Tetrahedron Vol. 46, No. 19, pp. 6821-6830, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

STUDIES ON ENAMIDES. PART-4[1] : PHOTOCHEMICAL INVESTIGATIONS OF N-AROYLDIPHENYLAMINES[#]

Indira Datta, Tapas Kumar Das (in part) and Somnath Ghosh*
Department of Chemistry, Jadavpur University, Calcutta 700032, **INDIA**

ABSTRACT : Photolysis of N-aroyldiphenylamines affords 9-arylacridines or phenanthridone depending on the structure of the substrates. Additionally, carbazole and photomigrated products are also obtained.

(*Received in UK* 13 *June* 1990)

Recently it has been reported[1] from our laboratory that the photolysis of N-aroyldiphenylamines led to a unique synthesis of 9-arylacridines alongwith the formation of carbazole and the photomigrated products. Our further investigations in this field have culminated in the first photochemical synthesis of 6H-5-phenyl-phenanthridin-6-one[2], an important class of heterocyclic compound, through the intermediacy of a radical cyclisation reaction involving N-(2-iodobenzoyl)-diphenylamine as the substrate.

Irradiation of a methanolic solution of N-benzoyldiphenylamine (3a) by a low pressure mercury lamp (16W,>90% 254 nm) under nitrogen atmosphere at room temperature (32°) for 17 hr, neatly afforded, after usual workup and chromatography over silica gel, carbazole (4), the known[3] 2-benzoyl- (5a) and 4-benzoyldiphenylamine (6a). On the other hand, the same experiment when carried out in the presence of iodine as oxidant for 35 hr gave only 4, 6a and notably culminated in the photochemical synthesis of 9-phenylacridine (7a), mp. 183° (acetone-petroleum ether, 60-80°) (lit.[4] mp. 184-5°), MS (70 eV) m/z 255 ($M^{\cdot+}$, 100%) **(Scheme-1).**

The photochemical reaction was found to be consistent for other substrates[3(c-f)] leading to the formation of 6(c-f) and 7(c-f) in varying yields **(Table-1)**, thereby demonstrating the generality of the photochemical method for the synthesis of acridines. The only exception was observed in the photolysis of N-(2-methoxybenzoyl)-diphenylamine (3b) when the acridine (7b) was formed besides only ortho- migrated product (5b) in very poor yield.

In order to ascertain the mechanistic pathway for the formation of acridine, we carried out several photochemical and thermal experiments

---

Presented in the **Pre-IUPAC Symposium (17) on Chemistry of Natural Products, 1990, IICB, Calcutta.**

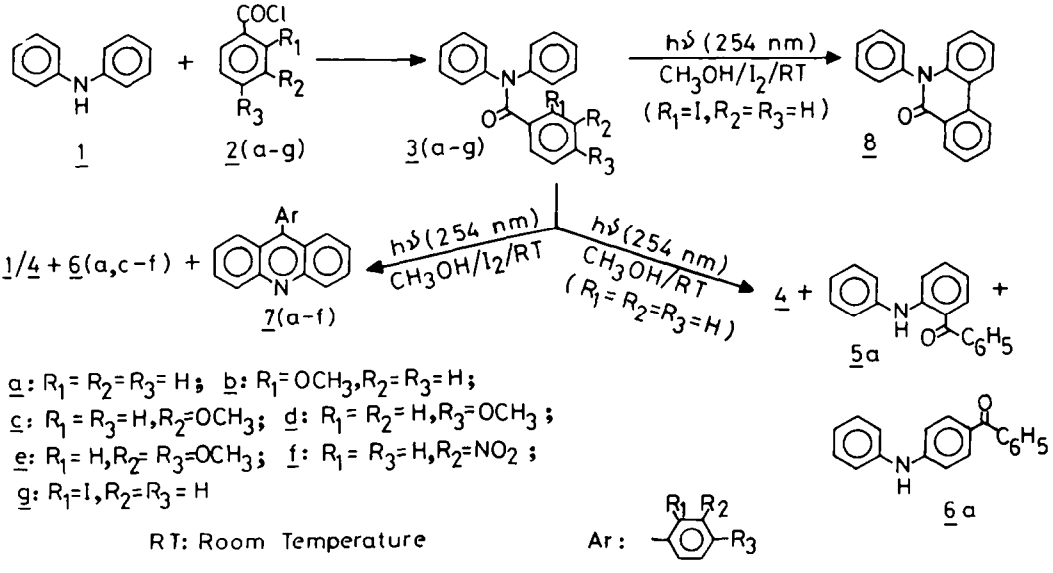
(Scheme-2) with parent substrate (5a) and the results of these experiments have been summarised in **Table-2.**

Thus, when a methanolic solution of 5a was allowed to stand at room temperature (32°) in dark in the presence of perchloric acid (70%) for 42 hr **(Scheme-2)** no acridine could be isolated **(Table-2,** entry 9), confirming thereby the role of light in the transformation of 5 to 7. The same reaction under refluxing condition in dark for only 2 hr gave acridine (7a) in 25% yield **(Table-2,** entry 8). These few experiments unambiguously established a cationic pathway of the reaction under thermal condition[4]. On the other hand, the photolysis of 5a in methanol in the presence of iodine gave 7a in 11% yield **(Table-2,** entry 4), indicating thereby a possible radical pathway for the formation of acridine (7a). Moreover, **Table-2** also shows :

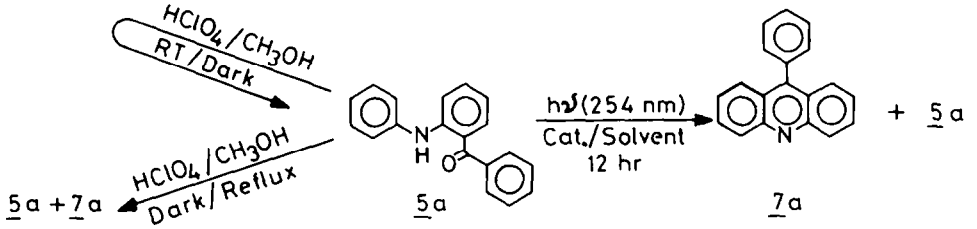
i) the optimum condition for the efficient photochemical conversion of 5a to 7a requires the use of iodine and hydriodic acid (entry 1); ii) compared to a radical initiator (entries 4,5) or an acid catalyst alone (entries 3,6), a combination of both (entries 1,2) gave an optimum yield of acridine; the exclusion of radical initiator or hydriodic acid drastically reduces the yield of acridine (7a) (entry 6).

Finally, the absence of 9-arylacridine (7) in the photolysis of 3 in methanol only **(Scheme-1)** also clearly indicates the catalytic role of iodine and possibly HI formed *in situ* **(Scheme-3)** in the formation of this compound.

SCHEME-1



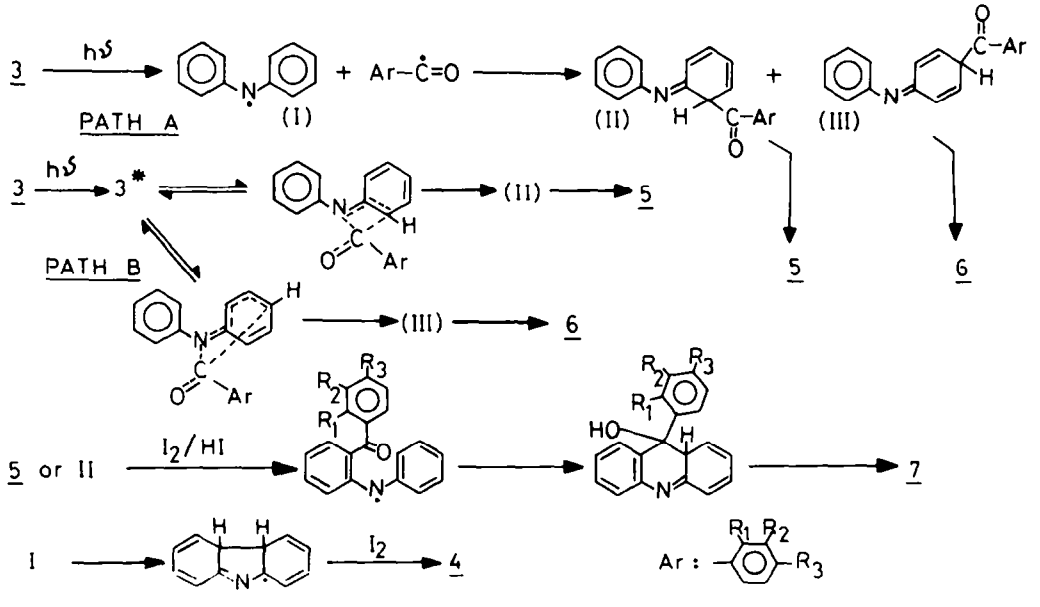
SCHEME-2



These foregoing facts **(Table-2)**, therefore, demonstrate that the major pathway for the formation of 9-arylacridines (7) under photochemical condition involves a radical mechanism via the sequences shown in **Scheme-3** in contrast to that of the thermal process (cationic mechanism) and may be considered as an example of a type of photo-Friedel-Crafts acylation reaction. The isolation of the photomigrated products [5 and 6] is accounted for by a photo-Fries rearrangement[1,5] and that of carbazole (4) by a photocyclisation of diphenylamine radical[1,6] (I) **(Scheme-3)**.

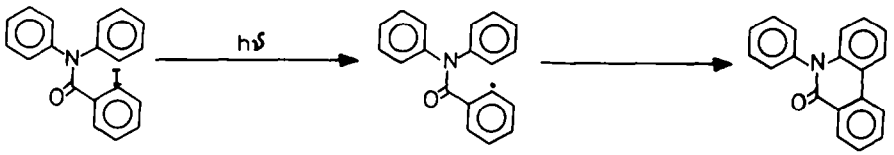
At this stage we became interested to study the photochemical behaviour of an ortho- halogen subsituted N-aroyldiphenylamine and for this purpose we had chosen N-(2-iodobenzoyl)-diphenylamine (3g). As anticipated, the oxidative photolysis of 3g in methanol/iodine solution at 254 nm afforded 6H-5-phenyl-phenanthridin-6-one (8), mp. 225° (acetone-petroleum ether, 60-80°)(lit.[2] mp. 225°), IR (KBr) ν_{max} 3060, 1655, 1605, 1505, 1430, 750 and 700 cm^{-1} as the sole product.

SCHEME-3



The 200 MHz ^1H NMR spectrum of 8 in $CDCl_3$ revealed the presence of two peri-protons at δ 8.36 (1H, dd, J_1=7.6 Hz, J_2=2.2 Hz, C_1-H) and 8.31 (1H, dd, J_1=7.6 Hz, J_2=2.2 Hz, C_{10}-H) indicating clearly the presence of a phenanthridone moiety. The spectrum could also characteristically account for the C_4-H at δ 8.58 (1H, dd, J_1=7.6 Hz, J_2=2.2 Hz). The remaining protons of the phenanthridone moiety were discernible at δ 7.78-7.87 (1H, m, C_2-H), 7.27-7.32 (1H, m, C_3-H) and 7.58-7.63 (3H, m, C_7-H, C_8-H, C_9-H). Additionally, a pair of double doublets appeared at δ 7.33 (2H, dd, J_1 = 7.6 Hz, J_2 = 2.2 Hz, $C_{3'}$ - H, $C_{5'}$ -H) and 7.65 (2H, dd, J_1 = 7.6 Hz, J_2 = 2.2 Hz, $C_{2'}$ -H $C_{6'}$ -H) and a one proton multiplet at δ 6.67 - 6.72 ($C_{4'}$ -H) due to the N-phenyl ring.

SCHEME-4



3g (IV) 8

The genesis of the photocyclised product (8) may be explained by a radical cyclisation reaction involving the radical (IV) (**Scheme-4**) which is readily formed by a photochemical homolytic cleavage of C—I bond[7-9] in 3g. It is also noteworthy to observe that the greater tendency of the substrate to form the radical (IV) precludes the formation of acridine, which arises first by the rearrangement of the aroyl group to the ortho-position followed by a radical cyclisation (**Scheme-3**). With an ortho-halogen group, the "hot" radical so generated undergoes concomitant cyclisation to afford the phenanthridone (8).

Thus we conclude that the oxidative photolysis of N-aroyldiphenylamines leads to the formation of 9-arylacridines or phenanthridone depending on the structure of the substrates and offers an easy access to the synthesis of two important classes of heterocyclic compounds.

EXPERIMENTAL

The melting points, recorded in H_2SO_4 bath are uncorrected. The IR spectra were obtained in a Perkin-Elmer 297 Infrared spectrometer, ^1H NMR spectra 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 a low pressure mercury lamp (16W, >90% 254 nm, Model 3016), manufactured by Applied Photophysics Ltd., England. Solvent abbreviations are : A-Acetone, B-Benzene, C-Chloroform 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 N-AROYLDIPHENYLAMINES [3(a-g)]:

N-benzoyldiphenylamine (3a) : 3a was prepared using diphenylamine (1) (5.1 g; 30 mmol) and benzoyl chloride (2a)(4.2 g; 30 mmol) by Schotten-Baumann reaction in strongly alkaline solution. A curdy white precipitate appeared, which on filtration and crystallisation from aqueous ethanol afforded 3a (5.0 g; 61%), mp. 180° (A-P)(lit.[10] mp. 180°). IR (KBr): ν_{max} 3060, 2910, 1650, 1590, 1485, 1110, 755 and 705 cm^{-1}.

N-(2-methoxybenzoyl)-diphenylamine (3b): Diphenylamine (1)(6.8 g; 40 mmol) dissolved in dry benzene (20 ml) was added to a well stirred suspension of sodium hydride (1.5 g; 63 mmol) in dry benzene (10 ml) at room temperature, followed by dropwise addition of 2-methoxybenzoyl chloride (2b), prepared from 2-methoxybenzoic acid (6.1 g; 40 mmol), in dry benzene (20 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 (3x25 ml), brine (4x25 ml) and dried over sodium sulphate. On removal of solvent, 3b was obtained in 35% yield (4.3 g), crystallised further from acetone-petroleum ether, 60-80°, mp. 127°.
IR (Nujol): ν_{max} 3040, 1650, 1590, 1450, 1250, 1020, 750 and 690 cm^{-1}.

N-aroyldiphenylamines [3(c-g)] were prepared by the above procedure using diphenylamine (1)(6.8 g; 40 mmol) and the acid chlorides [2(c-g)], obtained from the equimolar proportions of the respective acids.

N-(3-methoxybenzoyl)-diphenylamine (3c): Yield=1.5 g (12%); mp. 124°(A-P).

N-(4-methoxybenzoyl)-diphenylamine (3d): Yield=5.3g (43%); mp.141°(A-P) (lit.[11] mp. 143°).

IR (KBr): ν_{max} 3020, 2905, 1640, 1605, 1575, 1105, 760 and 700 cm^{-1}.

N-(3,4-dimethoxybenzoyl)-diphenylamine (3e): Yield=4.7g (35%);mp.164°(A-P).

IR (KBr): ν_{max} 3020, 3010, 1645, 1600, 1490, 1105, 760 and 700 cm^{-1}.

N-(3-nitrobenzoyl)-diphenylamine (3f): Yield=4.7g(37%);mp.115°(A-P) (lit.[12] mp. 118°).

IR (KBr): ν_{max} 3080, 3010, 1660, 1590, 1485, 1070, 760 and 695 cm^{-1}.

TABLE-1: RESULTS OF OXIDATIVE PHOTOLYSIS OF N-AROYLDIPHENYLAMINES [3(a-g)]

Substrate(3) MP.(Solvent)	Time (hr)	Diphenylamine(1) Yield: mg(%) Eluent	Carbazole(4) Yield: mg(%) Eluent	4-Aroyldiphenylamine(6) MP.(Solvent) Yield:mg(%) Eluent	9-Arylacridine(7) MP.(Solvent) Yield: mg(%) Eluent	Phenanthridone(8) MP.(Solvent) Yield: mg(%) Eluent
a 180°(A-P) (lit.[10] mp. 180°) (0.97 g; 3.6 mmol)	35	-	50(8) P	153°(A-P) (lit.[3] mp.154°) 571(59) P_1B_1	183°(A-P) lit.[4] mp.184-5°) 200(22) P_9B_1	-
b 127°(A-P) (1.04 g; 3.4 mmol)	30	-	62(11) P_9B_1	-	191°(A-P) 106(11) $P_1B_1+P_1B_3$	-
c 124°(A-P) (0.42 g; 1.4 mmol)	34	21(9) P	35(15) P_9B_1	145°(A-P) 148(35) P_1B_1	207-8°(A-P) 115(29) P_1B_3	-
d 141°(A-P) (lit.[11] mp. 143°) (0.84 g; 2.8 mmol)	31	35(7) P	-	164-5°(A-P) 451(54) $P_1B_1+P_1B_3$	212°(A-P) (lit.[13] mp.213°) 45(5) B	-
e 164°(A-P) (0.72 g; 2.2 mmol)	40	123(34) $P+P_9B_1$	-	190-91°(A-P) 114(16) B	232°(C-P) 185(27) P_1B_3	-
f 115°(A-P) (lit.[12] mp. 118°) (0.53 g; 1.7 mmol)	44	25(9) P_9B_1	-	153°(A-P) 79(15) P_1B_1	261°(A-P) 75(15) P_1B_1	-
g 129-30°(A-P) (1.08 g; 2.7 mmol)	25	85(19) P	-	-	-	225°(A-P) (lit.[2] mp.225°) 182(25) $P_1B_1+P_1B_3$

N-2-(iodobenzoyl)-diphenylamine (3g): Yield=8.1 g (51%); mp. 129-30° (A-P).

IR (Nujol): ν_{max} 3050, 1645, 1580, 1485, 1455, 1370, 1345, 755 and 700 cm^{-1}.

PHOTOLYSIS OF N-AROYLDIPHENYLAMINES [3(a-g)] :

Irradiation of N-benzoyldiphenylamine (3a): A solution of 3a (0.97 g; 3.6 mmol) and

TABLE-2: RESULTS OF PHOTOCHEMICAL AND THERMAL REACTIONS OF 2-BENZOYL-DIPHENYLAMINE (5a)

Entry	Method	2-Benzoyldiphenylamine(5a) mg	Recovered 5a mg(%)	Acridine(7a) mg(%)
1	hν/I_2/HI/CH_3OH	380	60(16)	225(63)
2	hν/HI/AIBN/CH_3OH	92	52(57)	27(31)
3	hν/HI/CH_3OH	160	106(66)	37(25)
4	hν/I_2/CH_3OH	60	42(70)	6(11)
5	hν/AIBN/CH_3OH	145	100(69)	5(4)
6	hν/$HClO_4$/CH_3OH	115	100(92)	4(4)
7	hν/AIBN/Petroleum ether, 60-80°	100	92(92)	-
8	$HClO_4$/CH_3OH/Dark/Reflux	156	118(76)	36(25)
9	$HClO_4$/CH_3OH/Dark/RT	68	55(81)	-

iodine (1.0 g; 3.9 mmol) in spectral methanol (350 ml) was irradiated for 35 hr under nitrogen atmosphere at room temperature (32°). The solvent was distilled off *in vacuo* and the crude product, after dilution with water (200 ml), was extracted with dichloromethane (3x50 ml). The combined organic layer was washed with saturated sodium thiosulphate solution (4x25 ml), brine (3x25 ml) and dried (Na_2SO_4). Evaporation of the solvent *in vacuo* afforded a residue, which on chromatography over silica gel gave carbazole (4), 4-benzoyldiphenylamine (6a) and 9-phenylacridine (7a). **Table-1** presents the experimental results and **Table-3** enlists the spectral data.

9-Phenylacridine (7a):

Found : C, 89.57%; H, 5.32% and N, 5.36%.

$C_{19}H_{13}N$ (255.32) requires C, 89.38%; H, 5.13% and N, 5.49%.

MS (70 eV): m/z 255 ($M^{\cdot+}$, 100%), 254 (99%), 161 (51%), 149(42%), 127(91%).

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

9-(2-Methoxyphenyl)-acridine (7b):

Found : C, 84.42%; H, 5.26% and N, 4.97%.

$C_{20}H_{15}NO$ (285.35) requires C, 84.19%; H, 5.29% and N, 4.91%.

9-(3-Methoxyphenyl)-acridine (7c) :

Found : C, 84.19%; H, 5.38% and N, 4.97%.

$C_{20}H_{15}NO$ (285.35) requires C, 84.19% ; H, 5.29% and N, 4.91%.

TABLE-3 : SPECTRAL DATA OF 4-AROYLDIPHENYLAMINES [6a,(c-f)] AND 9-ARYLACRIDINES [7(a-f)]

Product	IR (KBr): ν_{max} (cm^{-1})	^1H NMR ($CDCl_3$): δ(ppm) (J in Hz)
6a	3310,3050,1635,1600 1445,1170,750,740, 700	6.18(1H,s),7.01-7.12(3H,m),7.22(2H,dd, J=8.7, 1.3),7.30-7.40(2H,m),7.43-7.56(3H,m),7.76(2H,dd, J=6.1,1.8),7.79(2H,dd,J=6.7,1.7)
7a	3060,1630,1610,1515, 1440,755,710	7.47-7.52(3H,m),7.70(2H,d,J=10.5),7.72(2H,d, J=10.5), 7.83(2H,dd,J=10.5,2.0),7.97(2H,dd,J=8.0, 2.0),8.22 (2H,dd,J=9.0,2.0)
7b	3060,2950,1600,1515, 1460,1245,1025,830, 755	3.62(3H,s),7.18-7.28(3H,m),7.42(1H,dd,J=7.2,1.8), 7.46(1H,dd,J=7.2,1.8),7.59(1H,dd,J=9.0,1.8),7.67 (2H,dd,J=9.0,1.8),7.78(1H,dd,J=9.0,1.8),7.81(1H,dd, J=9.0,1.8),8.32(2H,dd,J=9.0,1.8)
6c	3330,3190,3010,1640, 1585,1245,1040,760, 710	3.86(3H,s),6.18(1H,s),7.06(2H,d,J=8.5),7.15(2H,dd, J=7.8,1.3),7.24(2H,dd,J=8.5,2.0),7.35(2H,dd,J=6.5, 2.0),7.36(1H,d,J=1.3),7.40(1H,d,J=7.8),7.42(1H,d, J=8.5),7.84(2H,d,J=8.5)
7c	3050,3010,2960,1600, 1585,1475,1255,1040, 1010,760,710	3.86(3H,s),7.02-7.06(1H,m),7.09(1H,d,J=2.0),7.16 (1H,dd,J=10.0,2.0),7.45(1H,dd,J=7.0,2.0),7.49(1H, dd,J=7.0,2.0),7.54(1H,dd,J=8.0,1.0),7.78(2H,dd,J=8.0, 2.0),7.83(2H,dd,J=8.0,2.0),8.32(2H,dd,J=10.0,2.0)
6d	3310,3040,3000,2850, 1635,1600,1590,1255, 1030,755,700	3.83(3H,s),6.17(1H,s),6.98-7.10(5H,m),7.25(2H,d,J= 8.0),7.38(2H,d,J=8.0),7.79(2H,d,J=8.0),7.83(2H,d, J=8.0)
7d	3060,3020,2840,1605, 1510,1245,1025,760, 725	3.96(3H,s),7.19(2H,dd,J=8.5,0.9),7.42(2H,dd,J=7.6, 0.9),7.49(2H,dd,J=8.5,1.9),7.80(2H,dd,J=8.5,1.9), 7.82(2H,dd,J=8.5,1.9),8.32(2H,dd,J=8.5,1.9)
6e	3320,2940,2850,1635, 1585,1255,1025,755, 705	3.88(3H,s),3.90(3H,s),6.13(1H,s),6.87(1H,d,J=8.8), 7.00(2H,d,J=8.8),7.06(1H,dd,J=7.4,1.5),7.17(2H,dd, J=7.4,1.5),7.31(1H,dd,J=8.8,2.2),7.35(2H,dd,J=8.8, 2.2),7.39(1H,d,J=2.2),7.73(2H,d,J=8.8)

TABLE-3 : SPECTRAL DATA OF 4-AROYLDIPHENYLAMINES [6a, (c-f)] AND 9-ARYLACRIDINES [7(a-f)] (Contd.)

Product	IR (KBr): ν_{max} (cm^{-1})	^1H NMR ($CDCl_3$): δ (ppm) (J in Hz)
7e	3060,3000,2950,1625, 1600,1580,1255,1030, 755	3.88(3H,s),4.04(3H,s),7.13-7.21(2H,m),7.28(1H,d, J=7.4),7.53(1H,dd,J=6.3,2.1),7.57(1H,dd, J=6.3,1.6),7.80-7.86(4H,m),8.25(2H,dd,J=8.4, 2.1)
6f	3330,3090,1640,1600, 1560,1435,1345,1160, 920,760,710	7.21-7.30(5H,m),7.38(4H,d,J=8.0),7.45(1H,s), 7.50(1H,d,J=8.0),7.86(1H,dd,J=8.0,2.0),8.22 (1H,dd,J=8.0,2.0),8.35(1H,d,J=2.0)
7f	3050,3030,1610,1530, 1490,1345,1105,1015, 755,745,705	7.49-7.66(4H,m),7.86(2H,dd,J=8.4,1.7),7.88 (2H,dd,J=8.4,1.7),8.37(2H,dd,J=8.4,1.7), 8.41(1H,d,J=1.7),8.50-8.57(1H,m)

4-(4-Methoxybenzoyl)-diphenylamine (6d) :

Found : C,79.08%; H, 5.98% and N, 5.18%.

$C_{20}H_{17}NO_2$ (303.36) requires C, 79.19%; H, 5.65% and N, 4.62%.

9-(3-Nitrophenyl)-acridine (7f) :

Found : C, 75.91%; H, 4.01% and N, 9.55%.

$C_{19}H_{12}N_2O_2$ (300.32) requires C, 75.99%; H, 4.03% and N, 9.33%.

6H-5-phenyl-phenanthridin-6-one (8) :

Found : C, 84.51%; H, 4.97% and N, 4.83%.

$C_{19}H_{13}NO$ (271.32) requires C, 84.11%; H, 4.83% and N, 5.16%.

ACKNOWLEDGEMENTS : The authors wish to thank Dr.R.V. Venkateswaran, IACS, Calcutta for recording 200 MHz ^1H NMR spectra and Dr.P. Maity, JU, Calcutta for microanalytical measurements. Financial assistance (to ID) from CSIR, New Delhi is also acknowledged.

REFERENCES

1. Part-3 : Datta,I.; Das,T.K.; Ghosh,S.N. **Tetrahedron Lett. 1989, 30**, 4009.
2. Moynehan,T.M.; Hey,D.H. **Proc. Chem. Soc. 1957**, 209.
3. Itier,J.; Casadevall, A. **Bull. soc. chim. Fr. 1969**, 2342.
4. Popp,F.D. **J. Org. Chem. 1962, 27**, 2658.
5. Bellus,D. **Advan. Photochem. 1971, 8**, 109.
6. Carruthers,W. **J. Chem. Soc. Chem. Commun. 1966**, 272.
7. Ghosh,S.N.; Datta,D.B.; Datta,I.; Das,T.K. **Tetrahedron 1989, 45**, 3775.
8. Sharma,R.K.; Kharasch,N. **Angew. Chem. Int. Ed. Engl. 1968, 7**, 36.
9. Wilson,R.M.; Commons,T.J. **J. Org. Chem. 1975, 40**, 2891.
10. Clarke,H.T. **"A Handbook of Organic Analysis : Qualitative and Quantitative"** Edward Arnold. London, **1952**, p. 202.
11. Grammaticakis,P. **Bull. soc. chim. Fr. 1964**, 924.
12. Grammaticakis,P. **Bull. soc. chim. Fr. 1960**, 1956.
13. Bergmann,E.; Rosenthal,W. **J. Prakt. Chem. 1932, 135**, 267.

NOTE : For carrying out experiments with perchloric acid in methanol as solvent, in actual practice we employed :

i) 0.2 ml of 70% aqueous perchloric acid in methanol (350 ml) for photolysis experiment and

ii) for thermal experiments 0.2 ml 70% perchloric acid (aqueous) in methanol (100 ml)

for the conversion of **5a** to **7a** (vide **Table-2**, entries 6, 8 and 9).