The design of molecules that spontaneously organize into helical architecture is of considerable interest because of their fascinating structural features as well as their potential applications. Since the pioneering discovery of cyclohept[b]indoles, an antidepressant agent, several reports on the synthesis of functionalised cyclohept[b]indoles have appeared. Merour et al. have reported the toxicity and structure activity relationship of benzocyclohept[b]indoles and these were found to be potent antiinflammatory and anticancer agents. Therefore, much effort has been directed towards the exploitation of efficient methodologies for the construction of heterocyclo-fused cyclohept[b]indoles, which will throw some light on the experimentations in synthetic organic chemistry.

1-Oxo-1,2,3,4-tetrahydrocarbazoles were successfully utilized by Prasad et al. for the synthesis of many carbazole alkaloids and this prompted us to synthesize 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles which can be used as potential precursors for the construction of highly functionalised heterocyclic rings appended to it. We envisioned that, developing a general and efficient route towards the synthesis of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole derivatives would significantly enhance the utility of it to attain our synthetic strategy.

2.1. Hydrazones

1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles have been obtained by using Japp-Klingemann method. According to this procedure, hydrazones can be conveniently synthesized by condensing β-dicarbonyl compounds with diazonium salts in solution. These hydrazones were starting materials in the Fischer indole synthesis, which lead to 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles.
Japp-Klingemann reaction\textsuperscript{193} is a special case of the coupling of diazonium salts with aliphatic or cyclic active methylene compounds. The first step involves the direct union of the anion of active methinyl compound and the diazonium cation. The second step is a simple cleavage of the formyl group, which is generally favoured by increasing the alkalinity of the solution.

2-Hydroxymethylenecycloheptanone (2) was prepared by formylation of cycloheptanone (1) (Scheme 2.1). Anisworth\textsuperscript{194} used sodium hydride in dry ether for the formylation of cyclohexanone. Mukherji and Bhattacharya\textsuperscript{195} condensed cyclohexanone with ethyl formate using dry sodium ethoxide in dry ether. Dry sodium methoxide\textsuperscript{196} was also used effectively. We used the later reagent for the preparation of 2-hydroxymethylene-1-cycloheptanone (2).

**Scheme 2.1**

![Chemical Structure](attachment:image.png)

Condensation of the diazotised aniline derivatives (4) with 2-hydroxymethylenecycloheptanone (2) under Japp-Klingemann conditions furnished the respective cycloheptan-1,2-dione-1-arylhydrazones (5) (Scheme 2.3). The IR spectrum (Fig 1) of an orange red prism of the compound 5b obtained by the reaction of diazotised p-toluidine (4b) with 2 showed the bands at 1654 cm\textsuperscript{-1} due to carbonyl stretching and 1624 cm\textsuperscript{-1} due to C=N stretching frequencies respectively. Its \textsuperscript{1}H NMR spectrum (Fig 2) registered a methyl proton signal as a singlet at \(\delta\) 2.30 and five methylene protons signal as multiplets at \(\delta\) 1.77-2.68. The resonance signal corresponding to four aromatic protons appeared as a multiplet at \(\delta\) 7.05-7.26 and a broad singlet at \(\delta\) 13.67 for -NH proton. The above spectrum clearly indicates the structure of the compound as cycloheptan-1,2-dione-1-(p-methylphenyl)hydrazone (5b). The mass spectrum (m/z 230) and elemental analysis: C 73.00%, H 07.98%, N 12.10% agreed very well with the proposed molecular formula C\textsubscript{14}H\textsubscript{18}N\textsubscript{2}O augmenting the structure of the compound as cycloheptan-1,2-dione-1-(p-
Fig 1. IR spectrum of cycloheptan-1,2-dione-1-(p-methylphenyl) hydrazone (5b)

Fig 2. $^1$H NMR spectrum of cycloheptan-1,2-dione-1-(p-methylphenyl) hydrazone (5b)
methylphenyl)hydrazone (5b). The generality of the reaction was tested with 4a, 4c, 4d and 4e (Scheme 2.3)

**Scheme 2.2**

![Scheme 2.2 diagram](image)

3, 4  
- **a:** R₁ = R₂ = R₃ = H
- **b:** R₁ = CH₃, R₂ = R₃ = H
- **c:** R₂ = CH₃, R₁ = R₃ = H
- **d:** R₃ = CH₃, R₁ = R₂ = H
- **e:** R₁ = Cl, R₂ = R₃ = H

**2.2. Synthesis of 1-oxo-1,2,3,4,5,10-hexahydrocyclohepta[b]indoles**

Kent's reagent (a 4:1 mixture of acetic acid and hydrochloric acid) was found to be superior to both gla acetic acid and 40% aq sulphuric acid for the cyclisation of hydrazones (5). Kapil and Chakraborty et al. had used this reagent successfully for this purpose.

A mixture of phosphorus pentoxide and orthophosphoric acid (1:5 w/w) was found to be a better cyclising agent, but it gave a mixture of isomeric 1-oxo-1,2,3,4,5,10-hexahydrocyclohepta[b]indoles when meta substituted hydrazone (6c) was reacted. In order to get a single product in such cases, we used Kent's reagent in our investigation.
The cycloheptan-1,2-dione-1-\((\rho\text{-methylphenyl})\)hydrazone (5b) upon acid cyclization using Kent’s reagent (CH\textsubscript{3}COOH : HCl, 4:1) gave a single product 7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6b). The structure of 6b was established on the basis of spectral data and elemental analysis. Its IR spectrum (Fig 3) exhibited a sharp and strong absorption band at 1618 cm\(^{-1}\) characteristic of \(\alpha,\beta\)-unsaturated carbonyl group and a band at 3328 cm\(^{-1}\) ascribable to -NH group. Its \(^1\)H NMR spectrum (Fig 4) displayed a singlet at \(\delta\) 2.45 for \(C_7\) - CH\textsubscript{3}, and four multiplets at \(\delta\) 1.95-2.02, \(\delta\) 2.05-2.11, \(\delta\) 2.82-2.85 and \(\delta\) 3.11-3.14 for \(C_3, C_4, C_2\) and \(C_5\) methylene protons respectively. Three aromatic protons envelop at \(\delta\) 7.16-7.42 (\(C_6, C_8\) and \(C_9\) protons) and -NH proton resonates as a broad singlet at \(\delta\) 8.86. The molecular ion peak in its mass spectrum appeared as a base peak at m/z 213. The elemental analysis: C 78.82%, H 07.15%, N 06.45% was compatible with the molecular formula C\textsubscript{14}H\textsubscript{15}NO. A series of similar compounds 6a, 6c, 6d and 6e were realized from 4a, 4c, 4d and 4e through the hydrazones 5a, 5c, 5d and 5e respectively (Scheme 2.3).

### Scheme 2.3

\[
\begin{align*}
4 \quad + \quad NaOAc, CH\textsubscript{3}OH & \quad \rightarrow \quad 5 \\
\text{H}_{2}O & \quad \rightarrow \quad 6
\end{align*}
\]

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

2.3. Synthesis of 2-benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles

After achieving the synthesis of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e), an efficient precursor for the synthesis of many novel heterocyclo- fused cyclohept[b]indoles, mixed aldol reaction\(^{198}\) of 7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6b) with benzaldehyde under basic conditions led to the
Fig. 3. IR spectrum of 7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[h]indole (6h)

Fig. 4. $^1$H NMR spectrum of 7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[h]indole (6h)
formation of 2-benzylidene-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7b) in 80% yield (Scheme 2.4).

Scheme 2.4

\[ R_1 \]  
\[ R_2 \]  
\[ R_3 \]  
\[ + \]  
\[ \text{alc. KOH} \]  
\[ \text{R}_1 \]  
\[ \text{R}_2 \]  
\[ \text{R}_3 \]  

6, b: \( R_1 = \text{CH}_3, R_2 = R_3 = H \)  
7: \( R_2 = \text{CH}_3, R_1 = R_3 = H \)  
\( R_i = R_2 = H \)  
\( R_1 = \text{Cl}, R_2 = R_3 = H \)  

e: 

Its IR spectrum (Fig 5) exhibited strong absorption bands at 1641 cm\(^{-1}\) characteristic of \( \alpha, \beta \)-unsaturated carbonyl group and at 3311 cm\(^{-1}\) ascribable to -NH group. The \(^1\)H NMR spectrum (Fig 6) showed the disappearance of \( C_2 \) methylene proton signal and the appearance of benzylic proton signal in the downfield as a singlet at \( \delta \) 7.78, which proved the mixed aldol condensation of 6b with benzaldehyde to give 7b. The aromatic cluster accounting for eight protons appeared at \( \delta \) 7.18-7.43 as a multiplet. The \( C_3 \) and \( C_5 \) methylene protons appeared as two multiplets at \( \delta \) 2.89-2.91 and \( \delta \) 3.18-3.21 respectively. The \( C_4 \) methylene proton resonates as a multiplet at \( \delta \) 2.17-2.23 while that of methyl group and indole -NH as a singlet at \( \delta \) 2.46 and as a broad singlet at \( \delta \) 8.99 respectively. The molecular ion peak in its mass spectrum at m/z 301 and elemental analysis: C 83.70%, H 06.39%, N 04.59% were in accordance with the molecular formula \( \text{C}_{21}\text{H}_{19}\text{NO} \). Mixed aldot condensation of 6a, 6c, 6d and 6e with benzaldehyde gave the corresponding 2-benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles 7a, 7c, 7d and 7e in 80-90% yield (Scheme 2.4).

2.4. Synthesis of 4,5,6,11-tetrahydro-3-phenylisoxazolo[4',3':6,7]cyclohept[b]indoles

In a typical experiment, when 2-benzylidene-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7b) was reacted with hydroxylamine hydrochloride in pyridine,\(^{199}\) it afforded white solid, mp 227°C, which had IR band around 3284 cm\(^{-1}\)
Fig 5. IR spectrum of 2-benzylidene-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclopenta[b]indole (7b)

Fig 6. $^1$H NMR spectrum of 2-benzylidene-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclopenta[b]indole (7b)
assignable to -NH group (Fig 7). Its $^1$H NMR spectrum (Fig 8) showed a singlet at $\delta$ 2.47 for the presence of C$_8$-CH$_3$. The multiplets at $\delta$ 2.12-2.17, $\delta$ 3.06-3.08 and $\delta$ 3.16-3.19 were due to the presence of methylene protons at C$_5$, C$_4$ and C$_6$ respectively. The aromatic region indicated a complex multiplet at $\delta$ 7.09-7.73 for eight protons. A broad singlet at $\delta$ 8.74 was due to a -NH proton. The molecular ion peak in its mass spectrum appeared as a base peak at m/z 314. Elemental analysis C 80.32%, H 05.66%, N 08.88% corroborated well with the proposed molecular formula C$_{21}$H$_{18}$N$_2$O. From these evidences, the structure was assigned to be 8-methyl-3-phenyl-4,5,6,11-tetrahydroisoxazolo[4',3':6,7]cyclohept[b]indole (8b). Similarly, the other 3-phenyl-4,5,6,11-tetrahydroisoxazolo[4',3':6,7]cyclohept[b]indole derivatives 8a, 8c, 8d and 8e were obtained from 7a, 7c, 7d and 7e respectively under identical conditions and their structures confirmed by spectral and analytical data (Scheme 2.5).

Scheme 2.5


Accordingly, when 2-benzylidene-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7b) was reacted with hydrazine hydrate in ethanol, it gave 8-methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolino[4',3':6,7]cyclohept[b]indole (9b) in 81% yield. The IR spectrum (Fig 9) revealed the presence of C=N (1590 cm$^{-1}$) thereby indicating the absence of carbonyl absorption. The $^1$H NMR spectrum (Fig 10) of 9b showed three proton singlet at $\delta$ 2.44, which was associated with methyl group. It showed multiplets at $\delta$ 2.75-2.82, $\delta$ 3.06-3.25 and $\delta$ 4.41-4.45, which were assignable to C$_{3a}$, C$_6$ and C$_3$ protons.
Fig 7. IR spectrum of 8-methyl-3-phenyl-4,5,6,11-tetrahydroisoxazolo[4',3',6,7]cyclohept[6]indole (8b)

Fig 8. $^1$H NMR spectrum of 8-methyl-3-phenyl-4,5,6,11-tetrahydroisoxazolo[4',3',6,7]cyclohept[6]indole (8b)
respectively. The C₄ and C₅ methylene protons also appeared as a multiplet in the region δ 2.10-2.20. The aromatic cluster accounting for eight protons appeared as a multiplet at δ 7.04 -7.54. The proton of indole NH was found to resonate as a singlet at δ 8.51 and that of pyrazolino NH as a broad singlet at δ 5.94. The mass spectrum showed the molecular ion peak at m/z 315. The elemental analysis agreed well with the proposed molecular formula C₂₁H₂₁N₃ augmenting the structure of the compound to be 9b. The generality of the above reaction was tested with 7a, 7c, 7d and 7e (Scheme 2.6).

Scheme 2.6

![Scheme 2.6](image)

7,9 a: R₁ = R₂ = R₃ = H  
b: R₁ = CH₃, R₂ = R₃ = H  
c: R₂ = CH₃, R₁ = R₃ = H  
d: R₃ = CH₃, R₁ = R₂ = H  
e: R₁ = Cl, R₂ = R₃ = H


The indole nucleus is associated with wide spectrum of pharmacological properties such as antitumor, antidepressant, antiinflammatory, antibacterial, antifungal and antituberculosis activities.⁴¹-⁵⁶ Besides these, many indolocarbazoles display interesting biological activities,²⁰¹-²⁰⁶ in particular the derivatives of indolo[2,3-α]carbazoles (10)²⁰⁷-²⁰⁹ such as the alkaloid k-252a²¹⁰,²¹¹ and staurosporine²¹²,²¹³ where both are potent PKC inhibitors. Recently, Jan Bergman et al¹¹² have synthesized cyclohept[1,2-b:5,4-b']bisindole (11) in two steps and reported to be sensitive towards oxidation, but it was however reasonably stable when stored in a freezer.
Fig 9. IR spectrum of 8-methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolino[4',3':6,7]cyclohept[b]indole (9b).

Fig 10. $^1$H NMR spectrum of 8-methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolino[4',3':6,7]cyclohept[b]indole (9b).
On the basis of these facts, we focussed our interest in the development of an efficient route to derive stable and hitherto unknown indolo[2',3':7,6]cyclohept[b]indole (12) in a single step, a related two indole rings fused with cycloheptane. This required the treatment of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6) with phenyl hydrazine in acetic acid (Scheme 2.7).

**Scheme 2.7**

![Scheme 2.7](image)

6 - 12  

- **a:** R1 = R2 = R3 = H
- **b:** R1 = CH3, R2 = R3 = H
- **c:** R2 = CH3, R1 = R3 = H
- **d:** R3 = CH3, R1 = R2 = H
- **e:** R1 = Cl, R2 = R3 = H

The reaction of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a) with phenyl hydrazine in presence of glacial acetic acid afforded a single product and identified to be 5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indole (12a) on the basis of its analytical and spectral data. The disappearance of carbonyl stretching frequency and the appearance of -NH stretching frequency at 3413 cm⁻¹ in its IR spectrum (Fig 11) revealed the formation of compound 12a. The ¹H NMR spectrum (Fig 12) exhibited two multiplets one at δ 2.15-2.21 corresponding to C6 protons and at δ 3.12-3.19 for C5 and C7 methylene protons. The eight protons aromatic envelop resonate as a multiplet in the region δ 7.10-7.59. Further, the appearance of -NH signal as a broad singlet at δ 8.00 of two proton intensity confirmed the structure of compound 12a as 5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indole. The mass spectrum of the compound showed the molecular ion peak at m/z 272. The elemental analysis further advocated the proposed molecular formula C19H16N2. Thus, it was assumed that the reaction commenced via the formation of hydrazone, which loses ammonia molecule as in Fischer indole synthesis. 

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Fig 11. IR spectrum of $5H,6,7,12,13$-tetrahydroindolo[2',3':7,6]cyclohept[f]indole (12a)

Fig 12. $^1$H NMR spectrum of $5H,6,7,12,13$-tetrahydroindolo[2',3':7,6]cyclohept[f]indole (12a)
Studies in Heterocycles

5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indole (12a). 1-Oxo derivatives 6b-e gave similar outcome leading to 12b-e.

2.7. An attempt to device a synthetic route for 4-oxopyrano[2',3':7,6]-cyclohept[b]indoles—Acetyl derivatives of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles

In further studies of our neat techniques, attention was focussed on to synthesize 2-methyl-4-oxopyrano[2',3':7,6]cyclohept[b]indoles (14) from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6). Hence, our interest was derived from an analogous situation in which the transformation of cycloheptanone (1) to 2-methyl-4-oxopyrano[2,3-a]cycloheptane (13) was effected using gla acetic acid and polyphosphoric acid (Scheme 2.8).

Scheme 2.8

With this view, 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a) was treated with the mixture of gla acetic acid and polyphosphoric acid at 100°C in an expectation that the reaction would proceed as shown in scheme 2.9, which primarily requires the enolisation of keto group.

Intriguingly, after work up, it yielded a different product (Scheme 2.10) melted at 219°C. The IR spectrum (Fig 13) of the compound showed two strong absorptions at 3298 cm⁻¹ and 1664 cm⁻¹ which were accountable for -NH and C=O stretching vibrations respectively. The ¹H NMR spectrum (Fig 14) exhibited the following resonances. A three proton singlet at 8 2.60, four two proton multiplets at 8 1.92-1.99, 8 2.03-2.09, 8 2.79-2.82 and 8 3.12-3.15 respectively, two doublets one at 8 7.33, J=8.76 Hz (ortho coupling) and the other at 8 7.92 with J=8.76 Hz (ortho coupling) and J=1.40 Hz (meta coupling), a
Fig 13. IR spectrum of 7-acetyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15a)

Fig 14. $^1$H NMR spectrum of 7-acetyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15a)
This was supported by the appearance of the molecular ion peak in its mass spectrum at m/z 241 whereas the expected product requires the molecular ion peak at m/z 265. A conclusive proof was derived from the elemental analysis C 74.52%, H 06.32%, N 05.78% that was in agreement with the molecular formula C_{15}H_{15}NO_2. The three proton singlet at δ 2.60 was accountable for the acetyl group protons, two doublets in the aromatic region at δ 7.33 with J=8.76 Hz and δ 7.92 with J=8.76 Hz and J=1.40 Hz were assignable for C_9 and C_8 protons respectively and a singlet at δ 8.28 was accountable for C_6 proton. Based on the above mentioned data, the appearance of four methylene proton signal as four multiplets and acetyl group protons as a singlet clearly ruled out the possibility of the formation of product (14a) and the structure of the product was assigned to be 7-acetyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15a) which is a simple Friedel crafts acylation.
product. This observation provoked us to study the orientation and reactivity effect of the substituents. Thus we have undertaken a systematic study of the reaction of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6b-e) with acetic acid and polyphosphoric acid, which gave the corresponding acylated products 15b-e.

When 7th position of 6a was blocked with either methyl (6b) or chloro (6e) group acylation occurred at 9th position (15b and 15e). When either 8th or 9th position (6c and 6d) was blocked by a methyl group the acetyl group entered the 7th position (15c and 15d). From the above observation it can be concluded that 7th position is more active towards an electrophile compared to other positions. This can be supported by the fact that the 7th position is para to the ring nitrogen atom. Further, when 7th position was substituted with chloro group poor yield was obtained. This may be due to the deactivating effect of the chloro group (Scheme 2.10).

**2.7.1 Antibacterial and antifungal activities**

All the newly synthesized compounds were screened for their *in vitro* antibacterial and antifungal activities by disc diffusion method. *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi* were the pathogens used for antibacterial studies. *Candida albicans*, *Trichophyton rubrum* and *Aspergillus niger* were used for antifungal studies. The minimal inhibitory concentration (MIC) values were determined by serial dilution method (Table 2.1).
Table 2.1 Antibacterial and antifungal activities of the compounds 15a-e

<table>
<thead>
<tr>
<th>Minimum inhibitory values (µg/mL)</th>
</tr>
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<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>15a</td>
</tr>
<tr>
<td>15b</td>
</tr>
<tr>
<td>15c</td>
</tr>
<tr>
<td>15d</td>
</tr>
<tr>
<td>15e</td>
</tr>
</tbody>
</table>

The screening results indicate that the chloro compound exhibited moderate inhibition against *S. aures*, *E. coli* and all the fungi tested. Compounds 15a and 15d inhibited the growth of *T. rubrum* at 50 µg/mL and 70 µg/mL.


Pyrido carbazoles such as ellipticine, olivacine are naturally occurring cytotoxic and antibiotic alkaloids of the fascinating heterocyclic compounds. It is well established that the pyridocarbazole ring is an appropriate skeleton to design DNA intercalating drugs.\(^5^6\) There has been a widespread interest in the unprecedented structures, the biogenesis and the synthesis of these pyridocarbazoles, due to the discovery of promising anticancer activities associated with this system.\(^5^5,1^5^7-1^6^0\) Ellipticinium is used clinically as a drug to treat advanced breast cancer and solid tumour.\(^1^6^1\) Further, progress were made thereafter by the synthesis of aminocarbazole, a biologically closely related member, which gives an ingenious pathway to prepare pyridocarbazole. A review of synthetic procedures towards aminocarbazoles from research reports and patent applications showed that most efforts suffer from some limitations such as complicated procedures, low yields or difficulty in accessing starting materials.\(^1^0^3-1^0^7\) Benzocyclohept[b]indoles were reported, to be a potent antitumour and antiinflammatory agent.\(^6^1-6^3,1^2^4,1^2^6\) These findings contemplated us to derive a new methodology to build up a related pyridine ring fused to cyclohept[b]indoles, pyrido[2',3':7,6]cyclohept[b]indoles from the precursor 1-amino-2-oxocyclohept[b]indoles (25).
Our appetite towards the synthesis of 1-amino-2-oxocyclohept[b]indole (25) was based on an analogous situation in which the transformation of 1-hydroxyimino-4-methylcyclohexanone (16) to keto group transposed product (21), upon reaction with acetyl chloride in acetic anhydride followed by hydrolysis\(^{216}\) (Scheme 2.11).

**Scheme 2.11**

![Scheme 2.11 Diagram]

Proceeding on the same lines, as above, we demonstrated the reaction on 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole derivatives (22) possessing the similar structural features and expected the keto group transposed product in order to derive pyrido[2',3':7,6]cyclohept[b]indoles (Scheme 2.12).

**Scheme 2.12**

![Scheme 2.12 Diagram]
2.9. Synthesis of 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indoles

In this context, 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a) on treatment with hydroxylamine hydrochloride in pyridine afforded white solid, mp 106°C which showed IR bands (Fig 15) at 3448 cm⁻¹ and 3200 cm⁻¹ indicating the presence of -OH and -NH groupings respectively. Its ¹H NMR spectrum showed (Fig 16) four multiplets at δ 1.82–2.05, δ 2.71–2.80, δ 2.90–3.10 and δ 3.25–3.40 correspond to the methylene protons present at C₄, C₅, C₃ and C₂ respectively. The aromatic cluster accounting for four protons appeared at δ 6.80–7.61 as a multiplet. Two broad singlets one at δ 8.71 for -NH proton and the other at δ 9.99 for -OH proton clearly indicate the product formation. The elemental analysis and the mass spectrum (m/z 214) of the compound corroborated well with the proposed molecular formula C₁₃H₁₄N₂O thereby confirming the compound 22a as 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole. A similar series of compounds 22b, 22c, 22d and 22e were obtained from 6b, 6c, 6d and 6e respectively (Scheme 2.12).

2.10. Synthesis of 1-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[b]indoles

After successfully obtaining 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22a), it was refluxed with acetyl chloride, acetic anhydride and pyridine in order to obtain 2-acetoxy-1-N,N-diacetylamino-3,4,5,10-tetrahydrocyclohept[b]indole (23a) as shown in Scheme 2.12. The IR spectrum (Fig 17) of the product showed -NH absorption at 3385 cm⁻¹. Its ¹H NMR spectrum (Fig 18) showed the following signals.

a. a '2H' multiplet at δ 2.01–2.07 (C₄-H₂)
b. a '3H' singlet at δ 2.37 (COCH₃)
Fig 15. IR spectrum of 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22a)

Fig 16. $^1$H NMR spectrum of 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22a)
c. two '2H' multiplets at δ 2.54 and δ 3.04 (C3-H2 and C5-H2)
d. a '1H' triplet at δ 5.85 (NHCOCH3)
e. two '1H' triplets at δ 7.04 and δ 7.12 (C7-H and C8-H, J = 7.2 Hz)
f. two '1H' doublets at δ 7.20 and δ 7.45 (C6-H and C9-H, J = 7.2 Hz)
g. two '1H' broad singlet at δ 7.63 and 12.01 (NH and OH)

The above mentioned data corresponds to the enol form of 1-N-acetylamino-2-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (24a). The analytical values (C15H16N2O2) and the molecular ion peak at m/z 256 in its mass spectrum also correspond to 1-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[b]indole (26a). It was pertinent to point out here that the product 1-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[b]indole (26a) was obtained in a single step directly from 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22a) without the formation of the anticipated 2-acetoxy-1-N,N-diacetylamino-3,4,5,10-tetrahydrocyclohept[b]indole (23a). 22b, 22c and 22d gave similar outcome leading to 26b, 26c and 26d respectively (Scheme 2.13).

Scheme 2.13

6, 22, 24, 26 a: R1 = R2 = R3 = H
b: R1 = CH3, R2 = R3 = H
c: R2 = CH3, R1 = R3 = H
d: R3 = CH3, R1 = R2 = H

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Fig 17. IR spectrum of 1-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[\(\beta\)]indole (26a)

Fig 18. \(^1\)H NMR spectrum of 1-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[\(\beta\)]indole (26a)
Our attempt to hydrolyse l-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[b]indoles (24) to l-amino-2-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles a good precursor to obtain pyrido[2',3':7,6]cyclohept[b]indoles using hydrochloric acid was unsuccessful.

![Chemical structure](image)

2.11. Reaction of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles with o-aminoacetophenone

At this stage, synthesis of quinolines by Friedlander's method\textsuperscript{217,218} caught our attention. So, in our expected effort to synthesize pyrido[2',3':7,6]cyclohept[b]indoles, the synthon, 7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole 6b was reacted with o-aminoacetophenone in glacial acetic acid in presence of few drops of conc sulphuric acid for 8 h at 120°C (Scheme 2.14). Interestingly, the reaction mixture showed two spots on tlc. These two products were separated by column chromatography. The fraction eluted with petroleum ether-ethyl acetate in the ratio 98:2, yielded a compound, which crystallised as yellow prisms (mp 139°C). The IR spectrum (Fig 19) revealed the absence of carbonyl stretching frequency but the presence of C=N stretching frequency at 1588 cm\textsuperscript{-1} and NH stretching frequency at 3350 cm\textsuperscript{-1}.

The \textsuperscript{1}H NMR spectrum (Fig 20) registered the following assignable signals

a. a ‘2H’ multiplet at δ 2.17-2.23 (C\textsubscript{8}-H\textsubscript{2})

b. a ‘3H’ singlet at δ 2.49 (C\textsubscript{11}-CH\textsubscript{3})

c. a ‘3H’ singlet at δ 2.72 (C\textsubscript{6}-CH\textsubscript{3})

d. a ‘4H’ multiplet at δ 3.16-3.22 (C\textsubscript{7}-H\textsubscript{2}, C\textsubscript{9}-H\textsubscript{2})

e. two ‘1H’ doublets at δ 7.11 and 7.34 (C\textsubscript{12}-H, C\textsubscript{13}-H, J = 8.2 Hz)

f. a ‘1H’ singlet at δ 7.40 (C\textsubscript{10}-H)

g. a ‘2H’ multiplet at δ 7.47-7.64 (C\textsubscript{3}-H, C\textsubscript{4}-H)

h. two ‘1H’ doublets at δ 8.00 and 8.05 (C\textsubscript{2}-H, C\textsubscript{5}-H, J = 8.2 Hz)

i. a ‘1H’ broad singlet at δ 9.75 (NH)
Fig 19. IR spectrum of 6,11-dimethyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27b)

Fig 20. $^1$H NMR spectrum of 6,11-dimethyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27b)
The elemental analysis C 84.64%, H 06.53%, N 09.01% and molecular ion peak at m/z 312 (48%) in its mass spectrum supported the molecular formula C$_{22}$H$_{20}$N$_2$. Further, in the mass spectrum the fragment peaks at m/z 130 and m/z 142 were characteristic of substituted quinoline nucleus. On the basis of above mentioned data the product was attested to be 6,11 dimethyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27b) which can be considered as benzo substituted pyrido [2',3':7,6]cyclohept[b]indole. A similar series of compounds 27a, 27c, 27d and 27e were obtained from the corresponding 6a, 6c, 6d and 6e respectively (Scheme 2.14)

The petroleum ether-ethyl acetate (95:5) fraction afforded colourless crystals on crystallization from chloroform (mp 116 °C). Its IR spectrum (Fig 21) showed absorption at 1683 cm$^{-1}$. The $^1$H NMR spectrum (Fig 22) exhibited two singlets each of three proton intensity at δ 2.28 and δ 2.99, a singlet of one proton intensity at δ 7.74, eight protons aromatic multiplet at δ 7.23-8.65 and a broad singlet at δ 12.99. The $^{13}$C NMR spectrum (Fig 23) showed signals at 19.30, 25.52, 121.51, 121.81, 123.37, 124.06, 125.01, 126.90, 129.11, 129.37, 130.20, 130.59, 138.86, 146.15, 158.01, and 168.79 ppm. The mass
Fig 21. IR spectrum of 12-methyl-6-(1'-propene-2'-ol)-dibenzo[h,f][1,5]diazocine (29)

Fig 22. $^1$H NMR spectrum of 12-methyl-6-(1'-propene-2'-ol)-dibenzo[h,f][1,5]diazocine (29)
Fig 23. $^{13}$C NMR Spectrum of 12-methyl-6-(1'-propene-2'-ol)-dibenzo[\textit{h},\textit{i}][1,5]\textit{diazocine (29)}
spectrum showed the molecular ion peak at m/z 276. From the above mentioned spectral and analytical data the structure of the product was attested to be 12-methyl-6-(1'-propene-2'-ol)-dibenzo[b,f][1,5]diazocine (29) (Scheme 2.14). The elemental analysis was compatible with the molecular formula C_{18}H_{16}N_{2}O. Reaction of other 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles 6a, 6c, 6d and 6e gave the same 12-methyl-6-(1'-propene-2'-ol)-dibenzo[b,f][1,5]diazocine (29). Due to the formation of similar product 29 in all the cases, it was concluded that o-aminoacetophenone gets dimerised and one of the two symmetrical methyl groups gets acetylated to 12-methyl-6-(1'-propene-2'-ol)-dibenzo[b,f][1,5]diazocine (29) in presence of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6).\textsuperscript{218a} Based on the following experimental observation that the reaction did not yield the dimerised product in the absence of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6) (Scheme 2.15).

The plausible mechanism has been proposed for the formation of 12-methyl-6-(1'-propene-2'-ol)-dibenzo[b,f][1,5]diazocine (29) (Scheme 2.15), in which, 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6) acts as an acid catalyst for the dimerisation of o-aminoacetophenone to yield the intermediate I. One of the two symmetrical methyl groups of I gets acylated with acetic acid in presence of the compound 6 to the intermediate II followed by tautomerisation to yield the product 12-methyl-6-(1'-propene-2'-ol)-dibenzo[b,f][1,5]diazocine (29).

**Scheme 2.15**

**Mechanism**

A number of oxazole derivatives have been isolated from natural sources and are characterized. Oxazole derivatives \(31\) synthesized from the ketoximes \(30\) with acetyl chloride in acetic anhydride have been used as optical whitening agents, sensitizing dyes, photo reducing pigments and muscle relaxants. Some of the derivatives were found to be effective against wide range of enteric infections and appetite depressants.

Our subsequent interest was to experiment the same 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indoles \((22)\) with acetyl chloride\(^{185}\) to afford oxazolo[4',5':7,6]cyclohept[b]indoles (Scheme 2.16) thus provide an easy and direct access to these hitherto unknown compounds. The study of the behavior of various ketoximes of 1-oxo-1,2,3,4-tetrahydrocarbazoles towards acetyl chloride and acetic anhydride has been in progress for some time in our laboratory. Thus, 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole \(22a\) was treated with acetyl chloride at room temperature. After workup it yielded a single product. In its IR spectrum (Fig 24) two bands at 3265 cm\(^{-1}\) and 1650 cm\(^{-1}\) were assigned to NH stretching and carbon nitrogen double bond stretching respectively. Its \(^1\)H NMR spectrum (Fig 25) showed the presence of a singlet at \(\delta 2.23\) of three proton intensity for \(C_2-CH_3\). The \(C_4\), \(C_5\) and \(C_6\) methylene proton signals appeared as three multiplets at \(\delta 2.14\), \(\delta 2.83\) and \(\delta 2.95\) respectively. The aromatic region showed a multiplet between \(\delta 7.06-\delta 7.47\), assigned for \(C_7\), \(C_8\), \(C_9\) and \(C_{10}\) protons. A broad singlet at \(\delta 8.98\) corresponds to NH proton. The molecular ion peak in its mass spectrum at \(m/z 238\) and elemental analysis were in agreement with the molecular formula \(C_{15}H_{14}N_2O\). Based on all the above details the compound was assigned the structure 2-methyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indole \((32a)\). Similarly other 2-methyl-4,5,6,11-
Fig 24. IR spectrum of 2-methyl-4,5,6,11-tetrahydroazolo[4',5':7,6]cyclohept[\textit{h}]indole (32a)

Fig 25. $^1$H NMR spectrum of 2-methyl-4,5,6,11-tetrahydroazolo[4',5':7,6]cyclohept[\textit{h}]indole (32a)
tetrahydrooxazolo[4',5':7,6]cyclohept[b]indole derivatives (32b-e) were prepared and their structures confirmed by spectral and elemental analyses (Scheme 2.16).

**Scheme 2.16**

![Chemical structure](image)

\[22, 32\ a: R_1 = R_2 = R_3 = H \]
\[b: R_1 = CH_3, R_2 = R_3 = H \]
\[c: R_2 = CH_3, R_1 = R_3 = H \]
\[d: R_3 = CH_3, R_1 = R_2 = H \]
\[e: R_1 = Cl, R_2 = R_3 = H \]

2.13. Synthesis of 4,5,6,11-tetrahydro-1,2,3-selenadiazolocyclohept[b]indoles

Further development of our search on the synthesis and reactivity of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles, we wished to synthesize 1,2,3-selenadiazolocyclohept[b]indoles (34) from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6) (Scheme 2.17).

Arsenium is a disease with severe damage to human health resulting from long-term exposure to high arsenic levels in the environment. Recently, Wuji et al. reported that selenium was used to prevent the accumulation of arsenic in the human body and rectify the damages. Hence, it was desired to obtain selenium incorporated 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles. This necessitated to treat 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6) with semicarbazide hydrochloride to get the intermediates 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (33), which were then reacted with selenium dioxide in acetic acid (Scheme 2.17).

2.13.1. Synthesis of 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indoles

1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a) was condensed with semicarbazide hydrochloride in ethanol in presence of sodium acetate to afford 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33a) melting at 149°C. The IR
spectrum (Fig 26) showed a strong and broad absorption at 3313 cm\(^{-1}\) due to NH stretchings (indole NH, CONH\(_2\) and \(-\text{NHCO}\)). The amide carbonyl stretching frequency appeared at 1672 cm\(^{-1}\). The analytical values (C\(_{14}\)H\(_{16}\)N\(_2\)O) and the molecular ion peak at m/z 256 (32%), and base peak at m/z 239 by the elimination of ammonia molecule in its mass spectrum also corresponded to the anticipated intermediate 33a. Examination of the \(^1\)H NMR spectrum (Fig 27) revealed that it was none other than the desired 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33a) and the resonances were assigned as below.

a. two '4H' multiplet at \(\delta 1.79-1.91\) (C\(_3\)-H\(_2\) and C\(_4\)-H\(_2\))
b. two '2H' multiplet at \(\delta 2.66-2.69\) and \(\delta 2.90-2.93\) (C\(_5\)-H\(_2\) and C\(_2\)-H\(_2\))
c. a '2H' broad singlet at \(\delta 6.51\) (NH\(_2\))
d. two '1H' triplets at \(\delta 6.95\) and \(\delta 7.12\) with \(J=7.20\) Hz (C\(_7\)-H and C\(_8\)-H)
e. two '1H' doublets at \(\delta 7.27\) with \(J=8.08\) Hz and \(\delta 7.46\) with \(J=7.88\) Hz (C\(_9\)-H and C\(_6\)-H)
f. two singlets at \(\delta 9.30\) and \(\delta 10.97\) (Indole -NH and \(-\text{NHCO}\))

Scheme 2.17

2.13.2. Synthesis of 4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept-[b]indoles

In an effort to arrive selenium metal incorporated cyclohept[b]indoles, we cyclised the above synthon 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33a) by
Fig 26. IR spectrum of 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33a)

Fig 27. $^1$H NMR spectrum of 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33a)
oxidative cyclisation using selenium dioxide in presence of gla acetic acid. It was identified as 4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4’,5’:6,7]cyclohept[b]indole (34a) on the basis of analytical (C_{13}H_{11}N_{1}Se) and spectral data collected on it. In its IR spectrum (Fig 28) the disappearance of strong -NH stretchings and carbonyl stretching frequencies and the appearance of strong N≡N stretching frequency at 1613 cm\(^{-1}\) confirmed that the compound 33a gets converted to 34a. The \(^1\)H NMR spectrum (Fig 29) also showed the disappearance of C\(_2\) methylene signal around \(\delta\) 2.90-2.93, NH\(_2\) proton signal at \(\delta\) 6.51 and NHCO proton signal at \(\delta\) 10.97. The C\(_5\) methylene proton appeared as a pentet at \(\delta\) 2.14-2.19. The C\(_6\) and C\(_4\) methylene protons appeared as two multiplets at \(\delta\) 3.15-3.18 and \(\delta\) 3.32-3.35 respectively. The aromatic cluster accounting for four protons resonates as two triplets and two doublets at \(\delta\) 7.08 (J = 7.46 Hz), \(\delta\) 7.18 (J = 7.54 Hz), \(\delta\) 7.34 (J = 8.08 Hz) and \(\delta\) 7.49 (J = 7.88 Hz) for C\(_8\), C\(_9\), C\(_{10}\) and C\(_7\) protons respectively. -NH proton appeared as a singlet at \(\delta\) 9.16. Its mass spectrum showed the molecular ion peak at m/z 288 and the base beak at m/z 179. A series of similar compounds 34b-e were realized from 6b-e through the intermediates 33b-e under identical conditions (Scheme 2.17).

**Antibacterial activity**

The compounds 4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4’,5’:6,7]cyclohept[b] indoles 34a-e were screened for their antibacterial activity against bacterial strains such as Bacillus Subtilis, Escherichia coli and Salmonella typhii. The compounds 34a-d showed only moderate activity and halogen substituted 4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4’,5’:6,7]cyclohept[b]indole 34e was found to be highly active.

2.14. Conclusion

Thus we have developed a facile method for the preparation of the following new cyclohept[b]indole derivatives utilizing the easily accessible 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles obtained by Japp Klingemann reaction of diazotised anilines and 2-hydroxymethylenecycloheptanone followed by acid catalysed cyclisation.

(i) 2-Benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles derived from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles were used as synthons to
Fig 28. IR spectrum of 4,5,6,11-tetrahydro-1,2,3-selenadiazo[4,5:6,7]cyclohept[6]pyridole (34a)

Fig 29. $^1$H NMR spectrum of 4,5,6,11-tetrahydro-1,2,3-selenadiazo[4,5:6,7]cyclohept[6]pyridole (34a)
derive 3-phenyl-4,5,6,11-tetrahydroisoaxazolo- and 3-phenyl-4,5,6,11- 

(ii) 5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indoles.

(iii) An attempt to device a synthetic route for 2-methyl-4-
oxopyranolo[2',3':7,6]cyclohept[b]indoles results the formation of acetyl 
derivatives of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles.

(iv) An attempt to device a synthetic route for 1-amino-2-oxo-1,2,3,4,5,10-
hexahydrocyclohept[b]indoles results the formation of 1-N-acetylamino-2-
hydroxy-1,2,3,4,5,10-hexahydrocyclohept[b]indoles.

(v) 6-methyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indoles and 12-
methyl-6-(1'-propene-2'-ol)-dibenzo[b,f][1,5]diazocine.

(vi) 2-methyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indoles.

(vii) 4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indoles from 1-
semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indoles obtained from the 
corresponding 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles.

The mechanism has also been proposed for the formation of new products.

Experimental

Preparation of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e)

(i) Preparation of 2-hydroxymethylene cycloheptanone (2)

General procedure: Cycloheptanone (1, 0.02 mol) was added in portions over a period of 
five minutes to a well-cooled, vigorously stirred mixture of sodium methoxide (from 5.17 g 
of sodium in 5 mL of absolute methanol), dry ether (4 mL) and ethyl formate (1.8 mL, 0.02 
mol). The mixture was stirred in the ice bath for 1 h and then allowed to stand at room 
temperature for 24 h. At the end of the period, ice and water were added to the yellow solid 
and acidified with conc hydrochloric acid. The oil that separated was extracted with ether, 
washed with cold water and brine and dried over anhydrous sodium sulphate. The 
residual oil after the removal of the solvent was distilled under reduced pressure to give 2-
hydroxymethylene cycloheptanone (2) as viscous liquid with 70 % yield.
(ii) Preparation of cycloheptan-1,2-dione-1-aryihydrazones (5a-e) from 2-hydroxymethylene cycloheptanone (2)

Mixtures of 2-hydroxymethylene cycloheptanone (2, 0.004 mol) and sodium acetate trihydrate (1 g) in methanol (6 mL) were cooled in ice. A solution of appropriate aniline derivative (0.004 mol) in aq hydrochloric acid (1.8 mL of hydrochloric acid in 2.12 mL water) was diazotised with cold saturated solution of sodium nitrite (0.35 g in 0.8 mL water) between 0°C and -5°C. The diazotised solution was added in small portions to the ice cooled mixture containing 2-hydroxymethylene cycloheptanone (2) over a period of 0.5 h with constant stirring. After standing for 0.5 h more, the resulting solid cycloheptan-1,2-dione-1-arylhydrazone (5) was filtered, washed with water, dried and crystallised from ethanol.

**Cycloheptan-1,2-dione-1-phenylhydrazone (5a)**

| Aniline (3a) | 0.372 g (0.004 mol) |
| 2-Hydroxymethylene cycloheptanone (2) | 0.560 g (0.004 mol) |
| Yield | 0.647 g (75%) |
| Mp | 87°C |
| IR (KBr) [v max cm⁻¹] | 3290, 1601, 1596, 1434, 1294, 1151, 1120, 1093, 999, 808, 748, 694, 542 |
| Analysis (C₁₃H₁₆N₂O) Calcd | C, 72.19; H, 07.46; N, 12.95% |
| Found | C, 72.28; H, 07.40; N, 12.91% |

**Cycloheptan-1,2-dione-1-(p-methylphenyl)hydrazone (5b)**

| p-Toluidine (3b) | 0.428 g (0.004 mol) |
| 2-Hydroxymethylene cycloheptanone (2) | 0.560 g (0.004 mol) |
| Yield | 0.727 g (79%) |
| Mp | 85°C |
| IR (KBr) [v max cm⁻¹] | 3271, 1654, 1624, 1517, 1448, 1417, 1226, 1166, 1085, 941, 819, 752, 507 |
| ¹H NMR (CDCl₃) [δ ppm] (Fig 2) | 1.77-2.68 (m, 10H, C₂-H₂, C₃-H₂, C₄-H₂, C₅-H₂, C₆-H₂), 2.30 (s, 3H, CH₃), 7.05-7.26 (m, 4H, C₂-H, C₃-H, C₅-H, C₆-H), 13.67 (bs, 1H, NH) |
| Analysis (C₁₄H₁₈N₂O) Calcd | C, 73.01; H, 07.88; N, 12.16% |
| Found | C, 73.00; H, 07.98; N, 12.10% |
Cycloheptan-1,2-dione-1-(m-methylphenyl)hydrazone (5c)

m-Toluidine (3c) : 0.428 g (0.004 mol)
2-Hydroxymethylene cycloheptanone (2) : 0.560 g (0.004 mol)
Yield : 0.662 g (72%)
Mp : 73°C
IR (KBr) [v max cm\(^{-1}\)] : 3250, 1633, 1604, 1519, 1425, 1240, 1157, 1080, 939, 810, 750, 623, 434
Analysis (C\(_{14}\)H\(_{18}\)N\(_2\)O) Calcd : C, 73.01; H, 07.88; N, 12.16%
Found : C, 73.07; H, 07.90; N, 12.20%

Cycloheptan-1,2-dione-1-(o-methylphenyl)hydrazone (5d)
o-Toluidine (3d) : 0.428 g (0.004 mol)
2-Hydroxymethylene cycloheptanone (2) : 0.560 g (0.004 mol)
Yield : 0.635 g (69%)
Mp : 90°C
IR (KBr) [v max cm\(^{-1}\)] : 3282, 1629, 1583, 1521, 1446, 1321, 1151, 1114, 943, 813, 742, 678, 623, 524, 501
Analysis (C\(_{14}\)H\(_{18}\)N\(_2\)O) Calcd : C, 73.01; H, 07.88; N, 12.16%
Found : C, 73.13; H, 07.98; N, 12.18%

Cycloheptan-1,2-dione-1-(p-chlorophenyl)hydrazone (5e)
p-Chloro aniline (3e) : 0.508 g (0.004 mol)
2-Hydroxymethylene cycloheptanone (2) : 0.560 g (0.004 mol)
Yield : 0.770 g (77%)
Mp : 105°C
IR (KBr) [v max cm\(^{-1}\)] : 3289, 1627, 1595, 1521, 1448, 1226, 1161, 1082, 941, 825, 663, 503, 432
Analysis (C\(_{13}\)H\(_{15}\)N\(_2\)Cl) Calcd : C, 62.28; H, 06.03; N, 11.17%
Found : C, 62.30; H, 06.10; N, 11.19%

Preparation of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e) from cycloheptan-1,2-dione-1-arylhydrazones (5a-e)

**General procedure:** The appropriate hydrazone (5, 0.001 mol) in a mixture of acetic acid (20 mL) and cone hydrochloric acid (5 mL) was refluxed on an oil bath pre-heated to 125-130°C for 2 h. The content was then cooled and poured into ice water with stirring. The separated brown solid was filtered and purified by passing through a column of silica gel.
and eluting with petroleum ether-ethyl acetate (95:5) mixture yielded l-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6).

1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a)

Cycloheptan-1,2-dione-1-phenyl hydrazone (5a)

Yield: 0.129 g (61%)

Mp: 151°C

IR (KBr) [v_max cm⁻¹]: 3292, 1635, 1569, 1531, 1436, 1261, 1205, 1153, 966, 894, 729, 588, 435

¹H NMR (CDCl₃) [δ ppm] (Fig 30):

- 1.99-2.04 (m, 2H, C₃-H₂), 2.06-2.12 (m, 2H, C₄-H₂), 2.83-2.87 (m, 2H, C₂-H₂), 3.14 -3.17 (m, 2H, C₅-H₂), 7.11-7.67 (m, 4H, C₆-H, C₇-H, C₈-H, C₉-H) and 8.96 (b s, 1H, NH)

Analysis (C₁₃H₁₃NO) Calcd: C, 78.36; H, 06.58; N, 07.03%

Found: C, 78.43; H, 06.49; N, 07.10%

7-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6b)

Cycloheptan-1,2-dione-1-(p-methyl) phenyl hydrazone (5b)

Yield: 0.136 g (64%)

Mp: 178°C

IR (KBr) [v_max cm⁻¹] (Fig 3): 3328, 1618, 1575, 1537, 1433, 1328, 1226, 1188, 968, 800, 713, 659, 428

¹H NMR (CDCl₃) [δ ppm] (Fig 4):

- 1.95-2.02 (m, 2H, C₃-H₂), 2.05-2.11 (m, 2H, C₄-H₂), 2.45 (s, 3H, C₇-CH₃), 2.82 -2.85 (m, 2H, C₂-H₂), 3.11-3.14 (m, 2H, C₅-H₂), 7.16-7.42 (m, 3H, C₆-H, C₈-H, C₉-H) and 8.86 (b s, 1H, NH)

Analysis (C₁₄H₁₅NO) Calcd: C, 78.84; H, 07.09; N, 06.57%

Found: C, 78.82; H, 07.15; N, 06.45%

8-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6c)

Cycloheptan-1,2-dione-1-(m-methyl) phenyl hydrazone (5c)

Yield: 0.143 g (67%)

Mp: 120°C

IR (KBr) [v_max cm⁻¹]: 3329, 1610, 1569, 1527, 1433, 1350, 1257, 1230, 1157, 956, 800, 756, 663, 434

¹H NMR (CDCl₃) [δ ppm]: 1.91-2.01 (m, 2H, C₃-H₂), 2.06-2.11 (m, 2H,
9-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6d)

Cycloheptan-1,2-dione-1-(o-methyl) phenyl hydrazone (5d)

Yield: 0.230 g (0.001 mol)
Mp: 0.138 g (65%)

IR (KBr) [\(v_{\text{max}} \text{ cm}^{-1}\)]
: 3298, 1605, 1537, 1442, 1351, 1257, 1228, 1180, 952, 785, 621, 542, 476

\(^1\)H NMR (CDCl\textsubscript{3}) [\(\delta \text{ ppm}\)]
: 1.97-2.02 (m, 2H, C\_3-H\_2), 2.06-2.13 (m, 2H, C\_4-H\_2), 2.49 (s, 3H, C\_9-CH\textsubscript{3}), 2.83-2.86 (m, 2H, C\_2-H\_2), 3.13-3.17 (m, 2H, C\_5-H\_2), 7.03 - 7.67 (m, 3H, C\_6-H, C\_7-H, C\_8-H) and 8.84 (b s, 1H, NH)

Analysis (C\textsubscript{14}H\textsubscript{15}NO) Calcd
: C, 78.84; H, 07.09; N, 06.57%
Found
: C, 78.91; H, 07.23; N, 06.82%

7-Chloro-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6e)

Cycloheptan-1,2-dione-1-(p-chloro) phenyl hydrazone (5e)

Yield: 0.250 g (0.001 mol)
Mp: 0.139 g (60%)

IR (KBr) [\(v_{\text{max}} \text{ cm}^{-1}\)]
: 3325, 1620, 1572, 1434, 1363, 1262, 1248, 1160, 792, 651, 530

\(^1\)H NMR (CDCl\textsubscript{3}) [\(\delta \text{ ppm}\)]
: 1.96-2.06 (m, 2H, C\_3-H\_2), 2.08-2.12 (m, 2H, C\_4-H\_2), 2.83-2.86 (m, 2H, C\_2-H\_2), 3.08-3.11 (s, 2H, C\_5-H\_2), 7.26-7.31 (m, 2H, C\_9-H, C\_10-H), 7.62 (s, 1H, C\_6-H), and 8.99 (b s, 1H, NH)

Analysis (C\textsubscript{13}H\textsubscript{12}NOCI) Calcd
: C, 66.81; H, 05.17; N, 06.00%
Found
: C, 66.78; H, 05.03; N, 05.97%
Preparation of 2-benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (7a-e) by mixed aldol reaction with benzaldehyde from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e)

**General procedure:** A mixture of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6, 0.001 mol) and benzaldehyde (0.001 mol) was treated with 4% alcoholic potassium hydroxide (10 mL) and stirred for 12 h at room temperature. The precipitated crystalline product was filtered off and washed with 50% ethanol. A further crop of condensation product was obtained on neutralisation with acetic acid and dilution with water. The products were crystallised from methanol.

**2-Benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7a)**

<table>
<thead>
<tr>
<th>1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a)</th>
<th>Yield</th>
<th>Mp</th>
<th>IR (KBr) [v max cm⁻¹]</th>
<th>Analysis (C₂₀H₁₇NO) Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.199 g (0.001 mol)</td>
<td></td>
<td>161°C</td>
<td>C, 83.59; H, 05.96; N, 04.88%</td>
<td>C, 83.55; H, 05.98; N, 04.80%</td>
</tr>
</tbody>
</table>

**2-Benzylidene-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7b)**

<table>
<thead>
<tr>
<th>7-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6b)</th>
<th>Yield</th>
<th>Mp</th>
<th>IR (KBr) [v max cm⁻¹] (Fig 5)</th>
<th>¹H NMR (CDCl₃) [δ ppm] (Fig 6)</th>
<th>Analysis (C₂₁H₁₉NO) Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.213 g (0.001 mol)</td>
<td></td>
<td>182°C</td>
<td>2.17-2.23 (m, 2H, C₄-H₂), 2.46 (s, 3H, C₇-CH₃), 2.89-2.91 (m, 2H, C₃-H₂), 3.18-3.21 (m, 2H, C₅-H₂), 7.18-7.43 (m, 8H, C₆-H, C₈-H, C₉-H, C₉-6-H), 7.78 (s, 1H, benzylic proton), 8.99 (b s, 1H, NH)</td>
<td>C, 83.69; H, 06.35; N, 04.65%</td>
<td>C, 83.70; H, 06.39; N, 04.59%</td>
</tr>
</tbody>
</table>
2-Benzylidene-8-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7c)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>Mp</th>
<th>IR (KBr) [v max cm⁻¹]</th>
<th>Analysis (C₂₁H₁₉NO) Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>7c</td>
<td>0.213 g (0.001 mol)</td>
<td>185°C</td>
<td>3315, 1641, 1568, 1530, 1429, 1324, 970, 770, 695</td>
<td>C, 83.69; H, 06.35; N, 04.65%</td>
<td>C, 83.78; H, 06.28; N, 04.73%</td>
</tr>
</tbody>
</table>

2-Benzylidene-9-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7d)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>Mp</th>
<th>IR (KBr) [v max cm⁻¹]</th>
<th>Analysis (C₂₁H₁₉NO) Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>7d</td>
<td>0.213 g (0.001 mol)</td>
<td>165°C</td>
<td>3301, 1637, 1577, 1523, 1490, 1433, 1328, 1251, 1159, 983, 950, 779, 740, 694, 540</td>
<td>C, 83.69; H, 06.35; N, 04.65%</td>
<td>C, 83.58; H, 06.25; N, 04.76%</td>
</tr>
</tbody>
</table>

2-Benzylidene-7-chloro-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7e)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>Mp</th>
<th>IR (KBr) [v max cm⁻¹]</th>
<th>Analysis (C₂₀H₁₆NOCI) Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>7e</td>
<td>0.233 g (0.001 mol)</td>
<td>181°C</td>
<td>3340, 1636, 1579, 1560, 1527, 1431, 1336, 991, 798, 765, 694</td>
<td>C, 74.65; H, 05.01; N, 04.35%</td>
<td>C, 74.52; H, 05.21; N, 04.32%</td>
</tr>
</tbody>
</table>

Preparation of 3-phenyl-4,5,6,11-tetrahydroisoxazolo[4',3';6,7]cyclohept[b]indoles (8a-e) from 2-benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (7a-e)

**General procedure:** The appropriate 2-benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7, 0.001 mol) was treated with hydroxylamine hydrochloride (1.5 g) in dry pyridine (5 mL) at 130°C for 10 h. The reaction mixture was then poured into crushed ice, the resulting semi-solid separated was extracted with chloroform and washed successively with dil hydrochloric acid and water, dried over...
anhydrous sodium sulphate. Evaporation of the solvent yielded a crude product, which was purified by passing through a silica gel column and eluting with petroleum ether-ethyl acetate (98:2). The product thus obtained was recrystallised from the same solvent system.

3-Phenyl-4,5,6,11-tetrahydroisoxazolo[4′,3′:6,7]cyclohept[b]indole (8a)

2-Benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7a)
Yield : 0.287 g (0.001 mol)
M.p : 207°C

IR (KBr) [v max cm⁻¹]
3274, 1598, 1541, 1485, 1458, 1421, 1352, 1328, 1266, 1161, 979, 746, 719, 690

¹H NMR (CDCl₃) [δ ppm]
2.13-2.18 (m, 2H, C₅-H₂), 3.07-3.10 (m, 2H, C₄-H₂), 3.19-3.22 (m, 2H, C₆-H₂), 7.12-7.73 (m, 9H, C₇-H, C₈-H, C₉-H, C₁₀-H, C₁-6'-H), 8.82 (bs, 1H, NH)

Analysis (C₂₀H₁₆N₂O) Calcd: C, 79.98; H, 05.37; N, 09.33%
Found: C, 79.62; H, 05.42; N, 09.21%

8-Methyl-3-phenyl-4,5,6,11-tetrahydroisoxazolo[4′,3′:6,7]cyclohept[b]indole (8b)

2-Benzylidene-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7b)
Yield : 0.301 g (0.001 mol)
M.p : 227°C

IR (KBr) [v max cm⁻¹]
3284, 1600, 1541, 1481, 1425, 981, 804, 750, 692, 648, 630, 603

¹H NMR (CDCl₃) [δ ppm]
2.12-2.17 (m, 2H, C₅-H₂), 2.47 (s, 3H, C₈-CH₃), 3.06-3.08 (m, 2H, C₄-H₂), 3.16-3.19 (m, 2H, C₆-H₂), 7.09-7.73 (m, 8H, C₇-H, C₉-H, C₁₀-H, C₁-6'-H), 8.74 (bs, 1H, NH)

Analysis (C₂₁H₁₈N₂O) Calcd: C, 80.23; H, 05.77; N, 08.91%
Found: C, 80.32; H, 05.66; N, 08.88%

9-Methyl-3-phenyl-4,5,6,11-tetrahydroisoxazolo[4′,3′:6,7]cyclohept[b]indole (8c)

2-Benzylidene-8-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7c)
Yield : 0.301 g (0.001 mol)
M.p : 197°C

IR (KBr) [v max cm⁻¹]
3250, 1558, 1484, 1404, 1263, 1029, 796, 746, 690

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10-Methyl-3-phenyl-4,5,6,11-tetrahydroisoxazolo[4',3':6,7]cyclohept[b]indole (8d)

2-Benzylidene-9-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7d)

Yield: 0.173 (55%)

Mp: 210°C

IR (KBr) [v max cm⁻¹]: 3200, 1558, 1530, 1480, 979, 800, 755, 696, 610

1H NMR (CDCl₃) [δ ppm] (Fig 36): 2.14-2.17 (m, 2H, C₅-H₂), 2.55 (s, 3H, C₉-CH₃), 2.94-2.97 (m, 2H, C₄-H₂), 3.13-3.16 (m, 2H, C₆-H₂), 7.07-7.69 (m, 8H, C₇-H, C₈-H, C₉-H, C₁₀-H, C₁₁-H), 8.92 (b s, 1H, NH)

Analysis (C₂₃H₁₈N₂O) Calcd

: C, 80.23; H, 05.47; N, 08.36%

: C, 80.22; H, 05.47; N, 08.32%

8-Chloro-4,5,6,11-tetrahydroisoxazolo[4',3':6,7]cyclohept[b]indole (8e)

2-Benzylidene-7-chloro-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7e)

Yield: 0.134 (49%)

Mp: 235°C

IR (KBr) [v max cm⁻¹]: 3277, 1508, 1465, 1423, 1263, 1060, 987, 808, 748, 693, 669

1H NMR (CDCl₃) [δ ppm] (Fig 37): 2.11-2.17 (m, 2H, C₅-H₂), 3.06-3.09 (m, 2H, C₄-H₂), 3.13-3.16 (m, 2H, C₆-H₂), 7.20-7.73 (m, 8H, C₇-H, C₈-H, C₁₀-H, C₁₁-H), 8.92 (b s, 1H, NH)

Analysis (C₂₀H₁₅N₂OCl) Calcd

: C, 71.75; H, 04.51; N, 08.37%

: C, 71.65; H, 04.55; N, 08.36%
Preparation of 3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4',3':6,7]cyclohept[7a-e]indoles (9a-e) from 2-benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[7a-e]indoles (7a-e)

**General procedure:** A mixture of 2-benzylidene-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[7a-e]indole (7, 0.001 mol) dissolved in absolute ethanol (20 mL) and 0.5 mL of hydrazine hydrate was refluxed for 2 h. The excess solvent was distilled off, and the crude reaction mixture was washed with water, extracted with chloroform and the combined organic layers were dried over anhydrous sodium sulphate. Evaporation of the solvent followed by crystallisation yielded 3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4',3':6,7]cyclohept[7a-e]indole (9).

3-Phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4',3':6,7]cyclohept[7a-e]indole (9a)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>0.287 g (0.001 mol)</td>
</tr>
<tr>
<td>Mp</td>
<td>222°C</td>
</tr>
<tr>
<td>IR (KBr) [v max cm⁻¹]</td>
<td>3309, 2914, 1599, 1492, 1452, 829, 752, 711</td>
</tr>
<tr>
<td>¹H NMR (CDCl₃) [δ ppm] (Fig 38)</td>
<td>2.11-3.29 (m, 4H, C₄-H₂, C₅-H₂), 2.78-2.85 (m, 1H, C₃a-H), 3.07-3.29 (m, 2H, C₆-H₂), 4.42-4.46 (m, 1H, C₃-H), 5.99 (b s, 1H, pyrazolo NH), 7.07-7.58 (m, 9H, C₇-H, C₈-H, C₉-H, C₁₀-H, C₂-H, C₃-H, C₄-H, C₅-H, C₆'-H) and 8.61 (s, 1H, indole NH)</td>
</tr>
</tbody>
</table>

Analysis (C₂₀H₁₉N₃) Calcd: C, 79.70; H, 6.35; N, 13.94%  
Found: C, 79.82; H, 6.38; N, 13.85%

8-Methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4',3':6,7]cyclohept[7a-e]indole (9b)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>0.301 g (0.001 mol)</td>
</tr>
<tr>
<td>Mp</td>
<td>200°C</td>
</tr>
<tr>
<td>IR (KBr) [v max cm⁻¹] (Fig 9)</td>
<td>3310, 2952, 1590, 1483, 1434, 826, 750</td>
</tr>
</tbody>
</table>
| ¹H NMR (CDCl₃) [δ ppm] (Fig 10) | 2.44 (s, 3H, C₈-CH₃), 2.10-2.20 (m, 4H, C₄-H₂, C₅-H₂), 2.75-2.82 (m, 1H, C₃a-H), 3.06-3.25 (m, 2H, C₆-H₂), 4.41-4.45 (m, 1H, C₃-
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Analysis (C_{21}H_{21}N_{3}) Calcd Found

9-Methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolino[4',3':6,7]cyclohept[b]indole (9c)

2-Benzylidene-8-methyl-1-oxo-1,2,3,4, 5,10-hexahydrocyclohept[b]indole (7c)

Yield : 0.244 (75%)
Mp : 219°C
IR (KBr) [\nu_{\text{max}} \text{ cm}^{-1}] : 3390, 1595, 1483, 1432, 816, 750, 713

\[^1^H\text{NMR (CDCl}_3\text{)} [\delta \text{ ppm}]\text{ (Fig 39)}\]

Analysis (C_{21}H_{21}N_{3}) Calcd Found

10-Methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolino[4',3':6,7]cyclohept[b]indole (9d)

2-Benzylidene-9-methyl-1-oxo-1,2,3,4, 5,10-hexahydrocyclohept[b]indole (7d)

Yield : 0.238 (76%)
Mp : 196°C
IR (KBr) [\nu_{\text{max}} \text{ cm}^{-1}] : 3310, 1592, 1486, 816, 752, 711

\[^1^H\text{NMR (CDCl}_3\text{)} [\delta \text{ ppm}]\text{ (Fig 40)}\]

Analysis (C_{21}H_{21}N_{3}) Calcd Found

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**8-Chloro-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolino[4',3':6,7]cyclohept[b]indole (9e)**

2-Benzylidene-7-chloro-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (7e)

Yield: 0.276 (76%)

Mp: 195°C

IR (KBr) [$\nu_{\text{max}}$ cm$^{-1}$]: 3311, 2950, 1596, 1485, 1439, 827, 752

$^1$H NMR (CDCl$_3$) [$\delta$ ppm] (Fig 41):

- 2.11-2.25 (m, 4H, C$_4$-H$_2$, C$_5$-H$_2$), 2.73-2.81 (m, 1H, C$_3$a-H), 3.05-3.20 (m, 2H, C$_6$-H$_2$), 4.43-4.47 (m, 1H, C$_3$-H), 5.96 (b s, 1H, pyrazolino NH), 7.15-7.53 (m, 8H, C$_7$-H, C$_9$-H, C$_10$-H, C$_2$'-H, C$_3$'-H, C$_4$'-H, C$_5$'-H, C$_6$'-H), and 8.62 (s, 1H, indole NH)

Analysis (C$_{26}$H$_{18}$N$_5$Cl) Calcd: C, 71.53; H, 05.40; N, 12.51%

Found: C, 71.40; H, 05.56; N, 12.32%

**Preparation of 5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indoles (12a-e)**

from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e)

General procedure: A mixture of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a, 0.001 mol) and phenyl hydrazine (0.001 mol) in glacial acetic acid (0.36 mL) was refluxed for 5 h. After cooling, the reaction mixture was poured into crushed ice, extracted with chloroform and dried over anhydrous sodium sulphate. The residue from the solvent evaporation was purified by silica gel column chromatography using 97:3 petroleum ether: ethyl acetate mixture. The product thus obtained was recrystallised from the same solvent system.

**5H,6,7,12,13-Tetrahydroindolo[2',3':7,6]cyclohept[b]indole (12a)**

1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a)

Yield: 0.207 g (76%)

Mp: 204°C

IR (KBr) [$\nu_{\text{max}}$ cm$^{-1}$] (Fig 11):

$^1$H NMR (CDCl$_3$) [$\delta$ ppm] (Fig 12):

- 2.15-2.21 (m, 2H, C$_6$-H$_2$), 3.12-3.19 (m, 4H, C$_5$-H$_2$, C$_7$-H$_2$), 7.10-7.59 (m, 8H, aromatic-H), 8.00 (s, 2H, N$_{12}$-H, N$_{13}$-H)

Analysis (C$_{19}$H$_{16}$N$_2$) Calcd: C, 83.79; H, 05.92; N, 10.29%

Found: C, 83.62; H, 05.55; N, 10.17%

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<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>Mp</th>
<th>IR (KBr) [ν max cm⁻¹]</th>
<th>¹H NMR (CDCl₃) [δ ppm]</th>
<th>Analysis (C₂₀H₁₈N₂) Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-Methyl-5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indole (12b)</td>
<td>0.213 g (0.001 mol)</td>
<td>190°C</td>
<td>3412, 1452, 1236, 863, 754</td>
<td>2.42 (s, 3H, C₉-CH₃), 2.21-2.22 (m, 2H, C₆-H₂), 3.10-3.21 (m, 4H, C₅-H₂, C₇-H₂), 7.02-7.53 (m, 7H, aromatic-H), 7.92 &amp; 8.02 (2 s, 2H, N₁₂-H, N₁₃-H)</td>
<td>C, 83.92; H, 06.29; N, 09.77%</td>
<td>C, 83.85; H, 06.54; N, 09.72%</td>
</tr>
<tr>
<td>10-Methyl-5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indole (12c)</td>
<td>0.213 g (0.001 mol)</td>
<td>175°C</td>
<td>3413, 1453, 1237, 862, 753</td>
<td>2.47 (s, 3H, C₁₀-CH₃), 2.19-2.29 (m, 2H, C₅-H₂), 3.10-3.20 (m, 4H, C₅-H₂, C₇-H₂), 6.82-7.55 (m, 7H, aromatic-H), 7.90 &amp; 8.01 (2 s, 2H, N₁₂-H, N₁₃-H)</td>
<td>C, 83.92; H, 06.29; N, 09.77%</td>
<td>C, 83.82; H, 06.54; N, 09.60%</td>
</tr>
<tr>
<td>11-Methyl-5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indole (12d)</td>
<td>0.213 g (0.001 mol)</td>
<td>200°C</td>
<td>3420, 1456, 1236, 870, 752</td>
<td>2.53 (s, 3H, C₁₁-CH₃), 2.17-2.23 (m, 2H, C₅-H₂), 3.14-3.17 (m, 4H, C₅-H₂, C₇-H₂), 6.99-7.56 (m, 7H, aromatic-H), 8.05 &amp; 8.22 (2 s, 2H, N₁₂-H, N₁₃-H)</td>
<td>C, 83.92; H, 06.29; N, 09.77%</td>
<td>C, 83.72; H, 06.52; N, 09.89%</td>
</tr>
</tbody>
</table>

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9-Chloro-5H,6,7,12,13-tetrahydroindolo[2',3':7,6]cyclohept[b]indole (12e)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>0.233 g (0.001 mol)</td>
</tr>
<tr>
<td>Mp</td>
<td>192°C</td>
</tr>
<tr>
<td>IR (KBr) [ν max cm⁻¹]</td>
<td>3411, 1152, 1235, 869, 751</td>
</tr>
<tr>
<td>¹H NMR (CDCl₃) [δ ppm] (Fig 44)</td>
<td></td>
</tr>
<tr>
<td>Analysis (C₁₉H₁₅N₁Cl) Calcd</td>
<td>C, 74.38; H, 04.93; N, 09.13%</td>
</tr>
<tr>
<td>Found</td>
<td>C, 74.33; H, 04.82; N, 09.23%</td>
</tr>
</tbody>
</table>

Preparation of acetyl derivatives of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (15a-e) from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e)

**General procedure:** Respective 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6, 0.001 mol) was heated with a mixture of acetic acid (0.002 mol) and polyphosphoric acid (10 gm P₂O₅ in 4 ml H₃PO₄) at 100°C for 8 h. The reaction mixture was cooled, poured into ice water; the precipitated product was filtered and dried. The crude residue was purified by passing through a column of silica gel and eluting with petroleum ether-ethyl acetate mixture (92:8).

7-Acetyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15a)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>0.199 g (0.001 mol)</td>
</tr>
<tr>
<td>Mp</td>
<td>219°C</td>
</tr>
<tr>
<td>IR (KBr) [ν max cm⁻¹] (Fig 13)</td>
<td>3298, 1664, 1612, 1434, 831</td>
</tr>
<tr>
<td>¹H NMR (CDCl₃) [δ ppm] (Fig 14)</td>
<td></td>
</tr>
<tr>
<td>Analysis (C₁₅H₁₅NO₂) Calcd</td>
<td>C, 74.67; H, 06.27; N, 05.80%</td>
</tr>
<tr>
<td>Found</td>
<td>C, 74.52; H, 06.32; N, 05.78%</td>
</tr>
</tbody>
</table>
9-Acetyl-7-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15b)

7-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6b)

Yield: 0.213 g (0.001 mol)
Mp: 0.198 g (72%)
IR (KBr) [ν max cm⁻¹]: 145°C

ν max cm⁻¹:
1H NMR (CDCl₃) [δ ppm]: 3299, 1658, 1613, 1432, 832

Analysis (C₁₆H₁₇NO₂) Calcd: C, 75.27; H, 06.71; N, 05.49%
Found: C, 75.40; H, 06.66; N, 05.30%

9-Acetyl-8-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15c)

8-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6c)

Yield: 0.213 g (0.001 mol)
Mp: 0.214 g (78%)
IR (KBr) [ν max cm⁻¹]: 195°C

ν max cm⁻¹:
1H NMR (CDCl₃) [δ ppm]: 3298, 1657, 1612, 1432, 830

Analysis (C₁₆H₁₇NO₂) Calcd: C, 75.27; H, 06.71; N, 05.49%
Found: C, 75.20; H, 06.62; N, 05.55%

9-Acetyl-9-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15d)

9-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6d)

Yield: 0.213 g (0.001 mol)
Mp: 0.192 g (70%)
IR (KBr) [ν max cm⁻¹]: 230°C

ν max cm⁻¹:
1H NMR (CDCl₃) [δ ppm]: 3295, 1654, 1612, 1436, 829

Analysis (C₁₆H₁₇NO₂) Calcd: C, 75.27; H, 06.71; N, 05.49%
Found: C, 75.20; H, 06.62; N, 05.55%
9-Acetyl-7-chloro-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (15e)

7-Chloro-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6e)
Yield: 0.233 g (0.001 mol)

Mp: 110°C
IR (KBr) [\( \nu_{\text{max}} \) cm\(^{-1} \)]
: 3294, 1650, 1609, 1428, 832

\(^1\)H NMR (CDCl\(_3\)) [\( \delta \) ppm]
: 2.00-2.05 (m, 2H, \( \text{C}_4\)-H\(_2\)), 2.22-2.25 (m, 2H, \( \text{C}_3\)-H\(_2\)), 2.70 (s, 3H, \( \text{C}_9\)-COCH\(_3\)), 2.75-2.82 (m, 2H, \( \text{C}_5\)-H\(_2\)), 3.19 (m, 2H, \( \text{C}_2\)-H\(_2\)), 7.69 (s, 1H, \( \text{C}_6\)-H), 8.52 (s, 1H, \( \text{C}_8\)-H), 9.09 (b s, 1H, NH)

Analysis (C\(_{16}\)H\(_{17}\)NO\(_2\)) Calcd Found
: C, 75.27; H, 06.71; N, 05.49% C, 75.26; H, 06.81; N, 05.32%

Preparation of 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (22a-e)
from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e)

**General procedure:** A mixture of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6, 0.005 mol), hydroxylamine hydrochloride (0.005 mol) in dry pyridine (3 mL) and absolute ethanol (10 mL) was refluxed for 3 h. The residue obtained on evaporation of excess solvent was diluted with water and extracted with chloroform. The extract was successively washed with dil hydrochloric acid and with water, dried over anhydrous sodium sulphate. Evaporation of the solvent followed by crystallisation with petroleum ether yielded 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22) as colourless prisms.

1-Hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22a)

1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a)
Yield: 0.995 g (0.005 mol)

Mp: 106°C
IR (KBr) [\( \nu_{\text{max}} \) cm\(^{-1} \)]
: 3448, 3200, 1556, 1446, 956, 790, 588

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$^1$H NMR (CDCl$_3$) [δ ppm]: 1.82-2.05 (m, 2H, C$_4$-H$_2$), 2.71-2.80 (m, 2H, C$_5$-H$_2$), 2.90-3.10 (m, 2H, C$_3$-H$_2$), 3.25-3.40 (m, 2H, C$_2$-H$_2$), 6.80-7.61 (m, 4H, C$_6$-H, C$_7$-H, C$_8$-H, C$_9$-H), 8.71 (b s, 1H, NH), 9.99 (b s, 1H, OH)

Analysis (C$_{13}$H$_{14}$N$_2$O) Calcd: C, 72.87; H, 06.59; N, 13.07%
Found: C, 72.50; H, 06.69; N, 13.17%

7-Methyl-1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22b)

Yield: 1.065 g (0.005 mol)
Mp: 114°C
IR (KBr) [ν max cm$^{-1}$]: 3450, 3211, 1556, 1447, 986, 789
$^1$H NMR (CDCl$_3$) [δ ppm]: 1.88-2.05 (m, 2H, C$_4$-H$_2$), 2.50 (s, 3H, C$_7$-CH$_3$), 2.70-3.10 (m, 6H, C$_2$-H$_2$, C$_3$-H$_2$, C$_5$-H$_2$), 7.00-7.71 (m, 3H, C$_6$-H, C$_8$-H, C$_9$-H), 8.51 (b s, 1H, NH), 9.97 (b s, 1H, OH)

Analysis (C$_{14}$H$_{16}$N$_2$O) Calcd: C, 73.66; H, 07.06; N, 12.27%
Found: C, 73.58; H, 07.27; N, 12.37%

8-Methyl-1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22c)

Yield: 1.065 g (0.005 mol)
Mp: 105°C
IR (KBr) [ν max cm$^{-1}$]: 3449, 3225, 1586, 1457, 1450, 987, 750, 580
$^1$H NMR (CDCl$_3$) [δ ppm]: 1.89-2.04 (m, 2H, C$_4$-H$_2$), 2.49 (s, 3H, C$_8$-CH$_3$), 2.70-2.82 (m, 2H, C$_5$-H$_2$), 2.92-3.10 (m, 4H, C$_2$-H$_2$, C$_3$-H$_2$), 6.99-7.77 (m, 3H, C$_6$-H, C$_7$-H, C$_9$-H), 8.52 (b s, 1H, NH), 9.97 (b s, 1H, OH)

Analysis (C$_{14}$H$_{16}$N$_2$O) Calcd: C, 73.66; H, 07.06; N, 12.27%
Found: C, 73.58; H, 07.27; N, 12.37%

9-Methyl-1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22d)

Yield: 1.065 g (0.005 mol)
Mp: 96°C
IR (KBr) [v max cm\(^{-1}\)]

\(^1\)H NMR (CDCl\(_3\)) [\(\delta\) ppm]

Analysis (C\(_{14}H_{16}N_2O\)) Calcd

Found

7-Chloro-1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22e)

Preparation of 1-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[b]indoles (26a-d) from 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (22a-d)

General procedure: To an ice cold solution of 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22, 0.003 mol) in acetic anhydride (2 mL) and pyridine (3 mL), acetyl chloride (1 mL) was added slowly and heated at 80°C for 10 h. The reaction mixture was diluted with ice water and extracted with chloroform. The chloroform extract was washed with dil hydrochloric acid and water, dried over anhydrous sodium sulphate. The residue obtained after evaporation of the solvent was chromatographed over a column of silica gel and eluted with petroleum ether-ethyl acetate (97:3) mixture to afford 1-N-acetylamino-2-hydroxy-3,4,5,10-tetrahydrocyclohept[b]indole (26) as colourless prisms.
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Mp : 212°C
IR (KBr) [v max cm⁻¹] : 3385, 1670, 1290
(Fig 17)

¹H NMR (CDCl₃) [δ ppm] : 2.01-2.07 (m, 2H, C₄-H₂), 2.37 (s, 3H, COCH₃), 2.54, 3.04 (2 m, 4H, C₃-H₂, C₅-H₂), 5.85 (t, 1H, NHCOCH₃), 7.04, 7.12 (2 t, 2H, C₇-H, C₈-H, J = 7.2 Hz), 7.20, 7.45 (2 d, 2H, C₆-H, C₉-H, J = 7.2 Hz), 7.63 (b s, 1H, NH), 12.01 (b s, 1H, OH)
(Fig 18)

Analysis (C₁₅H₁₆N₂O₂) Calcd
Found

: C, 70.29; H, 06.29; N, 10.93%
: C, 70.35; H, 06.59; N, 10.73%

1-N-Acetylamino-2-hydroxy-7-methyl-3,4,5,10-tetrahydrocyclohept[b]indole (26b)

7-Methyl-1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22b)

Yield : 0.684 g (0.003 mol)
Mp : 232°C
IR (KBr) [v max cm⁻¹] : 3410, 3386, 1672, 1293
¹H NMR (CDCl₃) [δ ppm] : 2.12 (m, 2H, C₄-H₂), 2.38 (s, 6H, C₇-CH₃, COCH₃), 2.75, 3.01 (2 m, 4H, C₃-H₂, C₅-H₂), 5.82 (t, 1H, NHCOCH₃), 6.90 (m, 3H, C₆-H, C₈-H, C₉-H), 8.00 (b s, 1H, NH), 12.02 (b s, 1H, OH)
(Fig 48)

Analysis (C₁₆H₁₆N₂O₂) Calcd
Found

: C, 71.09; H, 06.71; N, 10.36%
: C, 71.56; H, 06.81; N, 10.32%

1-N-Acetylamino-2-hydroxy-8-methyl-3,4,5,10-tetrahydrocyclohept[b]indole (26c)

8-Methyl-1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (c)

Yield : 0.684 g (0.003 mol)
Mp : 210°C
IR (KBr) [v max cm⁻¹] : 3444, 3392, 1673, 1293
¹H NMR (CDCl₃) [δ ppm] : 2.01-2.10 (m, 2H, C₄-H₂), 2.37 (s, 3H, COCH₃), 2.39 (s, 3H, C₅-CH₃), 2.56, 3.00 (2 m, 4H, C₃-H₂, C₅-H₂), 5.81 (t, 1H, NHCOCH₃), 7.04-7.47 (m, 3H, C₆-H, C₇-H, C₉-H), 7.70 (b s, 1H, NH), 12.04 (b s, 1H, OH)

Analysis (C₁₆H₁₆N₂O₂) Calcd
Found

: C, 71.09; H, 06.71; N, 10.36%
: C, 71.37; H, 06.52; N, 10.43%
1-N-Acetylamino-2-hydroxy-9-methyl-3,4,5,10-tetrahydrocyclohept[b]indole (26d)

9-Methyl-1-hydroxyimino-1,2,3,4,5,10-tetrahydrocyclohept[b]indole (22d)
Yield : 0.684 g (0.003 mol)
Mp : 222°C
IR (KBr) [ν max cm⁻¹] : 3441, 3399, 1669, 1439, 1252
¹H NMR (CDCl₃) [δ ppm] : 2.00-2.12 (m, 2H, C₄-H₂), 2.40 (s, 3H, COCF₃), 2.41 (s, 3H, C₅-CH₃), 2.55, 3.02 (2 m, 4H, C₃-H₂, C₃-H₂), 5.82 (t, 1H, NHCOCH₃), 7.04-7.48 (m, 3H, C₇-H, C₈-H, C₉-H), 7.79 (b s, 1H, NH), 12.00 (bs, 1H, OH)
Analysis (C₁₆H₁₈N₂O₂) Calcd : C, 71.09; H, 06.71; N, 10.36%
Found : C, 71.11; H, 06.77; N, 10.39%

Preparation of 6-methyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indoles (27a-e) from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e)

General procedure: A mixture of appropriate 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6, 0.01 mol) and o-aminoacetophenone (0.084 mL, 0.01 mol) in glacial acetic acid (2 mL) was refluxed for 8 h in presence of few drops of conc sulphuric acid. Then the reaction mixture was poured into the ice water with stirring and extracted with chloroform. The combined organic layers were dried and the excess solvent was removed by distillation to yield the crude product. Analysis by tlc showed the presence of two products and these were purified by column chromatography over silica gel and eluting with petroleum ether-ethyl acetate mixture. The product obtained by eluting with 98:2 petroleum ether-ethyl acetate fraction afforded the respective 6-Methyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27) and 95:5 petroleum ether-ethyl acetate fraction afforded 12-methyl-6-(1-propene-2-ol)-dibenzo[b,f][1,5]diazocine (29) in all the cases.

6-Methyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27a)

1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a)
Yield : 0.199 g (0.001 mol)
Mp : 136°C

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6,11-Dimethyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27b)

7-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6b)

Yield : 0.213 g (0.001 mol)

Mp : 139°C

IR (KBr) [\(\nu_{\text{max}}\) cm\(^{-1}\)]

\[3350, 1588, 1434, 1232, 980, 777\]

\(^1\)H NMR (CDCl\(_3\)) [\(\delta\) ppm]

\(2.17-2.23\) (m, 2H, C\(_8\)-H\(_2\)), 2.49 (s, 3H, C\(_{12}\)-CH\(_3\)), 2.72 (s, 3H, C\(_6\)-CH\(_3\)), 3.16-3.22 (m, 4H, C\(_7\)-H\(_2\), C\(_9\)-H\(_2\)), 7.11 & 7.34 (2 d, 2H, C\(_2\)-H, C\(_3\)-H, J = 8.2 Hz), 7.40 (s, 1H, C\(_{10}\)-H), 7.47-7.64 (m, 2H, C\(_3\)-H, C\(_4\)-H), 8.00 and 8.05 (2 d, 2H, C\(_2\)-H, C\(_5\)-H, J = 8.2 Hz), 9.75 (b s, 1H, NH)

Analysis (C\(_{22}\)H\(_{20}\)N\(_2\)) Calcd

: C, 84.58; H, 06.45; N, 08.97%

Found

: C, 84.64; H, 06.53; N, 08.91%

6,12-Dimethyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27c)

8-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6c)

Yield : 0.213 g (0.001 mol)

Mp : 135°C

IR (KBr) [\(\nu_{\text{max}}\) cm\(^{-1}\)]

\[3353, 1592, 1434, 1232, 980, 777\]

\(^1\)H NMR (CDCl\(_3\)) [\(\delta\) ppm]

\(2.18\) (m, 2H, C\(_8\)-H\(_2\)), 2.53 (s, 3H, C\(_{12}\)-CH\(_3\)), 2.72 (s, 3H, C\(_6\)-CH\(_3\)), 3.15-3.23 (m, 4H, C\(_7\)-H\(_2\), C\(_9\)-H\(_2\)), 7.11-8.25 (m, 7H, C\(_2\)-5-H, C\(_{10}\)-H, C\(_{11}\)-H, C\(_{13}\)-H), 9.74 (b s, 1H, NH)

Analysis (C\(_{22}\)H\(_{20}\)N\(_2\)) Calcd

: C, 84.58; H, 06.45; N, 08.97%

Found

: C, 84.32; H, 06.43; N, 08.96%

6,13-Dimethyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27d)

9-Methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6d)

Yield : 0.213 g (0.001 mol)

Analysis (C\(_{22}\)H\(_{20}\)N\(_2\)) Calcd

: C, 84.58; H, 06.45; N, 08.97%

Found

: C, 84.32; H, 06.43; N, 08.96%
Studies in Heterocycles

Yield: 0.196 g (63%)

Mp: 150°C

IR (KBr) [v max cm⁻¹]: 3354, 1589, 1452, 1332, 1239, 982, 733

¹H NMR (CDCl₃) [δ ppm] (Fig 50):
2.22 (m, 2H, C₆-H₂), 2.62 (s, 3H, C₁₃-CH₃), 2.73 (s, 3H, C₆-CH₃), 3.18-3.27 (m, 4H, C₇-H₂, C₉-H₂), 7.00-7.75 (m, 5H, C₃-H, C₄-H, C₁₀-H, C₁₁-H, C₁₂-H), 8.02 & 8.10 (2 d, 2H, C₂-H, C₅-H, J = 8.2 Hz), 9.75 (b s, 1H, NH)

Analysis (C₂₂H₂₀N₂): Calcd: C, 84.58; H, 06.45; N, 08.97%
Found: C, 84.55; H, 06.22; N, 09.01%

11-Chloro-6-methyl-7,8,9,14-tetrahydroquinolinol[2',3':7,6]cyclohept[b]indole (27e)

Yield: 0.233 g (0.001 mol)

Mp: 170°C

IR (KBr) [v max cm⁻¹]: 3350, 1593, 1435, 1233, 986, 776

¹H NMR (CDCl₃) [δ ppm] (Fig 51):
2.22 (m, 2H, C₆-H₂), 2.75 (s, 3H, C₁₃-CH₃), 3.16-3.22 (m, 4H, C₇-H₂, C₉-H₂), 7.59 (s, 1H, C₁₀-H), 7.21-8.08 (m, 6H, C₁₂-H, C₁₃-H, C₂-H, C₅-H), 9.77 (b s, 1H, NH)

Analysis (C₂₁H₁₇N₂Cl): Calcd: C, 75.78; H, 05.15; N, 08.42%
Found: C, 75.79; H, 05.22; N, 08.56%

12-methyl-6-(1'-propene-2'-ol)-dibenzo[l,5]diazocine (29)

The respective 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6) of 0.01 mol was reacted with o-aminouctophenone (0.01 mol) in gla acetic acid (2 mL) and refluxed for 8 h in presence of few drops of conc sulphuric acid. In all the cases the same 12-methyl-6-(1'-propene-2'-ol)-dibenzo[b,f][1,5]diazocine (29) was obtained.

Mp: 116°C

IR (KBr) [v max cm⁻¹]: 2810, 1683, 1599, 1312, 760

¹H NMR (CDCl₃) [δ ppm] (Fig 21):
2.28 and 2.99 (2 s, 6H, C₁₂-CH₃, (CH₃ of 1'-propene-2'-ol), 7.74 (s, 1H, olefinic proton), 7.23-8.65 (m, 8H, aromatic-H), 12.99 (b s, 1H, enolic OH)
Preparation of 2-methyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indoles (32a-e) from 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (22a-e)

General procedure: Acetyl chloride was added slowly to 1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22, 0.001 mol) under cold condition and stirred at room temperature for 24 h. The contents were then poured into ice water with stirring and extracted with chloroform. The combined organic extracts were washed with water, dried over anhydrous sodium sulphate and the excess solvent was removed by distillation to yield the crude product. This was purified by column chromatography over silica gel column and eluting with petroleum ether-ethyl acetate mixture (80:20).

2-Methyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indole (32a)

1-Hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22a)
Yield: 0.214 g (0.001 mol)
Mp: 175°C
IR (KBr) [ν max cm⁻¹] (Fig 24):
1H NMR (CDCl₃) [δ ppm] (Fig 25):
Analysis (C₁₅H₁₄N₂O) Calcd Found
: C, 75.61; H, 05.92; N, 11.76%
: C, 75.69; H, 05.98; N, 11.67%

2,8-Dimethyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indole (32b)

1-Hydroxyimino-7-methyl-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22b)
Yield: 0.228 g (0.001 mol)
Mp: 169-170°C
IR (KBr) [ν max cm⁻¹] (Fig 52):
1H NMR (CDCl₃) [δ ppm] (Fig 52):
Analysis (C₁₅H₁₄N₂O) Calcd Found
: C, 75.61; H, 05.92; N, 11.76%
: C, 75.69; H, 05.98; N, 11.67%
2,9-Dimethyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indole (32c)

1-Hydroxyimino-8-methyl-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22c)

Yield: 0.228 g (0.001 mol)

Mp: 162°C

IR (KBr) [v max cm⁻¹]: 3274, 1654, 1493, 1419, 780

¹H NMR (CDCl₃) [δ ppm]: 2.14-2.23 (m, 2H, C₄-H₂), 2.40 (s, 3H, C₂-CH₃), 2.45 (s, 3H, C₉-CH₃), 2.70-2.93 (m, 4H, C₃-H₂, C₅-H₂), 7.01-7.29 (m, 3H, C₇-H, C₈-H, C₁₀-H), 8.74 (b s, 1H, NH)

Analysis (C₁₆H₁₆N₂O) Calcd: C, 76.16; H, 6.39; N, 11.10%
Found: C, 76.25; H, 6.40; N, 11.21%

2,10-Dimethyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indole (32d)

1-Hydroxyimino-9-methyl-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22d)

Yield: 0.228 g (0.001 mol)

Mp: 166°C

IR (KBr) [v max cm⁻¹]: 3288, 1620, 1489, 1400, 753

¹H NMR (CDCl₃) [δ ppm]: 2.17-2.26 (m, 2H, C₄-H₂), 2.26 (s, 3H, C₂-CH₃), 2.47 (s, 3H, C₁₀-CH₃), 2.90-3.01 (m, 4H, C₃-H₂, C₅-H₂), 7.01-7.35 (m, 3H, C₇-H, C₈-H, C₉-H), 8.80 (b s, 1H, NH)

Analysis (C₁₆H₁₆N₂O) Calcd: C, 76.16; H, 6.39; N, 11.10%
Found: C, 76.32; H, 6.41; N, 11.11%

8-Chloro-2-methyl-4,5,6,11-tetrahydrooxazolo[4',5':7,6]cyclohept[b]indole (32e)

7-Chloro-1-hydroxyimino-1,2,3,4,5,10-hexahydrocyclohept[b]indole (22e)

Yield: 0.248 g (0.000 mol)

Mp: 205°C

IR (KBr) [v max cm⁻¹]: 3299, 1652, 1486, 1422, 1317, 740

Analysis (C₁₆H₁₆ClN₂O) Calcd: C, 75.81; H, 6.37; Cl, 11.04; N, 11.05%
Found: C, 75.87; H, 6.40; Cl, 11.11; N, 11.05%
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$^1$H NMR (CDCl$_3$) [δ ppm] : 2.03-2.36 (m, 2H, C$_4$-H$_2$), 2.19 (s, 3H, C$_2$-CH$_3$), 2.80-3.00 (m, 4H, C$_3$-H$_2$, C$_5$-H$_2$), 7.01-7.41 (m, 3H, C$_7$-H, C$_9$-H, C$_{10}$-H), 8.90 (b s, 1H, NH)

Analysis (C$_{15}$H$_{13}$N$_2$OCl) Calcd: C, 66.06; H, 04.80; N, 10.29%
Found: C, 66.19; H, 04.92; N, 10.30%

Preparation of 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (33a-e) from 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (6a-e)

General procedure: 1-Oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6, 0.005 mol) semicarbazide hydrochloride (0.01 mol) and sodium acetate (0.01 mol) in 6mL water were refluxed in ethanol (30 mL) for 5 h. The solid that separated out from the solution on cooling was filtered and recrystallised from ethanol.

1-Semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33a)

 Yield : 0.995 g (0.005 mol)
Mp : 149°C
IR (KBr) [v max cm$^{-1}$] : 3313, 2923, 2860, 1672, 1576, 1464, 1324, 1230, 1133, 799, 598
$^1$H NMR (DMSO-d$_6$) [δ ppm] : 1.79-1.91 (2 m, 4H, C$_3$-H$_2$, C$_4$-H$_2$), 2.66-2.69 (m, 2H, C$_5$-H$_2$), 2.90-2.93 (m, 2H, C$_2$-H$_2$), 6.51 (b s, 2H, NH$_2$), 6.95 (t, 1H, C$_7$-H, J=7.20 Hz), 7.12 (t, 1H, C$_9$-H, J=7.20 Hz), 7.27 (d, 1H, C$_5$-H, J=8.08 Hz), 7.46 (d, 1H, C$_6$-H, J=7.88 Hz), 9.30 (s, 1H, Indole NH), 10.97 (s, 1H, NHCO)

Analysis (C$_{14}$H$_{16}$N$_4$O) Calcd: C, 65.61; H, 06.29; N, 21.86%
Found: C, 65.78; H, 06.32; N, 21.81%

7-Methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33b)

 Yield : 1.065 g (0.005 mol)
Mp : 119°C
IR (KBr) [v max cm$^{-1}$] : 3313, 2924, 2862, 1671, 1570, 1463, 1328, 799, 596
$^1$H NMR (DMSO-d$_6$) [δ ppm] : 1.79-1.84 (2 m, 4H, C$_4$-H$_2$, C$_3$-H$_2$), 2.35 (s,
8-Methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[\text{b}]indole (33c)

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<td>Mp</td>
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<tr>
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<td>(^1)H NMR (DMSO-d₆) [δ ppm] (Fig 54)</td>
<td>1.78-1.84 (2 m, 4H, C₄-H₂, C₃-H₂), 2.39 (s, 3H, C₈-CH₃), 2.62-2.68 (m, 2H, C₅-H₂), 2.87-2.93 (m, 2H, C₂-H₂), 6.50 (b s, 2H, NH₂), 6.79 (d, 1H, C₇-H, J=8.08 Hz), 7.07 (s, 1H, C₆-H), 7.33 (d, 1H, C₁₀-H, J=8.04 Hz), 9.26 (s, 1H, Indole NH), 10.81 (s, 1H, NHCO)</td>
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Analysis (C₁₅H₁₈N₄O) Calcd: C, 66.65; H, 6.71; N, 20.72%
Found: C, 66.60; H, 6.85; N, 20.83%

9-Methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[\text{b}]indole (33d)

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<td>Yield</td>
<td>1.065 g (0.005 mol)</td>
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<tr>
<td>Mp</td>
<td>162°C</td>
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<tr>
<td>IR (KBr) [ν max cm⁻¹]</td>
<td>3315, 2926, 2872, 1670, 1573, 1464, 1133, 799, 598</td>
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<tr>
<td>(^1)H NMR (DMSO-d₆) [δ ppm] (Fig 55)</td>
<td>2.01-2.17 (2 m, 4H, C₄-H₂, C₃-H₂), 2.56 (s, 3H, C₉-CH₃), 2.97-2.99 (m, 2H, C₅-H₂), 3.10-3.16 (m, 2H, C₂-H₂), 6.05 (b s, 2H, NH₂), 7.01-7.48 (m, 3H, C₆-H, C₇-H, C₈-H), 8.94 (s, 1H, Indole NH), 10.00 (s, 1H, NHCO)</td>
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Analysis (C₁₅H₁₈N₄O) Calcd: C, 66.65; H, 6.71; N, 20.72%
Found: C, 66.72; H, 6.79; N, 20.82%
7-Chloro-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33e)

Yield: 1.165 g (0.005 mol)
Mp: 147°C
IR (KBr) [\nu_{\text{max}} \text{ cm}^{-1}] : 3131, 2925, 2862, 1673, 1462, 799, 593
\textit{^1}H NMR (DMSO-d6) [\delta \text{ ppm}]: 1.78-1.85 (2 m, 4H, C_4-H_2, C_3-H_2), 2.66-2.67 (m, 2H, C_5-H_2), 2.89-2.90 (m, 2H, C_2-H_2), 6.49 (b s, 2H, NH_2), 7.11 (d d, 1H, C_7-H, J(,\tau,\nu)=8.56Hz, J_{\text{meta}}=1.98Hz), 7.28 (d, 1H, C_8-H, J=8.56Hz), 7.49 (s, 1H, C_6-H), 9.35 (s, 1H, Indole NH), 11.13 (s, 1H, NHCO)

Analysis (C_{14}H_{15}N_4OCl) Calcd: C, 57.83; H, 5.21; N, 19.27%
Found: C, 57.70; H, 0.19; N, 19.30%

Preparation of 4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indoles (34a-e) from 1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indoles (33a-e)

General procedure: 1-Semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33, 0.005 mol) was dissolved in glacial acetic acid (15 mL) and warmed gently (50-60°C) with stirring. To this, selenium dioxide powder (0.005 mol) was added in small quantities during 0.5-1 h and stirring was continued until the evolution of gas ceased. The reaction mixture was cooled and filtered to remove the deposited selenium. The filtrate was poured into crushed ice and extracted using ethyl acetate. The combined organic layers were washed with water dried over anhydrous sodium sulphate. Evaporation of the solvent yielded a crude product, which was purified by column chromatography using 98:2 petroleum ether-ethyl acetate mixture. The product thus obtained was 4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indole (34).

4,5,6,11-Tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indole (34a)

1-Semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33a) Yield: 1.280 g (0.005 mol)
Mp: 125°C
IR (KBr) [\nu_{\text{max}} \text{ cm}^{-1}]: 3409, 1613, 1522, 1437, 1363, 1322, 1255, 797
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$^1$H NMR (CDCl$_3$) [$\delta$ ppm] (Fig 29)

- $^1$H NMR (CDCl$_3$) $[\delta$ ppm $]$
  - 2.14-2.19 (m, 2H, C$_5$-H$_2$), 3.15-3.18 (m, 2H, C$_6$-H$_2$), 7.08 (t, 1H, C$_8$-H, J=7.46 Hz), 7.18 (t, 1H, C$_9$-H, J=7.54 Hz), 7.34 (d, 1H, C$_{10}$-H, J=8.08 Hz), 7.49 (d, 1H, C$_7$-H, J=7.88 Hz), 9.16 (s, 1H, NH)

Analysis (C$_{13}$H$_{11}$N$_3$Se) Calcd

- C, 54.18; H, 03.85; N, 14.58%

Found

- C, 54.28; H, 03.42; N, 14.63%

8-Methyl-4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indole (34b)

- 7-Methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33b)
  - Yield: 1.350 g (0.005 mol)
  - Mp: 139°C
  - IR (KBr) $[\nu_{max}$ cm$^{-1}$]
    - 3400, 1612, 1532, 1439, 1252, 766
  - $^1$H NMR (CDCl$_3$) $[\delta$ ppm $]$
    - 2.21-2.27 (m, 2H, C$_5$-H$_2$), 2.45 (s, 3H, C$_8$-CH$_3$), 3.22-3.25 (m, 2H, C$_6$-H$_2$), 3.39-3.43 (m, 2H, C$_4$-H$_2$), 7.04-7.57 (m, 3H, C$_7$-H, C$_9$-H, C$_{10}$-H), 9.12 (s, 1H, NH)

Analysis (C$_{14}$H$_{13}$N$_3$Se) Calcd

- C, 55.64; H, 04.34; N, 13.90%

Found

- C, 55.62; H, 04.25; N, 13.83%

9-Methyl-4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indole (34c)

- 9-Methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33c)
  - Yield: 1.350 g (0.005 mol)
  - Mp: 147°C
  - IR (KBr) $[\nu_{max}$ cm$^{-1}$]
    - 3998, 1612, 1539, 1436, 1322, 1256, 798
  - $^1$H NMR (CDCl$_3$) $[\delta$ ppm $]$
    - 2.14-2.20 (m, 2H, C$_5$-H$_2$), 2.41 (s, 3H, C$_9$-CH$_3$), 3.13-3.16 (m, 2H, C$_6$-H$_2$), 3.33-3.35 (m, 2H, C$_4$-H$_2$), 7.00-7.27 (m, 3H, C$_7$-H, C$_8$-H, C$_{10}$-H), 9.04 (s, 1H, NH)

Analysis (C$_{14}$H$_{13}$N$_3$Se) Calcd

- C, 55.64; H, 04.34; N, 13.90%

Found

- C, 55.68; H, 04.32; N, 13.93%

10-Methyl-4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indole (34d)

- 9-Methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33d)
  - Yield: 1.350 g (0.005 mol)
  - Mp: 155°C
  - IR (KBr) $[\nu_{max}$ cm$^{-1}$]
    - 3998, 1612, 1539, 1436, 1322, 1256, 798
  - $^1$H NMR (CDCl$_3$) $[\delta$ ppm $]$
    - 2.14-2.20 (m, 2H, C$_5$-H$_2$), 2.41 (s, 3H, C$_9$-CH$_3$), 3.13-3.16 (m, 2H, C$_6$-H$_2$), 3.33-3.35 (m, 2H, C$_4$-H$_2$), 7.00-7.27 (m, 3H, C$_7$-H, C$_8$-H, C$_{10}$-H), 9.04 (s, 1H, NH)

Analysis (C$_{14}$H$_{13}$N$_3$Se) Calcd

- C, 55.64; H, 04.34; N, 13.90%

Found

- C, 55.68; H, 04.32; N, 13.93%

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IR (KBr) [\(\nu_{\text{max}}\) cm\(^{-1}\)]

\(^1\)H NMR (CDCl\(_3\)) [\(\delta\) ppm]

(Fig 59)

Analysis (C\(_{14}H_{13}N_3Se\)) Calcd

Found

\[\text{C, 55.64; H, 04.34; N, 13.90}\%\]

8-Chloro-4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4';5':6,7]cyclohept[b]indole (34e)

7-Chloro-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33e)

Yield

MP

IR (KBr) [\(\nu_{\text{max}}\) cm\(^{-1}\)]

\(^1\)H NMR (CDCl\(_3\)) [\(\delta\) ppm]

(Fig 60)

Analysis (C\(_{13}H_{16}N_3SeCl\)) Calcd

Found

\[\text{C, 48.39; H, 03.13; N, 13.02}\%\]

\[\text{C, 48.20; H, 03.19; N, 13.11}\%\]
**Fig. 30.** $^1$H NMR spectrum of 1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6a)

**Fig. 31.** $^1$H NMR spectrum of 8-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6c)
Fig 32. $^1$H NMR spectrum of 9-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6d)

Fig 33. $^1$H NMR spectrum of 7-chloro-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[b]indole (6e)
Fig 34. $^1$H NMR spectrum of 3-phenyl-4,5,6,11-tetrahydroisoxazol[4',3':6,7]cyclohept[b]indole (8a)

Fig 35. $^1$H NMR spectrum of 9-methyl-3-phenyl-4,5,6,11-tetrahydroisoxazol[4',3':6,7]cyclohept[b]indole (8c)
Fig 36. $^1$H NMR spectrum of 10-methyl-3-phenyl-4,5,6,11-tetrahydroisoxazolo[4',3':6,7]cyclohept[h]indole (8d)

Fig 37. $^1$H NMR spectrum of 8-chloro-4,5,6,11-tetrahydroisoxazolo[4',3':6,7]cyclohept[h]indole (8e)
Fig 38. $^1$H NMR spectrum of 3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4',3':6,7]cyclohept[b]indole (9a)

Fig 39. $^1$H NMR spectrum of 9-methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4',3':6,7]cyclohept[b]indole (9c)
Fig. 40. $^1$H NMR spectrum of 10-methyl-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4,3,6,7]cyclohept[6]indole (9d).

Fig. 41. $^1$H NMR spectrum of 8-chloro-3-phenyl-4,5,6,11-tetrahydro-2H-pyrazolo[4,3,6,7]cyclohept[6]indole (9e).
Fig 42. $^1$H NMR spectrum of 9-methyl-5H,6,7,12,13-tetrahydroidolo[2,3':7,6]cyclohept[b]indole (12b)

Fig 43. $^1$H NMR spectrum of 10-methyl-5H,6,7,12,13-tetrahydroidolo[2,3':7,6]cyclohept[b]indole (12c)
Fig 44. $^1$H NMR spectrum of 9-chloro-5H,6,7,12,13-tetrahydroidolo[2,3;7,6]cyclohept[6]indole (12e)

Fig 45. $^1$H NMR spectrum of 7-acetyl-8-methyl-1-oxo-1,2,3,4,5,10-hexahydrocyclohept[6]indole (15e)
Fig. 46. $^1$H NMR spectrum of 7-acetyl-9-methyl-1-oxo-1,2,3,4,5,10-hexahydrolidopyridine (15d).

Fig. 47. $^1$H NMR spectrum of 9-methyl-1-hydroxyimino-1,2,3,4,5,10-hexahydrolidopyridine (22d).
Fig 48. $^1\text{H}$ NMR spectrum of 1-N-acetylamino-2-hydroxy-8-methyl-3,4,5,10-tetrahydrocyclohept[b]indole (26b)

Fig 49. $^1\text{H}$ NMR spectrum of 6-methyl-7,8,9,14-tetrahydroquinolino[2',3':7,6]cyclohept[b]indole (27a)
Fig 50. $^1$H NMR spectrum of 6,13-dimethyl-7,8,9,14-tetrahydroquinolino[2',3':7,6']cyclohept[h]indole (27d)

Fig 51. $^1$H NMR spectrum of 11-chloro-6-methyl-7,8,9,14-tetrahydroquinolino[2',3':7,6']cyclohept[h]indole (27e)
Fig 52. "H NMR spectrum of 2,8-dimethyl-4,5,6,11-tetrahydrooxazolo[4',5',6',7,8]cyclohept[6]indole (32b)

Fig 53. "H NMR spectrum of 8-chloro-2-methyl-4,5,6,11-tetrahydrooxazolo[4',5',6',7,8]cyclohept[6]indole (32e)
Fig 54. $^1$H NMR spectrum of 9-methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33c)

Fig 55. $^1$H NMR spectrum of 9-methyl-1-semicarbazono-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33d)
**Fig 56.** $^1$H NMR spectrum of 7-chloro-1-semicolonbazone-1,2,3,4,5,10-hexahydrocyclohept[b]indole (33e)

**Fig 57.** $^1$H NMR spectrum of 8-methyl-4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indole (34h)
Fig 58. $^1$H NMR spectrum of 9-methyl-4,5,6,11-tetrahydron-1,2,3-selenadiazolo[4,5-b:6,7]cyclohept[h]indole (34c)

Fig 59. $^1$H NMR spectrum of 10-methyl-4,5,6,11-tetrahydron-1,2,3-selenadiazolo[4,5-b:6,7]cyclohept[h]indole (34d)
Fig 60. $^1$H NMR spectrum of 8-chloro-4,5,6,11-tetrahydro-1,2,3-selenadiazolo[4',5':6,7]cyclohept[b]indole (34e)