C, 71.85 %; H, 03.56 %; N, 05.47 %

Preparation of quinolino[2,3-b]carbazolo[6,5-a]pyran-7,8-diones (14a-14d)

General procedure: A mixture of 3,11-dihydro-2,4-dioxo-pyrano[2,3-a]carbazole (8, 0.001 mol) and vinyl acetate (0.001 mol) was treated with 4% sodium hydroxide (10 mL) for 1 h. The reaction mixture was poured into crushed ice, and neutralized with cold dil. HCl. The solid separated was filtered, dried and purified by column chromatography over silica gel using petroleum ether-ethyl acetate mixture (90:10) as an eluant to yield the corresponding quinolino[2,3-b]carbazolo[6,5-a]pyran-7,8-diones (14a-d).

12-Methylquinolino[2,3-b]carbazolo[6,5-a]pyran-7,8-dione (14a)

3,11-Dihydro-2,4-8-methyl-dioxopyrano[2,3-a]carbazole (8a) : 0.265 g (0.001 mol)

Yield : 0.124 g (65%)

Mp : >300°C

IR (KBr) [ν max cm$^{-1}$] (Fig 4.11) : 3413, 3274, 1643, 1595, 1531, 1417, 1390, 1261

$^1$H NMR (CDCl$_3$) [δ ppm] (Fig 4.12) : 2.58 (s, 3H, C$_{12}$-CH$_3$) 5.70 (b s, 1H, N$_2$-H), 7.56-7.62 (m, 8H, aromatic-H), 8.12 (s, 1H, C$_{11}$-H), 8.61 (b s, 1H, carbazole-NH), 11.01 (s, 1H, OH), (The ratio of quinone and quinol forms, 1:1)

Analysis (C$_{23}$H$_{14}$N$_2$O$_3$) Calcd : C, 75.40 %; H, 03.85 %; N, 07.64 %
(366.374) Found : C, 75.54 %; H, 03.76 %; N, 07.57 %

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13-Methylquinolino[2,3-b]carbazolo[6,5-a]pyran-7,8-dione (14b)

3,11-Dihydro-2,4-9-methyl-dioxopyrano[2,3-a]carbazole (8b)

<table>
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<td>Yield</td>
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<td>Mp</td>
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<td>IR (KBr) [v max cm⁻¹]</td>
<td>3415, 3278, 1643, 1595, 1533, 1390</td>
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¹H NMR (CDCl₃) [δ ppm] (Fig 4.29):

- 2.55 (s, 3H, C₃-CH₃)
- 5.68 (b s, 1H, N₂-H)
- 7.05-7.98 (m, 9H, aromatic-H)
- 8.62 (b s, 1H, carbazole-NH)
- 11.03 (s, 1H, OH)

(The ratio of quinone and quinol forms, 1:1)

Analysis (C₂₃H₁₄N₂O₃) Calcd:

- C, 75.40 %; H, 03.70 %; N, 07.64 %

Found:

- C, 75.34 %; H, 03.70 %; N, 07.59 %

14-Methylquinolino[2,3-b]carbazolo[6,5-a]pyran-7,8-dione (14c)

3,11-Dihydro-2,4-10-methyl-dioxopyrano[2,3-a]carbazole (8c)

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<td>IR (KBr) [v max cm⁻¹]</td>
<td>3413, 3274, 1643, 1595, 1531, 1417, 1390, 1261</td>
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</table>

¹H NMR (CDCl₃) [δ ppm] (Fig 4.30):

- 2.68 (s, 3H, C₁₄-CH₃)
- 5.68 (b s, 1H, N₂-H)
- 7.16-8.11 (m, 9H, aromatic-H)
- 8.62 (b s, 1H, carbazole-NH)
- 11.05 (s, 1H, OH)

(The ratio of quinone and quinol forms, 1:1)

Analysis (C₂₃H₁₄N₂O₃) Calcd:

- C, 75.40 %; H, 03.85 %; N, 07.64 %

Found:

- C, 75.34 %; H, 03.70 %; N, 07.59 %

Quinolino[2,3-b]carbazolo[6,5-a]pyran-7,8-dione (14d)

3,11-Dihydro-2,4-dioxopyrano[2,3-a]carbazole (8d)

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<td>Yield</td>
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**Mp** : >300°C

IR (KBr) [ν max cm⁻¹] : 3410, 3273, 1645, 1595, 1500, 1415, 1390, 1222, 1037, 696

¹H NMR (CDCl₃) [δ ppm] (Fig 4.31) : 5.67 (b s, 1H, N₂-H), 7.17-8.05 (m, 9H, aromatic-H), 8.61 (b s, 1H, Carbazole-NH), 11.09 (s, 1H, OH), (The ratio of quinone and quinol forms, 1:1)

Analysis (C₂₂H₁₂N₂O₃) Calcd (352.347) Found

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<td>C</td>
<td>74.99 %; H, 03.43 %; N, 07.99 %</td>
</tr>
<tr>
<td>C</td>
<td>74.84 %; H, 03.36 %; N, 07.87 %</td>
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**Preparation of 12,13-dihydro-5-oxoquinolino[2,3-a]carbazoles (17a-17d)**

**General procedure**

A mixture of the respective 1-hydroxycarbazole (2, 0.005 mol), anthranilic acid (0.005 mol), freshly fused powdered zinc chloride (3 g) and phosphorous oxychloride (4 mL) was kept at room temperature for 24 h, with occasional shaking. The reaction mixture was then poured into crushed ice and the precipitate obtained was filtered, washed with water, dried and this crude mixture showed two spots on TLC and then separated by column chromatography packed with silica gel. The yield of product, 1,7-dibenzoazocin-6,12-dione (16) obtained from removal of the solvent mixture eluting with petroleum ether-ethyl acetate mixture (99:1) was found to be around 20% in all the cases. The removal of solvent from the second fraction (petroleum ether – ethyl acetate, 97:3) afforded the respective 12,13-dihydro-5-oxoquinolino[2,3-a]carbazole (16) as white crystals.

**1,7-Dibenzoazocin-6-12-dione (16)**

Yield : 0.0357 g (~20%)

Mp : 146°C

IR (KBr) [ν max cm⁻¹] (Fig 4.13) : 3450, 2923, 1741, 1625, 1593, 1473, 1593, 1473, 1448, 1311, 1220, 1236, 744

¹H NMR (CDCl₃) [δ ppm] (Fig 4.14) : 6.49-7.79 (m, 8H, C₂, C₃, C₄, C₅, C₈, C₉, C₁₀, C₁₁-H), 8.20 (b s, 2H, N₁-H, N₇-H)

Analysis (C₁₄H₁₀N₂O₂) Calcd (238.245) Found

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<tr>
<td>C</td>
<td>70.58 %; H, 04.30 %; N, 11.76 %</td>
</tr>
<tr>
<td>C</td>
<td>70.68 %; H, 04.36 %; N, 11.67 %</td>
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12,13-Dihydro-9-methyl-5-oxoquinolino[2,3-a]carbazole (17a)

1-Hydroxy-6-methylcarbazole (2a)

Yield : 0.179 g (60%)

Mp : 185°C

IR (KBr) \( \nu_{\text{max}} \text{ cm}^{-1} \) : 3327, 1681, 1591, 1560, 1485, 1290, 1247, 1217, 1174, 1153, 1080

\( ^1\)H NMR (CDCl\(_3\)) \( \delta \text{ ppm} \)

Analysis (C\(_{20}\)H\(_{14}\)N\(_2\)O) Calcd : C, 80.46 %; H, 04.76 %; N, 09.45 %

: C, 80.55 %; H, 04.86 %; N, 09.57 %

12,13-Dihydro-10-methyl-5-oxoquinolino[2,3-a]carbazole (17b)

1-Hydroxy-7-methylcarbazole (2b)

Yield : 0.164 g (55%)

Mp : 178°C

IR (KBr) \( \nu_{\text{max}} \text{ cm}^{-1} \) : 3350, 1671, 1599, 1550, 1476, 1278, 1256, 1227, 1176, 1143, 1070

\( ^1\)H NMR (CDCl\(_3\)) \( \delta \text{ ppm} \)

Analysis (C\(_{20}\)H\(_{14}\)N\(_2\)O) Calcd : C, 80.46 %; H, 04.76 %; N, 09.45 %

: C, 80.61 %; H, 04.89 %; N, 09.31 %

12,13-Dihydro-11-methyl-5-oxoquinolino[2,3-a]carbazole (17c)

1-Hydroxy-8-methylcarbazole (2c)

Yield : 0.176 g (59%)

Mp : 175°C

IR (KBr) \( \nu_{\text{max}} \text{ cm}^{-1} \) : 3334, 1683, 1624, 1512, 1461, 1247, 1215
Synthetic Studies on Cyclopent[b]indoles and Carbazoles

$^1$H NMR (CDCl$_3$) [δ ppm] (Fig 4.33)

- 2.53 (s, 3H, C$_{11}$-CH$_3$), 5.84 (b s, 1H, N$_{13}$-H), 6.62 – 8.40 (m, 10H, aromatic 9H and N$_{13}$-H)

Analysis (C$_{20}$H$_{14}$N$_2$O)

Calcd (298.550) Found
- C, 80.46 %; H, 04.76 %; N, 09.45 %
- C, 80.54 %; H, 04.83 %; N, 09.37 %

12,13-Dihydro -5-oxoquinolino[2,3-a]carbazole (17d)

1-Hydroxy-carbazole (2d)

Yield : 0.183 g (0.001 mol)

Yield : 0.173 g (61%)

Mp : 180°C

IR (KBr) [$v_{max}$ cm$^{-1}$]

- 3332, 1676, 1616, 1560, 1485, 1438, 1325, 1215, 1085, 1043, 742, 759

$^1$H NMR (CDCl$_3$) [δ ppm] (Fig 4.34)

- 5.82 (b s, 1H, N$_{13}$-H), 6.75 – 8.24 (m, 11H, aromatic 10H and N$_{12}$-H)

Analysis (C$_{19}$H$_{12}$N$_2$O)

Calcd (284.316) Found
- C, 80.26 %; H, 04.25 %; N, 09.85 %
- C, 80.29 %; H, 04.36 %; N, 09.77 %
Fig 4.17 $^1$H NMR spectrum of 2-acetyl-8-methylfuro[2,3-$\alpha$]carbazole (4b)

Fig 4.18 $^1$H NMR spectrum of 2-acetyl-9-methylfuro[2,3-$\alpha$]carbazole (4c)
Fig 4.19 $^1$H NMR spectrum of 2-acetylfuro[2,3-a]carbazole (4d)

Fig 4.20 $^1$H NMR spectrum of 1-acetyloxy-7-methylcarbazole-2-carbaldehyde (6b)
Fig 4.21: $^1$H NMR spectrum of 1-acetyloxy-8-methylcarbazole-2-carbaldehyde (6c)

Fig 4.22: $^1$H NMR spectrum of 1-acetyloxy carbazole-2-carbaldehyde (6d)
Fig 4.25 $^1$H NMR spectrum of benzo[1,2-6]-1,4-thiazepino[7.6-<i>l</i>]carbazole (7d)

Fig 4.26 $^1$H NMR spectrum of 3,11-dihydro-2,4-dioxo-9-racemyl-pyran[2,3-a]carbazole (8b)
Fig 4.27 $^1$H NMR spectrum of 3,11-dihydro-2,4-dioxo-10-methylpyrano[2,3-a]carbazole (8c)

Fig 4.28 $^1$H NMR spectrum of 3,11-dihydro-2,4-dioxopyrano[2,3-a]carbazole (8d)
Fig 4.29 $^1$H NMR spectrum of 13-methylquinolino[2,3-b]carbazolo[6,5-o]pyran-7,8-dione (14b)

Fig 4.30 $^1$H NMR spectrum of 14-methylquinolino[2,3-b]carbazolo[6,5-o]pyran-7,8-dione (14c)
Fig 4.31 $^1$H NMR spectrum of quinolino[2,3-b]carbazolo[6,5-a]pyran-7,8-dione (14d)

Fig 4.32 $^1$H NMR spectrum of 12,13-dihydro-10-methyl-5-oxoquinolino[2,3-a]carbazole (17b)
Fig 4.33 $^1$H NMR spectrum of 12,13-dihydro-11-methyl-5-oxoquinolino[2,3-a]carbazole (17c)

Fig 4.34 $^1$H NMR spectrum of 12,13-dihydro-5-oxoquinolino[2,3-a]carbazole (17d)