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Note

Attempted synthesis of substituted carbazoles from 1-oxo-1,2,3,4-tetrahydro-carbazoles and 1-hydroxyimino-1,2,3,4-tetrahydrocarbazoles

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The reaction of 1-oxo-1,2,3,4-tetrahydrocarbazoles **1** with vinyl acetate in presence of alcoholic KOH affords hitherto unknown 7-methyl-1-oxo-2-(3′-methyl propan-1′-al)-1,2,3,4-tetrahydrocarbazole **2**. Similarly, the reaction of 1-hydroxyimino-1,2,3,4-tetrahydrocarbazoles **3** with vinyl acetate in the presence of *p*-toulenesulphonic acid results in the formation of a new compound viz., 2-acetoxy-1,2,3,3a,4,5-hexahydropyrrolo[3,4-*a*]carbazole **4**. All the compounds have been characterized by IR, NMR and mass spectra and elemental analysis.

Keywords: Carbazoles, tetrahydrocarbazoles, vinyl acetate, hexa-hydropyrrolo[3,4-*a*]carbazole

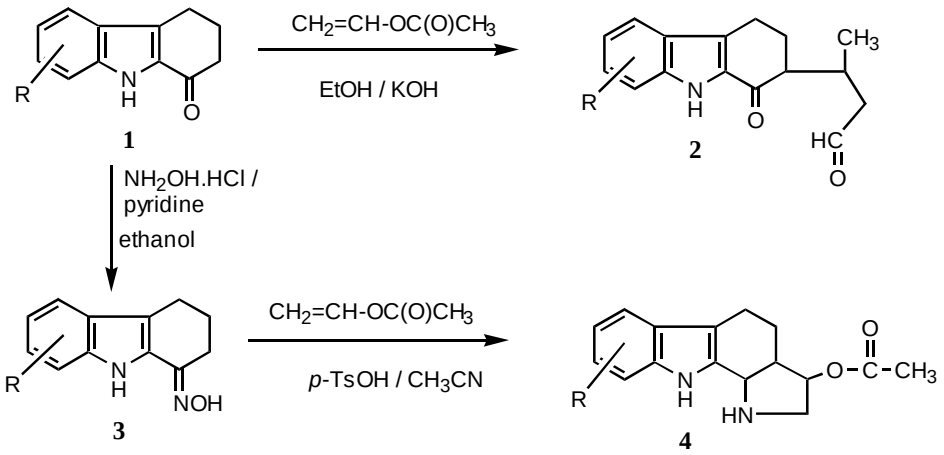
IPC: **Int.Cl.**[7] **C 07 D**

The emerging importance towards the various strategies applied to prepare carbazoles and their derivatives was due to their diverse pharmacological properties[1-3]. Over the past decades a large number of biologically active carbazole alkaloids have been obtained from terrestrial plants, marine resources and streptomycetes[1-10]. Development of new methods for the synthesis of functionalized carbazoles in particular, is attracting organic chemists due to the discovery of many carbazole alkaloids with varied pharmacological properties[6-10]. Recent discovery of the antitumor properties of naturally occurring carbazole alkaloids ellipticine and its isomer olivacine has created a wide interest towards the construction of various condensed systems[11,12]. To construct such tetracyclic systems with carbazole framework, the aim was to derive an intermediate, such that it could be a useful synthon to synthesize various annelated carbazole derivatives. Until now, the 1-oxo-1,2,3,4-tetrahydrocarbazole **1** and its derivatives have been exploited to a great extent to derive numerous annelated carbazoles of pharmacological importance[13-19]. It was felt worthwhile to introduce 2-vinylidene group in the second position of **1**, so 1-oxo-1,2,3,4-tetrahydrocarbazole[18] **1** was treated with vinyl acetate with a view to substituting a vinylic group at C-2 position of compound **1**.

With this as our aim the reaction of 7-methyl-1-oxo-1,2,3,4-tetrahydrocarbazole **1b** with vinyl acetate in the presence of alcoholic KOH gave a new product which melted at 121 °C. The IR spectrum of the product showed intense bands at 3256 cm^{-1} for the NH stretching and two intense bands at 1655 and 1639 cm^{-1} corresponding to the C=O group and C=C stretching vibrations, respectively. The ^1H NMR spectrum displayed multiplet in the region δ 1.19-1.27 with a three-proton intensity due to the methyl protons of the propanal group. Three multiplets appeared in the region δ 2.23-2.29, 2.62-2.68 and 2.97-3.26 corresponding to the C_2-H, C_4-2H and C_3-2H, respectively. A broad singlet at δ 2.47 corresponds to the C_7-methyl protons. A multiplet between the region δ 6.85-6.99 was for the C_3'-H and C_2'-2H. The aromatic protons at C_5 and C_6 and the carbazole-NH appeared as unresolved multiplet in the region δ 7.20-7.23. A singlet at δ 7.53 was due to the C_8-H. The formyl proton at C_1' appeared as a broad singlet at δ 8.93. The ^{13}C NMR spectrum showed two sharp singlets at δ 191.09 and 191.25 corresponding to the two carbonyl groups at C_1' and C_1. Moreover, the elemental analysis C, 75.78; H, 07.01; N, 05.12% also agreed well with the proposed molecular formula, $C_{17}H_{19}NO_2$. Based on the spectral and elemental data, the structure of the new compound obtained was found to be 7-methyl-1-oxo-2-(3′-methylpropan-1′-al)-1,2,3,4-tetrahydrocarbazole **2b** (**Scheme I**). The mass spectrum of **2b** (**Scheme II**) showed the molecular ion peak at m/z 269 (2%, M^+), the appearance of the fragment ion peak at m/z 241 (1%, $M^{+\cdot}$-28) due to the elimination of the ethylene fragment strongly supports the proposed structure.

A similar series of compounds, **2a**, **2c, 2d** and **2e** were realized from the respective 1-oxo-1,2,3,4-tetrahydrocarbazoles as **1a, 1c**, **1d** and **1e** (**Scheme I**).

The plausible mechanism for the formation of **2** could be explained as follows. The enolate ion of 1-oxo-1,2,3,4-tetrahydrocarbazole **I** undergoes Diels-



Scheme I

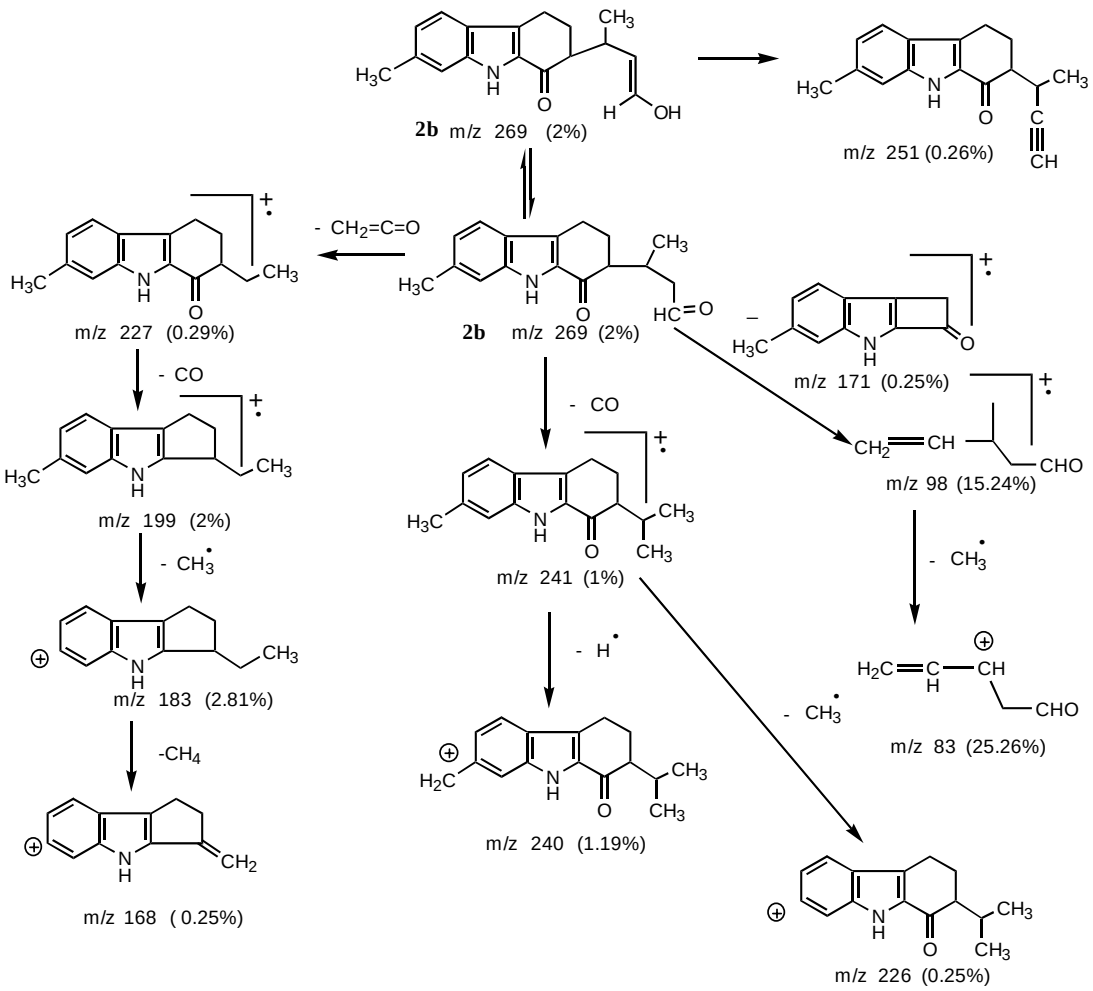
Alder reaction to afford the tetracyclic intermediate **II**. This undergoes cleavage in the presence of base to yield the 2-vinylidenecarbazole intermediate **III**. The tautomer of **III** adds again with vinyl acetate to give the 2-acetoxypyrano[2,3-*a*]carbazole **IV**. This cyclised intermediate **IV** gets cleaved by loosing the acetyl group in the presence of base to yield the product **2** (**Scheme III**).

The unsuccessful attempt towards the introduction of an active methylene group at the second position of the 1-oxo-1,2,3,4-tetrahydrocarbazoles **1** has induced us to attempt the same reaction on 1-hydroxyimino-1,2,3,4-tetrahydrocarbazoles[19] **3**. Tamura *et al.*[20] has used ethoxyvinyl acetate on cyclohexanone oximes in the presence of *p*-toulenesulphonic acid under Semmler-Wolff aromatization conditions to derive alkoxy acetanilides. In this regard, it was aimed to apply these reaction conditions by just changing the reactant, ethoxyvinyl acetate as vinyl acetate with an aim to obtain aminocarbazole derivatives. Interestingly, the reaction of 7-methyl-1-hydroxyimino-1,2,3,4-tetrahydrocarbazole **3b** with vinyl acetate in acetonitrile in the presence of *p*-TsOH resulted in the formation of hitherto unknown compound which was characterized as 3-acetoxy-1,2,3,3a,4,5-hexahydro-8-methylpyrrolo[2,3-*a*]carbazole **4b**.

The product in its IR spectrum showed strong bands at 3385 and 3210 cm^{-1} which were attributed to the two NH group-stretching vibrations. The C=O group stretching vibration was inferred from a strong band at 1670 cm^{-1}. The ^1H NMR spectrum showed two multiplets in the region between δ 2.17-2.32 and δ 2.62-2.69 corresponding to the methylene protons at C_4 and C_5 positions, respectively. The methyl protons at C_8 resonated as a broad singlet at δ 2.48. The multiplet in the region δ 2.97-3.00 of three proton intensity was accounted for the C_{1a}, C_{3a} methylene protons. A singlet at δ 3.25 was due to the acetyl protons. A multiplet in the region δ 6.86-7.21 was due to the protons at C_2 and C_3 positions. A doublet of one proton intensity appeared at δ 6.98 was due to the C_6 proton with a *J* value of 8.20 Hz. The C_9 proton appeared as a singlet at δ 7.39. A doublet of one proton intensity resonated at δ 7.53 with a *J* value of 8.20 Hz was accounted for the C_7 proton. The N_1H proton and the carbazole NH appeared as a multiplet between δ 8.86-8.97. The mass spectrum showed the molecular ion peak at m/z 225 which, may be due to loss of the acetoxy group during ionization. Moreover, the elemental analysis (C, 71.78; H, 07.11; N, 09.93%) augmented the formation of the new compound with a molecular formula, $C_{17}H_{20}N_2O_2$. From the spectral and analytical data the structure of the compound was found to be 3-acetoxy-1, 2, 3, 3a, 4,5-hexahydro-8-methylpyrrolo[2,3-*a*]carbazole **4b**. The repeatability of the experiment was tested on the compounds **3a**, **3c**, **3d** and **3e** to afford the respective 3-acetoxy-1, 2, 3, 3a, 4, 5-hexahydropyrrolo[2, 3-*a*]-carbazole derivatives as **4a**, **4c**, **4d** and **4e** (**Scheme I**).

Experimental Section

Melting points were determined with a Mettler FP 51 melting point apparatus and are uncorrected. IR spectra in KBr were recorded on a Shimadzu FTIR-8201 PC infrared spectrophotometer; ^1H NMR and ^{13}C NMR spectra in $CDCl_3$ on a Varian AMX 400

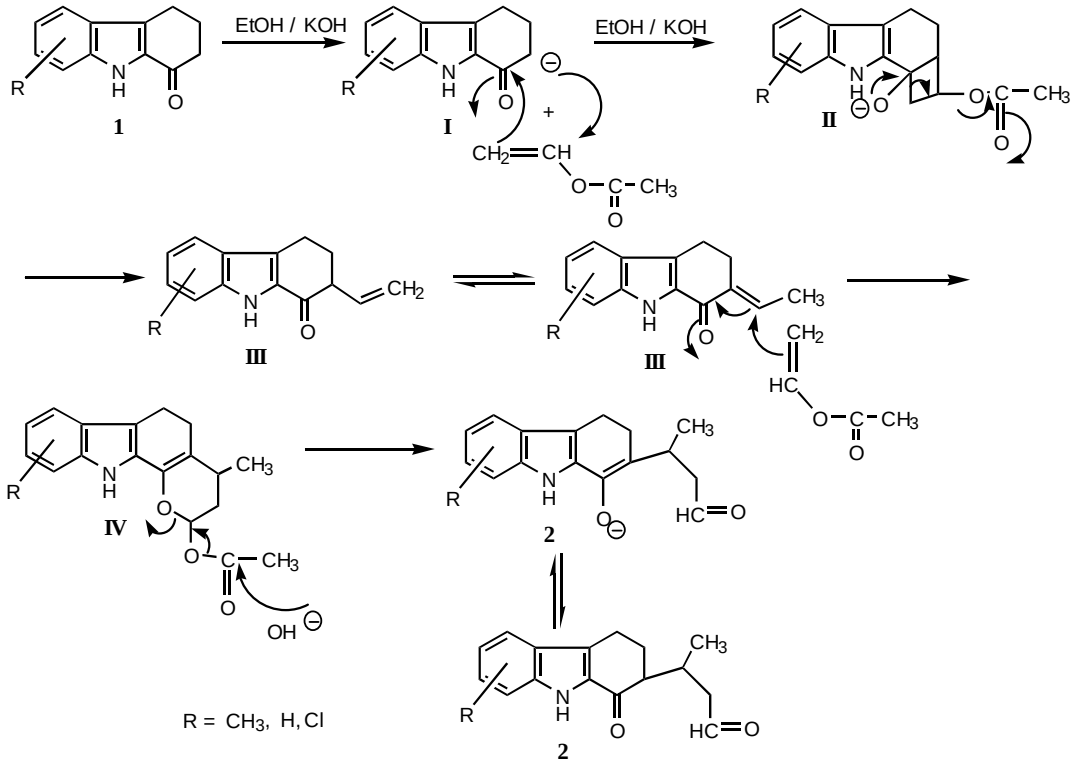


Scheme II- Mass spectral fragmentation of **2b**

FT-NMR spectrometer using TMS as internal reference (chemical shifts in δ, ppm); and mass spectra on a Jeol-JMS-D-300 mass spectrometer at 70 eV. Satisfactory C, H, N, analyses were obtained for all the compounds on a Perkin-Elmer Model 240 CHN analyzer. The purity of the products was checked by TLC on silica gel plate. All solvents were purified by distillation or were of HPLC grade.

Reaction of 1-oxo-1,2,3,4-tetrahydrocarbazoles 1 with vinyl acetate. General procedure. The respective 1-oxo-1,2,3,4-tetrahydrocarbazole (**1**, 0.001 mole) was dissolved in 4% alcoholic KOH solution and stirred at room temperature for 10 min. Then vinyl acetate (1 mL) was added and the mixture was further stirred for 24 hr. After one day the excess ethanol was removed and the reaction mixture was dissolved in cold water. Then it was neutralized with dil. HCl and extracted with ethyl acetate. The organic layer was thoroughly washed with water and dried over anhydrous sodium sulphate. The removal of solvent yielded a crude product. It was purified by column chromatography over silica gel using pet. ether-ethyl acetate mixture [99:1] as eluent. The purified product was obtained as yellow crystalline powder.

8-Methyl-1-oxo-2-(3′-methylpropan-1′-al)-1,2,3, 4-tetrahydrocarbazole 2a: Yellow crystalline powder from pet. ether-ethyl acetate mixture, m.p. 135°C, yield 80%; IR: 3298, 2925, 2857, 1647, 1630, 1542, 1477, 1327, 1178, 748 cm^{-1}; ^1H NMR: δ 1.22-1.27 (m, 3H, C_3'-CH_3) 2.24-2.33 (m, 1H, C_2-H), 2.49 (s, 3H, C_8-CH_3), 2.64-2.68 (m, 2H, C_4-2H), 2.94-3.03 (m, 2H, C_3-2H), 7.05-7.22 (m, 3H, C_3'-H, C_2'-2H), 7.34-7.67 (m, 4H, C_5-H, C_6-H, C_7-H, carbazole-NH), 8.83 (b s, 1H, C_1'-CHO); ^{13}C NMR: δ 21.08 (C_8-CH_3), 22.45 (C_3'-CH_3), 22.58 (C_2), 24.05 (C_4), 25.54 (C_5), 26.16



Scheme III

(C_{10b}), 38.22 (C_3), 38.49 (CH_3), 111.27 (C_{5a}), 113.29 (C_6), 121.01 (C_7), 121.58 (C_{9a}), 123.09 (C_9), 124.88 (C_8), 125.78 (C_{5b}), 129.24 (C_{10a}), 190.45 (C_1=O); MS: m/z (%) M^+ 269 (2.5), 251 (0.29), 241 (1), 240 (2.01), 227 (0.39), 226 (0.45), 199 (5), 183 (2.58), 171 (0.48), 168 (0.25), 98 (14.2), 83 (28.16).

7-Methyl-1-oxo-2-(3′-methylpropan-1′-al)-1,2,3,4-tetrahydrocarbazole 2b: Yellow crystalline powder from pet. ether-ethyl acetate mixture, m.p. 121°C, yield 78%; IR: 3256, 2934, 2855, 1655, 1639, 1536, 1474, 1212, 1169, 788 cm^{-1}; ^1H NMR: δ 1.19-1.27 (m, 3H, C_3'-CH_3), 2.23-2.29 (m, 1H, C_2-H), 2.47 (s, 3H, C_7-CH_3), 2.62-2.68 (m, 2H, C_4-2H), 2.97-3.26 (m, 2H, C_3-2H), 6.85-6.99 (m, 3H, C_3'-H, C_2'-2H), 7.20-7.23 (m, 3H, C_5-H, C_6-H, carbazole-NH), 7.53 (s, 1H, C_8-H), 8.93 (b s, 1H, C_1'-CHO); ^{13}C NMR: δ 20.04 (C_7-CH_3), 21.51 (C_3'-CH_3), 22.11 (C_2), 23.97 (C_4), 25.04 (C_5), 25.15 (C_{10b}), 37.78 (C_3), 38.20 (CH_3), 110.26 (C_{5a}), 112.19 (C_6), 120.99 (C_7), 121.46 (C_{9a}), 122.59 (C_9), 123.95 (C_8), 126.99 (C_{5b}), 129.70 (C_{10a}), 191.08 (C_1=O); MS: m/z (%) M^+ 269 (2), 251 (0.26), 241 (1), 240 (1.19), 227 (0.29), 226 (0.25), 199 (2), 183 (2.81), 171 (0.25), 168 (0.25), 98 (15.2), 83 (25.26).

6-Methyl-1-oxo-2-(3′-methylpropan-1′-al)-1,2,3,4-tetrahydrocarbazole 2c: Yellow crystalline powder from pet. ether-ethyl acetate mixture, m.p. 170°C, yield 75%; IR: 3273, 2920, 2856, 1643, 1630, 1539, 1479, 1321, 802 cm^{-1}; ^1H NMR: δ 1.19-1.27 (m, 3H, C_3'-CH_3), 2.22-2.33 (m, 1H, C_2-H), 2.45 (s, 3H, C_6-CH_3), 2.60-2.67 (m, 2H, C_4-2H), 2.96-3.01 (m, 1H, C_3-2H), 7.18-7.36 (m, 6H, C_3'-H, C_2'-2H, C_7-H, C_8-H, carbazole-NH), 7.42 (s, 1H, C_5-H), 9.12 (b s, 1H, C_1'-CHO); ^{13}C NMR: δ 20.48 (C_6-CH_3), 21.58 (C_3'-CH_3), 22.76 (C_2), 24.48 (C_4), 25.65 (C_5), 26.71 (C_{10b}), 38.15 (C_3), 39.49 (CH_3), 110.30 (C_{5a}), 112.89 (C_6), 122.34 (C_7), 122.68 (C_{9a}), 123.29 (C_9), 125.16 (C_8), 125.98 (C_{5b}), 129.03 (C_{10a}), 191.06 (C_1=O); MS: m/z (%) M^+ 269 (2), 251 (0.28), 241 (1), 240 (1.79), 227 (0.32), 226 (0.38), 199 (4), 183 (3.54), 171 (0.48), 168 (0.51), 98 (14.2), 83 (25.98).

1-Oxo-2-(3′-methylpropan-1′-al)-1,2,3,4-tetrahydrocarbazole 2d: Yellow crystalline powder from pet. ether-ethyl acetate mixture; m.p. 150°C, yield 75%; IR: 3288, 2934, 2855, 1647, 1635, 1569, 1541, 1474, 1329, 1246, 733 cm^{-1}; ^1H NMR: δ 1.23-1.27 (m, 3H, C_3'-CH_3), 2.24-2.31 (m, 1H, C_2-H), 2.66-2.69 (m, 2H, C_4-2H), 3.00-3.03 (m, 2H, C_3-2H), 7.13-7.17 (m, 3H, C_3'-H, C_2'-2H), 7.34-7.66 (m, 5H, C_5-H, C_6-H, C_7-H, C_8-H, carbazole-NH), 9.31 (b s, 1H, C_1'-CHO); ^{13}C NMR: δ 21.09 (C_3'-CH_3), 22.32 (C_2), 24.01 (C_4),

25.68 (C_5), 25.77 (C_{10b}), 37.85 (C_3), 38.43 (CH_3), 111.09 (C_{5a}), 112.55 (C_6), 121.11 (C_7), 121.69 (C_{9a}), 122.85 (C_9), 124.08 (C_8), 127.13 (C_{5b}), 129.87 (C_{10a}), 190.98 (C_1=O); MS: m/z (%) M^+ 255 (2), 237 (0.28), 227 (1), 226 (1.89), 213 (0.28), 212 (0.21), 185 (1.2), 169 (2.81), 157 (0.24), 154 (0.28), 84 (15.2), 69 (24.06).

6-Chloro-1-oxo-2-(3′-methylpropan-1′-al)-1,2,3,4-tetrahydrocarbazole 2e: Yellow crystalline powder from pet. ether-ethyl acetate mixture, m.p. 220°C, yield 70%; IR: 3265, 2925, 2856, 1654, 1639, 1537, 1468, 1379, 1317, 1263, 1086, 1020, 727 cm^{-1}; ^1H NMR: δ 1.20-1.25 (m, 3H, C_3'-CH_3), 2.24-2.30 (m, 1H, C_2-H), 2.65-2.68 (m, 2H, C_4-2H), 2.95-2.99 (m, 2H, C_3-2H), 7.29-7.39 (m, 6H, C_3'-CH, C_2'-2H, C_7-H, C_8-H, carbazole-NH), 7.63 (s, 1H, C_5-H), 9.07 (b s, 1H, C_1'-CHO); ^{13}C NMR: δ 20.98 (C_3'-CH_3), 22.35 (C_2), 24.54 (C_4), 25.69 (C_5), 26.34 (C_{10b}), 38.64 (C_3), 39.78 (CH_3), 111.44 (C_{5a}), 112.58 (C_6), 122.58 (C_7), 123.77 (C_{9a}), 124.09 (C_9), 125.56 (C_8), 126.19 (C_{5b}), 130.05 (C_{10a}), 191.21 (C_1=O); MS: m/z (%) M^+ 289 (2), 271 (0.25), 261 (1), 260 (1.51), 247 (0.35), 246 (0.38), 219 (4), 203 (3.54), 191 (0.48), 188 (0.52), 118 (15.2), 103 (20.44).

Reaction of 1-hydroxyimino-1,2,3,4-tetrahydrocarbazoles 3 with vinyl acetate. General procedure. 1-Hydroxyimino-1,2,3,4-tetrahydrocarbazoles (**3**, 0.001 mole) was dissolved in 15 mL of acetonitrile and added a catalytic amount of *p*-toluenesulphonic acid. To this mixture 1 mL of vinyl acetate was added and the reaction mixture was refluxed on a water-bath for 6 hr. At the end of the period the excess solvent was removed by distillation and was poured into crushed ice. The cold contents were neutralised with 10% sodium bicarbonate solution, extracted with ethyl acetate. The organic phase was thoroughly washed with water and dried over anhydrous sodium sulphate. On removal of the solvent the crude product obtained was purified by column chromatography over silica gel. The mixture of pet. ether:ethyl acetate (95:5) afforded crystalline powder as the product.

3-Acetoxy-1,2,3,3a,4,5-hexahydro-9-methylpyrrolo[2,3-*a*]carbazole 4a: Crystalline powder from pet. ether-ethyl acetate mixture, m.p. 234°C, yield 68%; IR: 3390, 3236, 2923, 2854, 1643, 1614, 1543, 1381, 1329, 1173, 1140 cm^{-1}; ^1H NMR: δ 2.24-2.30 (m, 2H, C_4-2H), 2.49 (s, 3H, C_9-CH_3), 2.64-2.69 (m, 2H, C_5-2H), 2.99-3.03 (m, 2H, C_{1a}-H, C_{3a}-H), 3.45 (s, 3H, C_3-$COCH_3$), 7.07-7.36 (m, 4H, C_2-2H, C_3-H, C_7-H), 7.50 (d, 1H, C_6-H, J = 8.00 Hz), 7.66 (d, 1H, C_8-H, J = 7.96 Hz), 8.82 (m, 2H, N_1H and carbazole-NH); ^{13}C NMR: δ 21.04 (C_9-CH_3), 22.55 (C_3'-CH_3), 22.71 (C_2), 24.17 (C_4), 25.25 (C_3), 38.08 (C_3'), 38.16 (C_2'), 109.15 (C_{9a}), 111.09 (C_{4b}), 121.54 (C_{8a}), 123.11 (C_{4a}), 127.09 (C_6), 134.11 (C_7), 137.03 (C_5), 139.46 (C_8), 190.24 ($C_{1'}$=O), 191.55 (C_1=O); MS: m/z (%) M^+ 225 (10), 200 (20), 199 (100), 198 (14), 171 (21), 170 (23), 157 (15), 144 (15), 143 (59), 142 (15), 115 (15).

3-Acetoxy-1,2,3,3a,4,5-hexahydro-8-methylpyrrolo[2,3-*a*]carbazole 4b: Crystalline powder from pet. ether-ethyl acetate mixture, m.p. 131°C, yield 71%; IR: 3385, 3210, 2925, 2857 1670, 1634, 1537, 1428, 1409, 1329, 1242, 1171, 1140 cm^{-1}; ^1H NMR: δ 2.17-2.32 (m, 2H, C_4-2H), 2.48 (s, 3H, C_8-CH_3), 2.62-2.69 (m, 2H, C_5-2H), 2.97-3.00 (m, 2H, C_{1a}-H, C_{3a}-H), 3.25 (s, 3H, C_3-$COCH_3$), 6.86-7.21 (m, 3H, C_2-2H, C_3-H), 6.98 (d, 1H, C_6-H, J = 8.20 Hz), 7.39 (s, 1H, C_9-H), 7.53 (d, 1H, C_7-H, J = 8.20 Hz), 8.86-8.97 (m, 2H, N_1H, carbazole-NH); ^{13}C NMR: δ 20.04 (C_8-CH_3), 21.50 (C_3'-CH_3), 22.11 (C_2), 23.97 (C_4), 25.03 (C_3), 37.78 (C_3'), 38.20 (C_2'), 110.26 (C_{9a}), 112.19 (C_{4b}), 120.99 (C_{8a}), 122.59 (C_{4a}), 126.99 (C_6), 133.78 (C_7), 137.53 (C_5), 138.26 (C_8), 191.09 ($C_{1'}$=O), 191.25 (C_1=O); MS: m/z (%) M^+ 225 (10), 200 (14), 199 (100), 198 (16), 171 (12), 170 (22), 157 (14), 144 (12), 143 (54), 142 (14), 115 (16).

3-Acetoxy-1,2,3,3a,4,5-hexahydro-7-methylpyrrolo[2,3-*a*]carbazole 4c: Crystalline powder from pet. ether-ethyl acetate mixture, m.p. 160°C, yield 65%; IR (KBr, ν cm^{-1}): 3395, 3273, 2926, 2855 1641, 1578, 1541, 1452, 1325, 1182, 1132; ^1H NMR: δ 2.23-2.29 (m, 2H, C_4-2H), 2.45 (s, 3H, C_7-CH_3), 2.63-2.67 (m, 2H, C_5-2H), 2.99-3.04 (m, 2H, C_{1a}-H, C_{3a}-H), 3.21(s, 3H, C_3-$COCH_3$), 7.18-7.33 (m, 5H, C_2-2H, C_3-H, C_8-H, C_9-H), 7.42 (s, 1H, C_6-H), 8.78-8.94 (m, 2H, N_1H, carbazole-NH); ^{13}C NMR: δ 20.04 (C_7-CH_3), 21.85 (C_3'-CH_3), 22.45 (C_2), 24.74 (C_4), 25.44 (C_3), 38.98 (C_3'), 39.07 (C_2'), 110.14 (C_{9a}), 112.49 (C_{4b}), 120.64 (C_{8a}), 125.41 (C_{4a}), 128.49 (C_6), 135.09 (C_7), 138.14 (C_5), 139.25 (C_8), 189.95 ($C_{1'}$=O), 191.01 (C_1=O); MS: m/z (%) M^+ 225 (11), 200 (18), 199 (100), 198 (12), 171 (20), 170 (24), 157 (13), 144 (10), 143 (58), 142 (12), 115 (19).

3-Acetoxy-1,2,3,3a,4,5-hexahydropyrrolo[2,3-*a*]-carbazole 4d: Crystalline powder from pet. ether-ethyl acetate mixture, m.p. 165°C, yield 70%; IR: 3399, 3285, 2923, 2854 1643, 1519, 1468, 1329, 1250 cm^{-1}; ^1H NMR: δ 2.25-2.31 (m, 2H, C_4-2H), 2.48 (s, 3H, C_8-CH_3), 2.65-2.69 (m, 2H, C_5-2H), 3.01-3.04 (m, 2H,

C_{1a}-H, C_{3a}-H), 3.38 (s, 3H, C_3-$COCH_3$), 7.15-7.39 (m, 5H, C_2-2H, C_3-H, C_7-H, C_8-H), 7.43 (d, 1H, C_6-H, J = 8.36 Hz), 7.66 (d, 1H, C_9-H, J = 8.04 Hz), 9.05 (b s, 2H, N_1H, carbazole-NH); ^{13}C NMR: δ 22.05 ($C_{3'}$-CH_3), 22.54 (C_2), 25.03 (C_4), 25.54 (C_3), 37.96 ($C_{3'}$), 39.27 ($C_{2'}$), 111.54 (C_{9a}), 112.58 (C_{4b}), 121.75 (C_{8a}), 126.01 (C_{4a}), 129.12 (C_6), 136.11 (C_7), 138.76 (C_5), 139.32 (C_8), 190.55 ($C_{1'}$=O), 191.51 (C_1=O); MS: m/z (%) M^+ 211 (11), 186 (12), 185(100), 184 (14), 157 (12), 156 (25), 143 (11), 130 (10), 129 (58), 128 (15), 101 (18).

3-Acetoxy-7-ch1oro-1,2,3,3a,4,5-hexahydropyrrolo[2,3-*a*]carbazole 4e: Crystalline powder from pet. ether-ethyl acetate mixture, m.p. 205°C, yield 60%; IR: 3355, 3245, 2924, 2856 1670, 1638, 1519, 1478, 1321, 1086, 1016 cm^{-1}; ^{1}H NMR: δ 2.24-2.30 (m, 2H, C_4-2H), 2.65-2.69 (m, 2H, C_5-2H), 2.95-2.99 (m, 5H, C_{1a}-H, C_{3a}-H, C_3-$COCH_3$), 7.29-7.36 (m, 4H, C_2-2H, C_3-H, C_6-H), 7.37 (d, 1H, C_8-H, J = 8.70 Hz), 7.62 (d, 1H, C_9-H, J = 8.70 Hz), 9.20 (b s, 2H, N_1H, carbazole NH); ^{13}C NMR: δ 22.97 ($C_{3'}$-CH_3), 23.51 (C_2), 24.99 (C_4), 25.75 (C_3), 38.76 ($C_{3'}$), 39.24 ($C_{2'}$), 111.34 (C_{9a}), 113.09 (C_{4b}), 121.45 (C_{8a}), 125.58 (C_{4a}), 128.49 (C_6), 137.05 (C_7), 138.84 (C_5), 139.65 (C_8), 190.15 ($C_{1'}$=O), 191.01 (C_1=O); MS: m/z (%) M^+ 245 (12), 220 (12), 219 (100), 218 (15), 191 (11), 190 (21), 177 (11), 164 (15), 163 (50), 162 (18), 135 (17).

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