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STUDIES ON ENAMIDES

PART-2[1] : A NOVEL PHOTOCHEMICAL SYNTHESIS OF 9H-INDOLO [3,2,1-de] PHENANTHRIDIN-9-ONE, A BENZCANTHINE ANALOGUE

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Abstract: The synthesis of 3-aroylcarbazoles [4(a-d)] and the unknown 1-aroylcarbazoles [5(a-c)] has been achieved by the photolysis of 9-aroylcarbazoles [3(a-d)] in polar solvent. Irradiation of 3(a-c) in non-polar solvent afforded regiospecifically 5(a-c), carbazole (1) and for the first time, 9H-indolo [3,2,1-de] phenanthridin-9-one (8) from 3b. The yield of 8 was significantly improved by UV exposure of 9-(2-iodobenzoyl)-carbazole (3e) in methanol and iodine, without providing any photomigrated product.

The photochemical rearrangement of 9-aroylcarbazoles [3(a-d)], as has been recently reported[1] from our laboratory, culminated in the synthesis of hitherto unknown 1-aroylcarbazoles [5(a-c)], 3-aroylcarbazoles [4(a-d)] and carbazole (1), depending on the wavelength of irradiation (Scheme-1). Our enduring interest in this subject led us to study the effects of sensitiser and solvent on the photolysis of 3(a-c) and 3e, whereby we could develop, for the first time, from 3b and 3e, a novel and efficient methodology for the synthesis of 9H-indolo [3,2,1-de] phenanthridin-9-one‡ (8), an analogue of naturally occurring canthine group of alkaloids[2].

Irradiation of a methanolic solution of 9-benzoylcarbazole (3a) in a quartz vessel (immersion type) by a medium pressure mercury lamp (400W, λ_{max} 365-366 nm) under nitrogen atmosphere in the presence of Michler's ketone (MK) as sensitiser failed to provide any new result, save the previously isolated[1] carbazole (1) and the photomigrated products 3-benzoyl- (4a) and 1-benzoylcarbazole (5a) in reasonable yield. The same result was also obtained when irradiation of 3a was carried out in methanol alone, using a low pressure mercury lamp (16W, > 90% 254 nm) (Scheme-1).

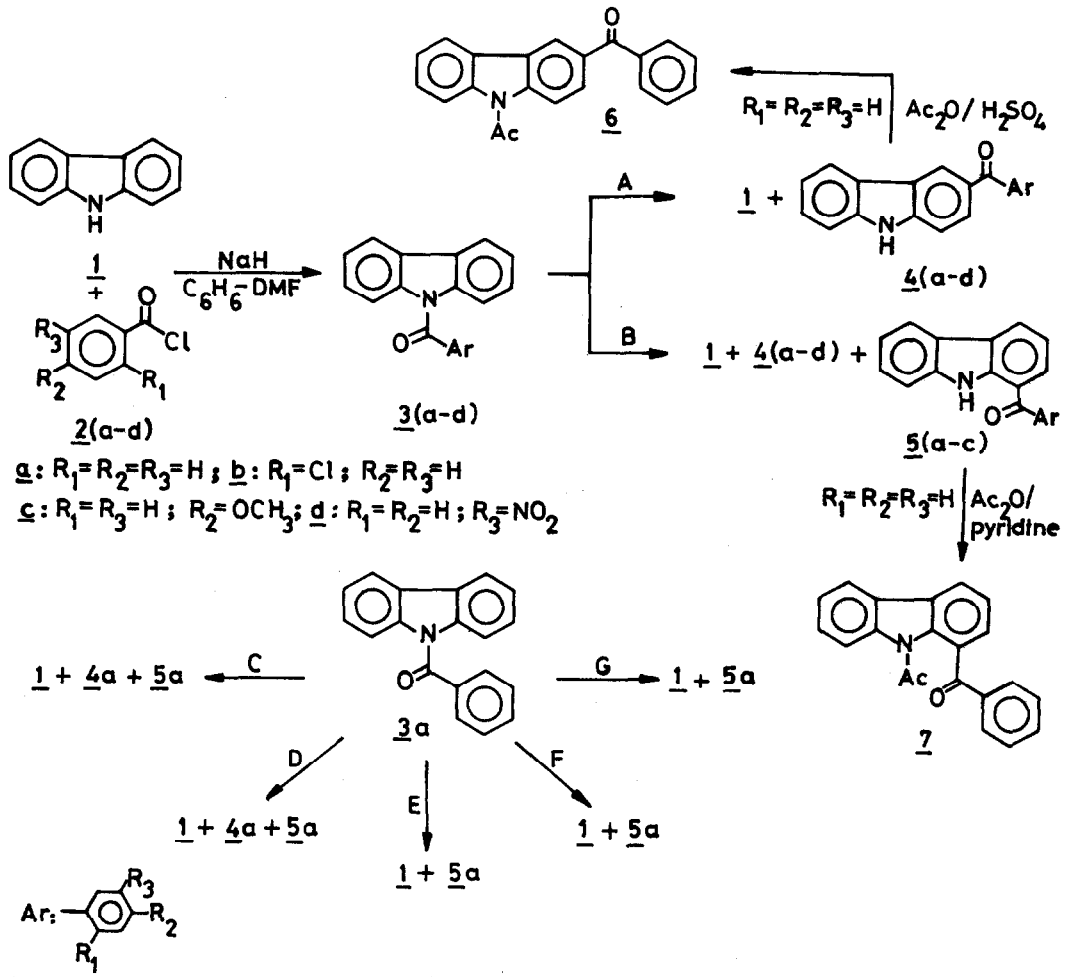
We next endeavoured to observe the photochemical behaviour of 3a in non-polar solvent such as benzene. Interestingly, the said photolysis in the absence or presence of sensitiser (MK) at 365-366 nm afforded 1 and the only migrated product 5a (Scheme-1). This experimental observation was also found to be consistent when a benzene solution of 3a was exposed to UV radiation (254 nm).

The remarkable regiospecificity so observed in the photolysis of 3a in non-polar solvent provided a distinct improvement of our earlier method[1] for the synthesis of unknown 5a, when the same was previously obtained alongwith 1 and 4a in the presence of methanol/iodine and also presently, in methanol or methanol/MK (Scheme-1).

Table-1 collectively presents an overview of all these experiments, Table-2 enlists the spectral data of the photomigrated products [4(a-d) and 5(a-c)] and Table-3 records a comparative ^{1}H NMR data of 4a, 5a and 2-benzoylcarbazole (13).

‡Also known as 19-ketophenanthridindocoline[4].

SCHEME-1



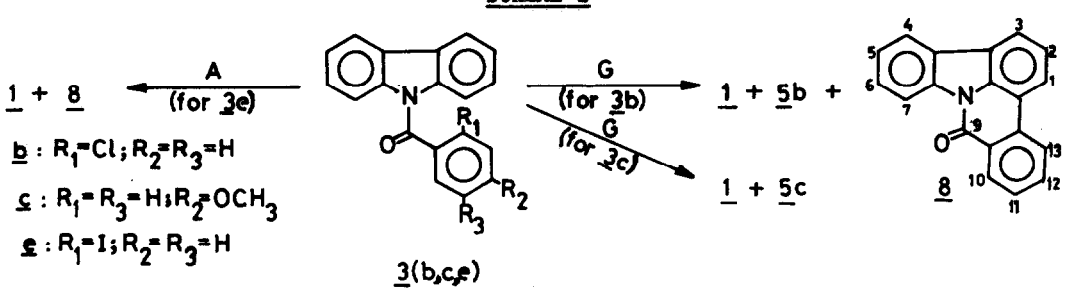
A: hν (254 nm)/CH_3OH/I_2; B: hν (365-366 nm)/CH_3OH/I_2; C: hν (254 nm)/CH_3OH; D: hν (365-366 nm)/CH_3OH/MK; E: hν (365-366 nm)/C_6H_6; F: hν (365-366 nm)/C_6H_6/MK; G: hν (254 nm)/C_6H_6.

prepared by the known procedure[3] (Scheme-4) alongwith their respective acetyl derivatives (6, 7 and 14).

In order to ascertain the generality of this regiospecific migration, we envisaged to investigate the photolysis of 3(b-c) in benzene at 254 nm (Scheme-2). While the irradiation of 3c afforded 1 and 5c as the sole migrated product, photolysis of 3b yielded 1, 5b and for the first time, 9H-indolo[3,2,1-de]phenanthridin-9-one (8) in 23% yield, mp. 225°(C-P)(lit.[4] mp. 227°), IR(KBr): ν_{max} 3040, 1695, 1665, 1605, 1580, 1505, 1465, 1445, 1420, 1350, 1340, 1305, 1275, 1160, 810, 765 and 695 cm^{-1}.

The 200 MHz ^1H NMR spectrum of 8 in $CDCl_3$ revealed the presence of four peri-

SCHEME-2

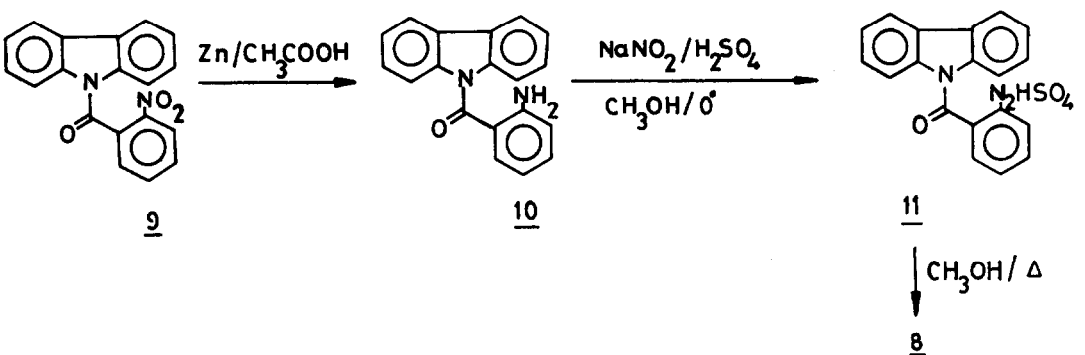


protons at δ 8.05 (1H, dd, J_1=8.0 Hz, J_2=2.4 Hz, C_1-H), 8.07 (1H, dd, J_1=8.0 Hz, J_2=2.4 Hz, C_4-H), 8.30 (1H, dd, J_1=8.0 Hz, J_2=1.6 Hz, C_{13}-H) and 8.67 (1H, dd, J_1=8.0 Hz, J_2=2.4 Hz, C_3-H), indicating clearly the presence of indolo[3,2,1-de]phenanthridone moiety. The spectrum could also characteristically account for C_7-H and C_{10}-H at δ 8.83 (1H, dd, J_1=8.0 Hz, J_2=2.4 Hz) and 8.15 (1H, d, J=8.0 Hz) respectively. The remaining aromatic protons were discernible at δ 7.50 (1H, dd, J_1=8.0 Hz, J_2=2.4 Hz, C_5-H), 7.58 (1H, d, J=8.0 Hz, C_2-H), 7.59 (1H, dd, J_1=8.0 Hz, J_2=1.6 Hz, C_{11}-H), 7.67 (1H, dd, J_1=8.0 Hz, J_2=2.4 Hz, C_6-H) and 7.82 (1H, m) for the C_{12}-H.

Encouraged by this observation, we incorporated in our ongoing project the photochemical study of 9-(2-iodobenzoyl)-carbazole (3e), as the irradiation of the same has not been reported so far[5,6]. As anticipated, the UV exposure of 3e at 254 nm in CH_3OH/iodine (Scheme-2) led exclusively to the desired phenanthridone (8) in excellent yield (67%) alongwith the formation of carbazole (1).

It is significant to note that the absence of any photomigrated products in the

SCHEME-3



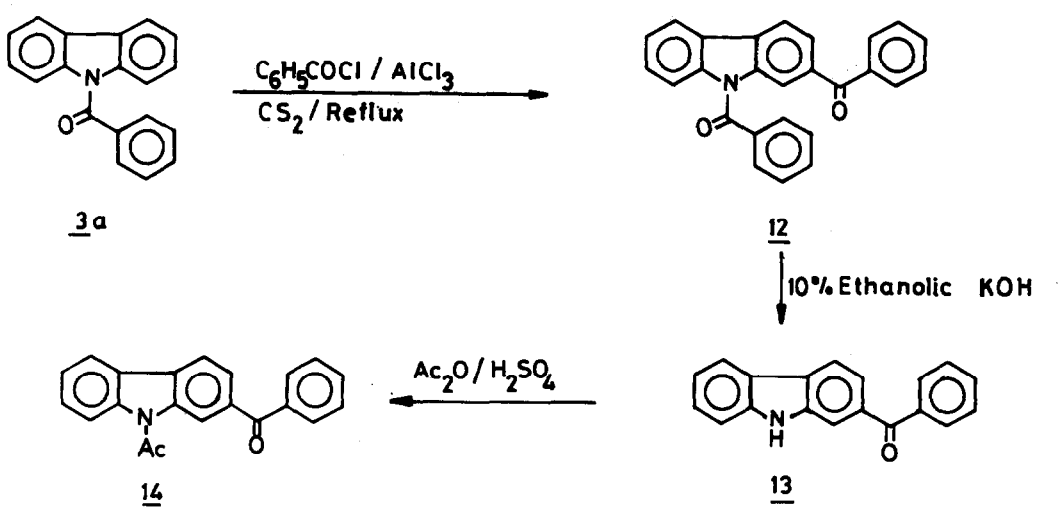
photolysis of 3e coupled with the higher yield of 8 compared to those of the results obtained with 3b, paved a superior photochemical pathway for the synthesis of naturally occurring benzcanthin-11-one[7] and their derivatives, studies of which are presently underway in our laboratory.

The structure of the photocyclised product (8) has also been confirmed by its independent synthesis (Scheme-3), following the reported procedure[4].

The genesis of the photomigrated products [4(a-d) and 5(a-c)] in methanol from the substrates [3(a-d)] may be rationalised by a normal photo-Fries rearrangement[1,8] either through a radical pathway[9] (Path A) involving the species (i) and (ii) or by a concerted mechanism[9] (Path B) through the intermediacy of (iii) and (iv). These mechanistic considerations have been shown in a generalised form in Scheme-5. Furthermore, the rearrangement of the aroyl group in the presence of methanol/iodine at 254 nm (Method A), for reasons not so clear, furnished 3-aroylcarbazoles [4(a-d)] as the sole photomigrated products. This type of [1,5]-migration is well documented in literature[10,11]. However, such regiospecificity was not observed when the photolysis was performed in methanol (Method C) or in the presence of sensitiser(Method D).

On the other hand, in non-polar solvent (benzene), the aroyl group from 3(a-c) possibly migrated regiospecifically from nitrogen to C_1 via a concerted α-tropic-[1,3]-shift (Path B_2). It appears, as though, the solvent controls the reaction course as against an insignificant role of the sensitiser or wavelength of irradiation.

SCHEME-4

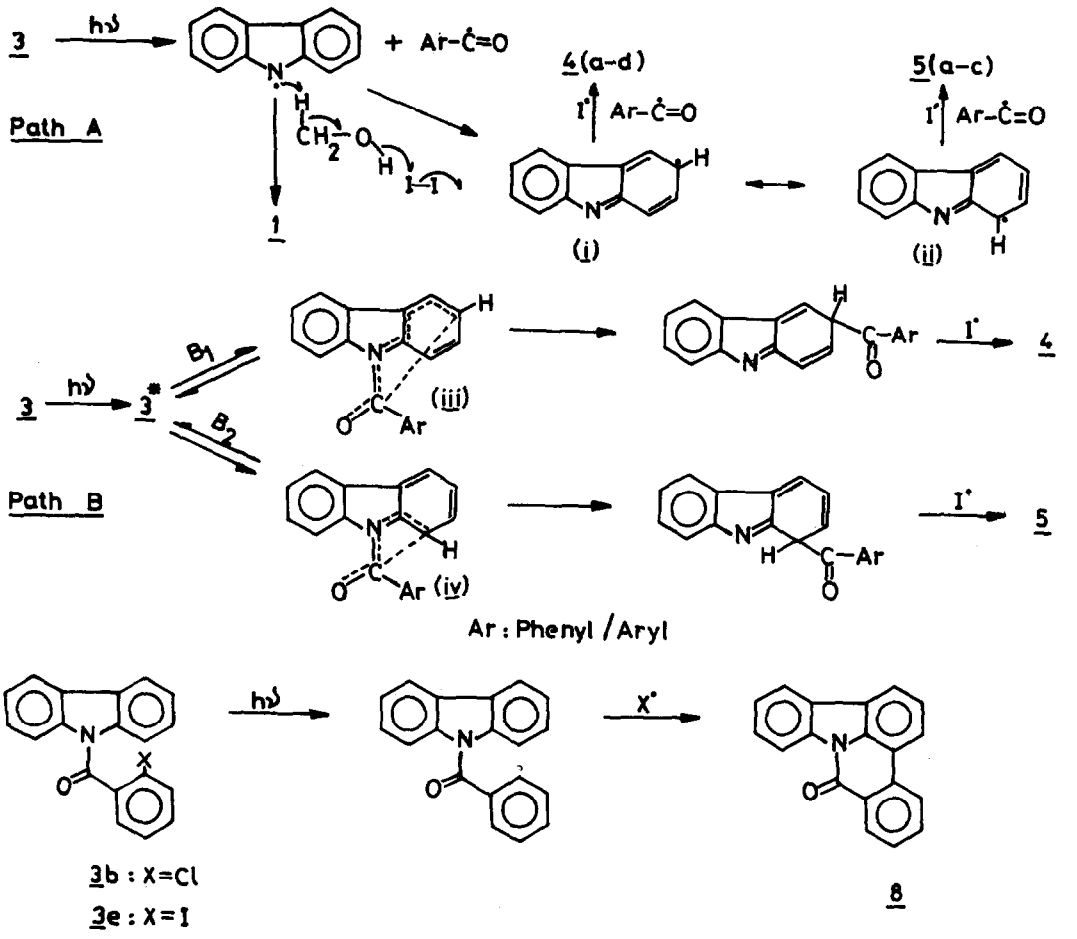


It is also of paramount importance to observe that the absence of any photomigrated products in the photolysis of 3e, albeit in methanol, in comparison to 3b, distinctly reflects a greater tendency of the iodo-derivative (3e) for radical formation[5,6], followed by a concomitant photocyclisation (Scheme-5) so as to afford phenanthridone (8) in higher yield.

Thus, it was observed that the photolysis of 9-aroylcarbazoles, save 3e, under the aforesaid conditions offers a convenient methodology for the synthesis of 3-aroylcarbazoles (prepared earlier by chemical method[12]) and the unknown 1-aroylcarbazoles,

while 3e, uniquely affords 9H-indolo[3,2,1-de]phenanthridin-9-one through a facile photocyclisation pathway.

SCHEME-5



EXPERIMENTAL

The melting points, recorded in H_2SO_4 bath are uncorrected. The IR spectra were obtained in a Perkin-Elmer 297 Infrared spectrophotometer, ^1H NMR spectra, unless otherwise stated, in $CDCl_3$ in a Varian XL 200 MHz spectrometer using TMS as internal standard, Mass spectra (70 ev) in a Hitachi RMU 6L Mass spectrometer and microanalyses were performed using a Perkin-Elmer 240C Elemental analyser. The photolysis experiments were carried out in quartz vessel (immersion type) in the presence of either low pressure mercury lamp (16W, >90% 254 nm, Model 3016) or medium pressure UV lamp

TABLE-1: Results of Photolysis of 9-Aroylcarbazoles[3(a-e)].

Substrate(3) MP.(Solvent)	Method (Time in hr)	Carbazole(1) Yield: mg(%) Eluent	3-Aroylcarbazole(4) MP. (Solvent) Yield: mg(%) Eluent	1-Aroylcarbazole(5) MP. (Solvent) Yield : mg(%) Eluent	Phenanthridone(8) MP.(Solvent) Yield: mg(%) Eluent
a 98°(aq.alc.) lit.[13] mp.98° (1.0 g; 3.69 mmol)	A (44)	360(58) P_3B_1	201-202°(A-P) (lit.[12] mp.203-205°) 300(30) P_1B_1+B	-	-
	B (10)	200(32) P_3B_1	202°(A-P) 50(5) P_1B_3	139°(A-P) 150(15) P_1B_1	-
	C (31)	300(48) P_9B_1	200(20) B	250(25) P_3B_1	-
	D (11)	200(32) P+P_9B_1	50(5) P_1B_4	100(10) P_4B_1	-
	E (12)	150(24) P+P_9B_1	-	100(10) P_9B_1+P_4B_1	-
	F (11)	250(40) P_9B_1	-	50(5) P_4B_1	-
	G (30)	50(8) P_9B_1+P_3B_1	-	80(8) P_1B_1	-
b 95°(B-P) (1.0 g; 3.27 mmol) (0.55 g; 1.80 mmol)	A (30)	100(18) P_3B_1+P_1B_1	198-200°(A-P) 200(20) B	-	-
	B (11)	150(27) P_3B_1	202°(A-P) 150(15) P_1B_3	181°(A-P) 300(30) P_1B_1	-
	G (27)	75(25) P_9B_1	-	52(9) P_3B_1	225°(C-P) (lit.[4] mp.227°) 110(23) P_3B_1+P_1B_1
c 111°(B-P) (1.0 g; 3.32 mmol)	A (29)	200(36) P_3B_1+P_1B_1	186-188°(A-P) 50(5) B	-	-
	B (10)	190(35) P_3B_1	190°(A-P) 150(15) P_1B_3	141°(A-P) 150(15) P_1B_1	-
	G (30)	145(50) P+P_9B_1	-	115(22) P_1B_1	-
d 151°(B-P) (1.0 g; 3.16 mmol)	A (32)	350(66) P_3B_1+P_1B_1	195°(crude) 20 B	-	-
	B (12)	200(38) P_3B_1	205°(A-P) 60(6) P_1B_3	-	-
e 88-89°(E-P) (1.77 g; 4.46 mmol)	A (17)	201(27) P_9B_1	-	-	225°(C-P) 803(67) P_3B_1+P_1B_1+P_1B_3

(400W, λ_{max} 365-366 nm, Model 3040), manufactured by Applied Photophysics Ltd.,England. Solvent abbreviations are: A-Acetone; B-Benzene; C-Chloroform; E-Diethyl ether and P-Petroleum ether, 60-80° with the subscripts referring to the proportions of the solvents used for chromatographic elution (silica gel, 60-120 mesh, BDH). The yield denotes the combined amounts of crystallised material obtained after chromatography.

PREPARATION OF 9-AROYLCARBAZOLES [3(a-e),9] :

9-Benzoylcarbazole (3a): Carbazole (1)(3.3 g; 20 mmol) dissolved in dry benzene (20 ml)-DMF (20 ml) was added to a well-stirred suspension of sodium hydride (1.8 g; 75 mmol) in dry benzene (20 ml) at room temperature, followed by dropwise addition of benzoyl chloride (2a)(2.85 g; 20 mmol) in dry benzene (10 ml) at 0° and kept overnight.

The reaction mixture was decomposed with ice-cold brine (150 ml) and extracted to exhaustion with dichloromethane (4x50 ml). The organic layer was washed with dil. HCl (2x25 ml), brine (2x25 ml) and dried (Na_2SO_4). On removal of solvent 3a was obtained in 60% yield (3.2 g), crystallised further from aq. alcohol, mp.98° (lit.[13] mp.98°).

IR(Nujol): ν_{max} 1675, 1595, 1445, 1325, 1300, 1150, 1070, 750, 720, 700 cm^{-1}.

9-Aroylcarbazoles [3(b-e),9] were prepared by the above procedure using 1 (2.0 g; 12 mmol) and the acid chlorides [2(b-e)] and of 2-nitrobenzoic acid, obtained from the respective acids (2.0 g).

9-(2-Chlorobenzoyl)-carbazole (3b): Yield=2.2 g (60%); mp. 95° (B-P).

IR($CHCl_3$): ν_{max} 3070, 3010, 1675, 1595, 1440, 1360, 1090, 1050, 950 cm^{-1}.

^{1}H NMR(100 MHz): δ 7.28-7.42 (2H,m), 7.42-7.48 (4H,m), 7.48-7.56 (4H,m), 8.03 (2H, dd, J_1=7.0 Hz, J_2=3.0 Hz).

9-(4-Methoxybenzoyl)-carbazole (3c): Yield=2.5 g (69%); mp. 111° (B-P).

IR($CHCl_3$): ν_{max} 3010, 1670, 1605, 1510, 1440, 1320, 1255, 1170, 1030, 840 cm^{-1}.

^{1}H NMR(100 MHz): δ 3.88 (3H, s), 6.99 (2H, dd, J_1=8.0 Hz, J_2=1.0 Hz), 7.30-7.44 (4H,m), 7.57 (2H, dd, J_1=7.0 Hz, J_2=3.0 Hz), 7.73 (2H, dd, J_1=8.0 Hz, J_2=1.0 Hz), 8.03 (2H, dd, J_1=7.0 Hz, J_2=3.0 Hz).

9-(3-Nitrobenzoyl)-carbazole (3d): Yield=2.65 g (70%); mp. 151° (B-P).

IR(Nujol): ν_{max} 3080, 1680, 1615, 1530, 1445, 1365, 1160, 1070, 755, 690 cm^{-1}.

^{1}H NMR(100 MHz): δ 7.26-7.40 (4H,m), 7.69 (1H, dd, J_1=8.0 Hz, J_2=1.0 Hz), 7.90-8.01 (4H,m), 8.39 (1H, d, J=2.0 Hz), 8.50 (2H, dd, J_1=7.0 Hz, J_2=2.0 Hz).

9-(2-Iodobenzoyl)-carbazole (3e): Yield=3.0 g (63%); mp. 88-89° (E-P).

IR(KBr): ν_{max} 3060, 1670, 1600, 1585, 1490, 1480, 1445, 1360, 1330, 1305, 1210, 1155, 1085, 1020, 950, 775, 760, 750, 725, 630 cm^{-1}.

^{1}H NMR(200 MHz): δ 7.38 (1H, dd, J_1=6.8 Hz, J_2=1.3 Hz), 7.42 (3H, dd, J_1=6.8 Hz, J_2=1.3 Hz), 7.49 (2H, dd, J_1=7.3 Hz, J_2=1.7 Hz), 7.56 (2H, dd, J_1=6.8 Hz, J_2=1.7 Hz), 7.64 (1H, dd, J_1=7.7 Hz, J_2=1.7 Hz), 8.03 (1H, dd, J_1=7.7 Hz, J_2=1.3 Hz), 8.05 (2H, dd, J_1=7.7 Hz, J_2=1.7 Hz).

9-(2-Nitrobenzoyl)-carbazole (9): Yield=1.5 g(40%); mp.149°(A-P)(lit.[4] mp.148-150°)

IR(KBr): ν_{max} 1665, 1570, 1515, 1475, 1440, 1360, 1330, 1305, 1205, 1155, 1065, 795, 745, 715 cm^{-1}.

^{1}H NMR(200 MHz): δ 7.41 (2H,dd,J_1=8.4 Hz, J_2=2.3 Hz), 7.65 (2H,dd,J_1=6.9 Hz, J_2=2.3 Hz), 7.87 (2H,dd,J_1=8.4 Hz,J_2=1.5 Hz), 7.89 (2H,dd, J_1=8.4 Hz, J_2=1.5 Hz), 8.05 (2H,dd,J_1=7.7 Hz, J_2=2.3 Hz), 8.43 (2H,dd,J_1=7.7 Hz, J_2=2.3 Hz).

PHOTOLYSIS OF 9-AROYLCARBAZOLES [3(a-e)] :

METHOD A: Irradiation with 16W UV lamp using methanol/iodine

Irradiation of 9-benzoylcarbazole (3a): A solution of 3a (1.0 g; 3.69 mmol) and iodine (0.5 g; 3.9 mmol) in spectral methanol (350 ml, BDH) was irradiated for 44 hr under nitrogen atmosphere. The solvent was distilled off in vacuo and the crude product, after dilution with water (200 ml) was extracted with dichloromethane (3x75 ml). The combined organic layer was washed with saturated sodium thiosulphate solution (3x25 ml), brine (2x25 ml) and dried (Na_2SO_4). Distillation of the solvent afforded a brownish-yellow residue which was chromatographed, whereby 1 and 3-benzoylcarbazole (4a) were isolated. Table-1 presents the experimental results and Table-2 enlists the spectral data.

3-Benzoylcarbazole (4a):

Found C,83.92%, H,5.21% and N,5.30%.

$C_{19}H_{13}NO$(271.3) requires C,84.11%; H,4.83% and N,5.16%.

Similar irradiation experiments were performed with 3(b-e) (1.0 g) and the results are given in Table-1.

3-(2-Chlorobenzoyl)-carbazole (4b) :

Found C,74.46%; H,4.24% and N,4.62%.

$C_{19}H_{12}NOCl$(305.8) requires C,74.64%; H,3.96% and N,4.58%.

3-(4-Methoxybenzoyl)-carbazole (4c) :

Found C,80.15%; H,5.15% and N,4.45%.

$C_{20}H_{15}NO_2$(301.3) requires C,79.72%; H,5.02% and N,4.65%.

3-(3-Nitrobenzoyl)-carbazole (4d): Vide Table-1.

^{1}H NMR (vide Table-2) recorded in 100 MHz (d_6-DMSO).

The compound 3e on photolysis under the aforesaid condition yielded 1 and 8.

9H-Indolo [3,2,1-de] phenanthridin-9-one (8) :

Found C,84.69%; H,4.25% and N,5.03%.

$C_{19}H_{11}NO$(269.3) requires C,84.74%; H,4.12% and N,5.20%.

METHOD B: Irradiation with 400W UV lamp using methanol/iodine

An analogous procedure (cf. Method A) was followed with 3a (1.0 g; 3.69 mmol) and usual work-up and chromatography afforded 1, 4a and 1-benzoylcarbazole (5a) (Table-1 and Table-2).

1-Benzoylcarbazole (5a) :

Found C,83.94%; H,4.85% and N,4.87%.

$C_{19}H_{13}NO$(271.3) requires C,84.11%; H,4.83% and N,5.16%.

TABLE-2: Spectral Data of 1-Aroyl-[5(a-c)] and 3-Aroylcarbazoles [4(a-d)].

Product	IR(KBr) ν_{max} (cm^{-1})	^1H NMR δ(ppm) (J in Hz)	MS m/z[rel. intensity(%)]
4a	3240,1640,1610, 1445,1410,1330, 1270,1245,1130, 955,750,705	7.35-7.39(1H,m),7.52-7.57(4H,m),7.59 (1H,dd,J_1=7.3,J_2=1.7),7.66(1H,d,J=7.6), 7.92(2H,dd,J_1=8.1,J_2=1.7),8.05(1H,dd, J_1=8.5,J_2=1.7),8.15(1H,dd,J_1=7.7,J_2= 1.7),8.57(1H,br.s),8.66(1H,d,J=1.7)	271($M^{\cdot+}$,43),270(100), 195(37),194(98),166 (84),149(99),139(37), 105(22),77(22)
5a	3410,3380,1627, 1590,1565,1490, 1445,1315,1265, 1220,1115,965, 840,750,720,700	7.29-7.34(1H,m),7.39(1H,dd,J_1=8.1,J_2= 1.9),7.46-7.52(1H,m),7.55-7.63(3H,m), 7.66(1H,d,J=7.5),7.86(1H,d,J=8.1), 7.87(2H,d,J=8.1),8.20(1H,dd,J_1=7.5, J_2=2.5),8.39(1H,dd,J_1=7.5,J_2=2.5), 10.56(1H,br.s)	271($M^{\cdot+}$,21),270(100), 253(26),240(72),193 (98),166(98),165(98), 148(98),139(74),195 (96),77(99)
4b	3300,1645,1620, 1590,1575,1450, 1335,1285,1130, 755,740,705	7.33-7.37(1H,m),7.47-7.56(7H,m),8.01 (1H,dd,J_1=8.0,J_2=1.7),8.12(1H,dd,J_1= 8.0,J_2=1.7),8.57(1H,br.s),8.62(1H,d, J=2.6)	307(14),305($M^{\cdot+}$,42), 194(54),149(100),111 (32),99(64),85(96)
5b	3400,1630,1620, 1570,1490,1430, 1315,1220,1115, 750	7.30-7.36(1H,m),7.41(1H,dd,J_1=6.8,J_2= 1.7),7.48-7.55(4H,m),7.56(2H,dd,J_1=6.8, J_2=1.7),7.63(1H,dd,J_1=6.8,J_2=1.7),8.21 (1H,dd,J_1=7.7,J_2=2.6),8.41(1H,dd,J_1= 7.7,J_2=2.6),10.75(1H,br.s)	
4c	3220,1640,1600, 1580,1325,1275, 1250,1020,740	3.94(3H,s),7.08(2H,d,J=8.0),7.34-7.38 (1H,m),7.50-7.58(3H,m),7.96(2H,d,J=8.0), 8.02(1H,dd,J_1=8.0,J_2=2.1),8.16(1H,dd, J_1=8.0,J_2=1.4),8.48(1H,br.s),8.61(1H, d,J=2.8)	301($M^{\cdot+}$,100),300(78), 270(75),195(72),194 (99),166(94),149(98), 141(24),139(38),135 (98),130(84),77(21)
5c	3420,3400,1637, 1625,1570,1480, 1260,1250,1175, 1020,840,755	3.90(3H,s),7.07(2H,d,J=8.9),7.32(1H,d, J=7.7),7.37(1H,dd,J_1=8.0,J_2=1.5),7.56 (1H,dd,J_1=6.8,J_2=1.3),7.59(1H,d,J=7.0), 7.87(2H,dd,J_1=8.8,J_2=3.0),7.89(1H,d,J= 8.9),8.19(1H,d,J=7.1),8.36(1H,d,J=7.6), 10.50(1H,br.s)	
4d	3240,1650,1625, 1575,1530,1450, 1350,1335,1270, 1250,1140,900, 820,780,720	7.18-7.80(4H,m),7.91(1H,d,J=8.0),7.93 (1H,dd,J_1=8.0,J_2=1.8),8.20(1H,dd,J_1= 8.0,J_2=2.0),8.25(1H,dd,J_1=8.0,J_2=2.0), 8.47(1H,dd,J_1=8.0,J_2=2.0),8.54(1H,d,J= 1.8),8.64(1H,d,J=2.0),11.84(1H,br.s)	

TABLE-3: Comparative ^{1}H NMR (200 MHz, $CDCl_3$) Spectral Data for 3-Benzoyl- (4a), 1-Benzoyl- (5a), 2-Benzoylcarbazole (13) and their respective Acetyl Derivatives (6, 7 and 14) [δ (ppm), J in Hz].

Compound	C_1-H	C_2-H	C_3-H	C_4-H	C_5-H	C_8-H	C_2-H + C_6-H	-NH	-NCOCH_3
4a	7.66 d J=7.6	8.05 dd J_1=8.5 J_2=1.7	-	8.66 d J=1.7	8.15 dd J_1=7.7 J_2=1.7	7.59 dd J_1=7.3 J_2=1.7	7.92 dd J_1=8.1 J_2=1.7	8.57 br.s	-
5a	-	7.86 d J=8.0	7.49 m	8.39 dd J_1=7.5 J_2=2.5	8.20 dd J_1=7.5 J_2=2.5	7.66 d J=7.5	7.87 d J=8.1	10.56 br.s	-
13	8.00 d J=1.6	-	7.75 dd J_1=8.0 J_2=1.6	8.18 d J=8.8	8.18 d J=8.8	7.58 m	7.90 dd J_1=8.0 J_2=2.0	8.37 br.s	-
6	8.01 dd J_1=8.0 J_2=2.0	8.14 d J=8.0	-	8.46 d J=2.0	8.33 dd J_1=8.0 J_2=2.0	7.92 dd J_1=8.0 J_2=2.0	7.82 dd J_1=8.0 J_2=2.0	-	2.88 s
7	-	8.09 dd J_1=7.0 J_2=2.1	7.47 m	8.73 dd J_1=7.0 J_2=2.1	8.17 dd J_1=7.0 J_2=2.1	7.59 dd J_1=7.7 J_2=1.4	7.47 m	-	2.25 s
14	8.76 d J=2.0	-	7.90 dd J_1=8.0 J_2=2.0	8.31 d J=8.0	8.13 d J=8.0	8.13 d J=8.0	7.90 dd J_1=8.0 J_2=2.0	-	2.94 s

1-(2-Chlorobenzoyl)-carbazole (5b) :

Found C,74.71%; H,4.03% and N,4.31%.

$C_{19}H_{12}NOCl$(305.8) requires C,74.64%; H,3.96% and N,4.58%.

3-(4-Methoxybenzoyl)-carbazole (5c) :

Found C,80.41%; H,5.52% and N,4.42%.

$C_{20}H_{15}NO_2$(301.3) requires C,79.72%; H,5.02% and N,4.65%.

3-(3-Nitrobenzoyl)-carbazole (4d): Vide Table-1.

METHOD C: Irradiation with 16W UV lamp in methanol

A solution of 3a (1.0 g; 3.69 mmol) in spectral methanol (350 ml) on exposure to 16W UV lamp for 31 hr gave a brown residue which after usual work-up and chromatography yielded 1, 3a and 5a (Table-1).

METHOD D: Irradiation using 400W UV lamp in methanol/sensitiser

Irradiation of 3a (1.0 g; 3.69 mmol) in methanol (350 ml) and sensitiser (MK,

0.1 g) using a 400W UV lamp for 11 hr afforded 1, 3a and 5a (Table-1).

METHOD E: Irradiation using 400W UV lamp in benzene

Irradiation of 3a (1.0 g; 3.69 mmol) in dry benzene (350 ml) for 12 hr at 365-366 nm furnished 1 and only 5a (Table-1).

METHOD F: Irradiation with 400W UV lamp in benzene/sensitiser

Photolysis of 3a (1.0 g; 3.69 mmol) in dry benzene (350 ml) and sensitiser (MK, 0.1 g) at 365-366 nm for 11 hr yielded as before 1 and 5a (Table-1).

METHOD G: Irradiation using 16W UV lamp in benzene

The compound 3a (1.0 g; 3.69 mmol) on photolysis (254 nm) for 30 hr in dry benzene (350 ml) afforded 1 and 5a (Table-1).

The photolysis of 3b under identical conditions gave 1, 5b and phenanthridone (8), while 3c afforded 1 and only 5c (Table-1).

9-(2-Aminobenzoyl)-carbazole (10): 9-(2-Nitrobenzoyl)-carbazole (9)(1.4 g; 8.62 mmol), zinc dust (1.5 g) in glacial acetic acid (30 ml) were taken and the standard procedure[4] followed to obtain 10 as a yellow crystalline solid (1.5 g; 61%), mp. 159-160° (aq. alcohol) (lit.[4] mp. 160-62°).

IR(KBr): ν_{max} 3490, 3380, 1655, 1610, 1590, 1440, 1320, 1305, 1265, 750 cm^{-1}.

9H-Indolo [3,2,1-de] phenanthridin-9-one (8): The compound (10)(1.16 g; 4.06 mmol) in methanol (30 ml) and conc. H_2SO_4 (2 ml) was diazotised at 0° with sodium nitrite solution ($NaNO_2$, 0.24 g in water, 5 ml) by the known procedure[4]. The diazotised product (11) after dilution with methanol (30 ml) was refluxed for 30 min. The product on chromatography yielded 8 (0.038 g; 4%), mp. 226° (C-P) (lit.[4] mp. 227°) with P_3B_1, P_1B_1 and P_1B_3 as eluents.

9-Acetyl-3-benzoylcarbazole (6): 3a (0.06 g; 0.22 mmol) on acetylation with acetic anhydride (6 ml) and conc. H_2SO_4 (0.1 ml) under reflux for 2 hr gave, after usual work-up and chromatography, 9-acetyl-3-benzoylcarbazole (6) (0.015 g; 22%), mp. 155° (A-P) (lit.[4] mp.154°) from P_1B_3 fraction.

IR(KBr): ν_{max} 3140, 3020, 1705, 1650, 1600, 1580, 1480, 1370, 1260, 1020, 755, 720 cm^{-1}.

9-Acetyl-1-benzoylcarbazole (7): Acetylation of 5a (0.026 g; 0.1 mmol) with acetic anhydride (2 ml) and pyridine (2 ml) under refluxing condition for 5 hr yielded after chromatography 7 (0.018 g; 60%), mp. 238-41°(d)(C-P) from the benzene fraction.

IR(KBr): ν_{max} 1705, 1655, 1605, 1555, 1485, 1440, 1380, 1335, 1110, 760,710 cm^{-1}.

2,9-Dibenzoylcarbazole (12): 2,9-Dibenzoylcarbazole (12) was prepared from 3a (1.8 g; 6.64 mmol) following the standard procedure[3] in 60% yield (1.5 g), mp. 124° (A-P) (lit.[14] mp. 124°), obtained in P_1B_1 fraction after chromatography.

IR(KBr): ν_{max} 3050, 1660, 1640, 1595, 1485, 1260, 1065, 915, 745, 720, 695 cm^{-1}.

^1H NMR(200 MHz): δ 7.41-7.53 (6H,m), 7.55-7.65 (4H,m), 7.73 (2H,dd,J_1=6.5 Hz, J_2=2.4 Hz), 7.77 (2H,dd,J_1=6.5 Hz,J_2=2.4 Hz), 7.94 (1H,d,J=1.8 Hz),8.13 (1H,dd,J_1=8.8 Hz,J_2=1.8 Hz),8.15(1H,d,J=7.6 Hz).

2-Benzoylcarbazole (13): Saponification of 12 (0.9 g; 2.4 mmol) with ethanolic potassium hydroxide (45 ml; 10%) for 1 hr followed by usual work-up and chromatography afforded 13 (0.55 g; 85%) in P_1B_3 fraction, mp. 164° (A-P) (lit.[3] mp. 163°).

IR(KBr): ν_{max} 3260, 3040, 1625, 1555, 1440, 1325, 1300, 1240, 880, 725, 710 cm^{-1}.

9-Acetyl-2-benzoylcarbazole (14): Standard procedure[3] was followed to convert 2-benzoylcarbazole (13) (0.1 g; 0.37 mmol) to its acetyl derivative (14) (0.035 g; 30%), mp. 134-36° (A-P) (lit.[3] mp. 136-37°), eluent: benzene-ethyl acetate (7:1).

IR(KBr): ν_{max} 1685, 1650, 1610, 1595, 1560, 1455, 1360, 1300, 1260, 1010, 885, 775, 760, 715 cm^{-1}.

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REFERENCES :

1. Part-1: Ghosh,S.N.; Das,T.K.; Datta,D.B.; Mehta,S. Tetrahedron Lett. 1987, 28, 4611.
2. Manske,R.H.F.; Holmes,H.L. "The Alkaloids. Chemistry and Physiology", 1952, vol. II, Academic Press Inc., New York.
3. Plant,S.G.P.; Rogers,K.M.; Williams,S.B.C. J.Chem.Soc. 1935, 741.
4. Plant,S.G.P.; Tomlinson,M.L. J.Chem.Soc. 1932, 2188.
5. Sharma,R.K.; Kharasch,N. Angew.Chem.Int.Ed.Engl. 1968, 7, 36.
6. Wilson,R.M.; Commons,T.J. J.Org.Chem. 1975, 40, 2891.
7. Marion,L.; Manske,R.H.F. Can.J.Research 1938, 16B, 432.
8. Bellus̆,D. Advan.Photochem. 1971, 8, 109.
9. Bouchet,P.; Joncheray,G.; Jacquier,R.; Elguero,J. J.Heterocycl.Chem. 1978, 15, 625.
10. Winkler-Lardelli,B.; Rosenkranz,H.J.; Hansen,H.J.; Schmid,H.; Blank,B.; Fischer,H. Helv.Chim.Acta. 1973, 56, 2628.
11. Lyubarskaya,A.E.; Pauli,G.D.; Bren,V.; Zhdanov,Yu.A.; Knyazhanskii,M.I.; Minkin, V.I.; Otekhnovich,L.P. Zh.Org.Chim. 1976, 12, 918.
12. Hunter,W.H.; Darling,S.F. J.Amer.Chem.Soc. 1931, 53, 4183.
13. Clarke,H.T. "A Handbook of Organic Analysis : Qualitative and Quantitative", 1949, 207, Edward Arnold, London.
14. Itier,J.; Casadevall,A. Bull.soc.chim.Fr. 1969, 2342.