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Synthesis and Spectral Studies of Substituted Phenyl and Naphthyl imino-1,2,3,4-tetrahydrocarbazoles

R. VELMURUGAN and M. SEKAR*
Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore- 641 020, India
E-mail: mmsekar7@yahoo.co.in

The reaction of 1-oxo-1,2,3,4-tetrahydrocarbazole (**1**) and aniline (**2a-c**) in ethanol and refluxed for 1 h at 120 °C afforded phenyl imino-1,2,3,4-tetrahydrocarbazole derivatives (**3a-c**). The same reaction of 1-oxo-1,2,3,4-tetrahydrcarbazole and naphthylamine (**4**) in ethanol and refluxed for 1 h at 120 °C yielded naphthyl imino-1,2,3,4-tetrahydrocarbazole (**5**).

Key Words: 1-Oxo-1,2,3,4-tetrahydrocarbazole, Phenyl imino carbazole, Naphthyl imino carbazole.

INTRODUCTION

Carbazole alkaloids represent a new and interesting variant in the large number of existing indole alkaloids which yielded several important drugs[1-4]. A large number of carbazole alkaloids have been isolated from plants[5]. The Indian Curry leaf plant *Murraya Koemigii Spereng* (*Rutaceae*) has been found to be the rich and rewarding source of many carbazole alkaloids[6]. The alkaloids ellipticine and olivacine have showed marked anticancer activity[7], Olivacine is also known for its antiulcer, antiheumatic properties[8]. Carbamycin A and carbamycin B have been found to be useful antibacterial and antifungal agents. It has been reported that pyridocarbazoles, oxotetrahydrocarbazoles[9], Mukonine isomers[10], Girinimbine isomers[11], pyrazino(3,2, 1-J,K)carbazoles, acetyl amino carbazoles[12] show marked anticancer and anti-HIV activities[13].

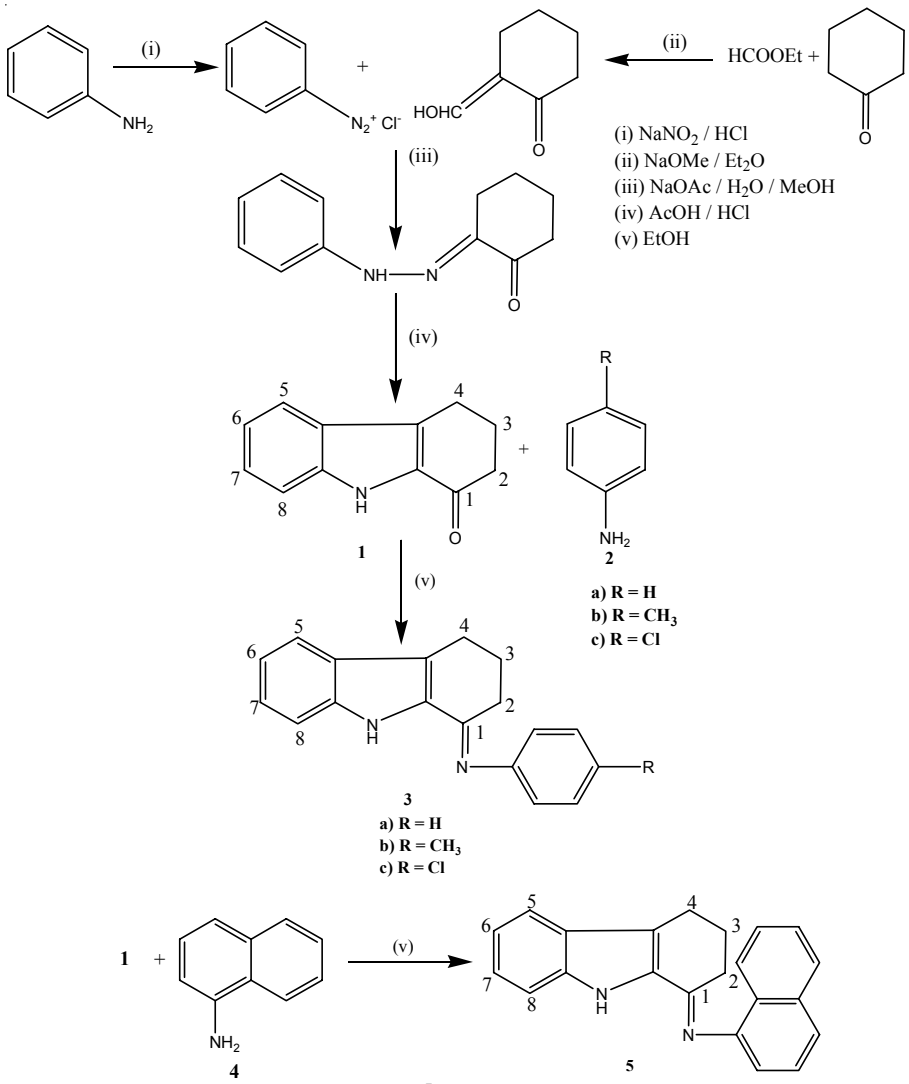
EXPERIMENTAL

The products were purified using column chromatographic method, packed with silica gel and petroleum ether, ethyl acetate mixture of solvents used for elution.

The melting points were determined using a metler FP-5 apparatus and are uncorrected. FT-IR spectra were recorded on a Perkin-Elmer-597, FT IR-8201 PC spectro-meter using potassium bromide. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian FX-90 FT-NMR and WH-270 NMR spectrometer using tetramethyl silane as an internal standard.

Preparation of phenyl imino-1,2,3,4-tetrahydrocarbazoles (3a-c): A mixture of the appropriate 1-oxo-1,2,3,4-tetrahydrocarbzole (**1**, 0.1 mol) and aniline (**2a-c**, 0.1 mol) both dissolved in ethanol and refluxed for 1 h. Then the contents were cooled and poured into crushed ice, the solid obtained was filtered off and recrystallized from petroleum ether and ethyl acetate (2:1) mixture (**Scheme-I**).

Preparation of naphthyl imino-1,2,3,4-tetrahydrocarbazoles (5): A mixture of the appropriate 1-oxo-1, 2,3,4-tetrahydrocarbzole (**1**, 0.1 mol) and naphthylamine (**4**, 0.1 mol) both dissolved in ethanol and refluxed for 1 h. Then the contents were cooled and poured into crushed ice, the solid obtained was filtered off and recrystallized from petroleum ether and ethyl acetate (2:1) mixture (**Scheme-I**).



Scheme-I

RESULTS AND DISCUSSION

1-Oxo-1,2,3,4-tetrahydrocarbazole and aniline (**2a-c**) both dissolved in ethanol and refluxed for 1 h to afford products (**3a-c**). Table-1 contains of the analytical data for compounds (**1-5**). FT-IR and ^{1}H NMR spectral values are given in Table-2.

TABLE-1

Compd.	Yield (%)	m.p. (ºC)	m.f. (m.w.)
1	85.00	158	$C_{12}H_{11}NO$ (185)
3a	76.92	148	$C_{18}H_{16}N_2$ (260)
3b	98.50	165	$C_{19}H_{18}N_2$ (274)
3c	84.80	Low melting point	$C_{18}H_{15}N_2Cl$ (294)
5	87.10	Low melting point	$C_{22}H_{18}N_2$ (310)

TABLE-2
IR, ^{1}H NMR AND ^{13}C NMR SPECTRAL DATA OF **1, 3a-c, 5**

Compd.	IR (ν_{max}, cm^{-1})	^{1}H NMR signals (δ ppm)
1	3300, 1640, 1540, 1480, 1340, 1260, 1200, 1140, 820 and 740	2.28 (p, 2H, C3-H, *J* = 6.25 Hz) 2.67 (t, 2H, C4-H, *J* = 6.45 Hz) 3.02 (t, 2H, C2-H, *J* = 6.58 Hz) 7.11-7.67 (m, 4H, C5, C6, C7, C8-H) 9.0 (singlet, N-H)
3a	3265, 2937, 1647, 1571, 1542, 1475, 1257, 1171, 746 and 731	3.018 (t, 2H, C2-H), 2.274 (p, 2H, C3-H) 2.676 (t, 2H, C4-H), 7.312-7.668 (m, 9H, C5, C6, C7, C8 and 2`,3`,4`,5`,6`-H).
3b	3285, 2928, 1642, 1571, 1541, 1616, 1474, 1329, 1188, 1169 and 748	3.15 (t, 2H,C2-H), 2.60 (s, 3H, CH_3), 2.30 (p, 2H, C3-H), 2.70 (t, 2H, C4-H), 7.37-7.78 (m, 8H, C5, C7, C8 and 2`,3`,5`,6`-H)
3c	3380, 3289, 2924, 2854, 1288, 1616, 1494, 1181, 1088, 820, 748, 731 and 697	3.20(t, 2H, C2-H), 2.35 (p, 2H, C3-H), 2.75 (t, 2H, C4-H), 7.40-7.85 (m, 8H, C5, C7, C8 and 2`,3`,5`,6`-H)
5	3341, 3230, 3024, 2937, 1643, 1573, 1457, 1643, 1573, 1457, 1288, 1171, 1087, 790 and 770	2.235 (p, 2H, C3-H), 2.959 (t, 2H, C2-H) 2.623 (t, 2H, C4-H) 6.732-7.775 (m, 11H, C5-H, C6-H, C7-H, C8-H and C2`-H, C3`-H, C4`-H, C5`-H, C6`-H, C7`-H, C8`-H).

The FT-IR spectrum of the compound (**3a**) showed two strong absorption bands at 3265 and 2937 cm^{-1} for NH and aromatic C-H stretching's respectively and C=N stretching appeared at 1647 cm^{-1}. Its ^{1}H NMR spectrum showed a multiplet at δ 7.312 to 7.668 ppm for 9 aromatic protons of C_5, C_6, C_7 and C_8 of carbazole phenyl moiety, C_2', C_3', C_4', C_5' and C_6' protons of imino phenyl moiety. Two protons of C_2-carbon atom appeared as triplet at δ 3.018 ppm. Another two protons at C_3 carbon atom appears as pentet centered at 2.274 ppm the splitting of the signal (pentet) is due to two adjacent C_2 and C_4 methylene protons. Triplet appearing at δ 2.676 ppm has been assigned to the C_4 methylene protons.

The presence of thirteen distinct peaks in the ^{13}C NMR spectrum of the synthesized compound **3a** confirms the molecular structure. The ipso carbon atoms present in the product appear as weak signals at δ 191.450 and 137.913 ppm. These data were in support of the structure of phenyl imino 1,2,3,4-tetrahydrocarbazole (**3a**).

The FT-IR spectrum of the compound (**3b**) showed a strong absorption band at 1642 cm^{-1} corresponding to C=N stretching and the two strong absorption bands at 2928 and 3285 cm^{-1} corresponds to C-H and N-H stretching frequencies, respectively. On the basis of spectral evidence (Table-2) the compound named as 1-(4′-methyl phenyl)imino-1,2,3,4-tetrahydrocarbazole (**3b**).

The FT-IR spectrum of the compound (**3c**) showed an absorption band at 3380 cm^{-1} for N-H stretching and the absorption of aromatic C-H stretching bands appears at 3289 cm^{-1}. The two strong absorption bands at 2924 and 1616 cm^{-1} are due to asymmetric C-H stretching of CH_2 group and C=N stretching. The C-Cl stretching is confirmed by the band at 697 cm^{-1}. On the basis of spectral evidence (Table-2) the compound was named as 1-(4′-chloro phenyl)imino-1,2,3,4-tetrahydrocarbazole (**3c**).

The FT-IR spectrum of the compound (**5**) showed absorption band at 3341 cm^{-1} for NH stretching and two strong absorption bands at 3230 and 1643 cm^{-1} for aromatic C-H stretching and C=N stretching. Its ^1H NMR spectrum showed a pentet at δ 2.25 ppm has been assigned to methylene protons at C_3 carbon atom of carbazole moiety. The triplet at δ 2.959 ppm assigned to two protons at C_2 carbon atom of the same moiety. Another triplet has its center at δ 2.623 ppm is due to two methylene protons of C_4 carbon and has been spilt in to triplet by two adjacent protons at C_3 carbon atom. The multiplet peaks appeared in the aromatic region from δ 6.732 to 7.775 ppm corresponds to eleven protons of the phenyl moiety in the carbazole and 1-naphthyl moiety in the compound. On the basis of spectral evidence of the compound was named as 1-(1′-naphthyl)imino-1,2,3,4-tetrahydrocar-bazole (**5**).

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