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STUDIES ON ENAMIDES. PART-3[1] : A NOVEL PHOTOCHEMICAL SYNTHESIS OF 9-ARYLACRIDINES

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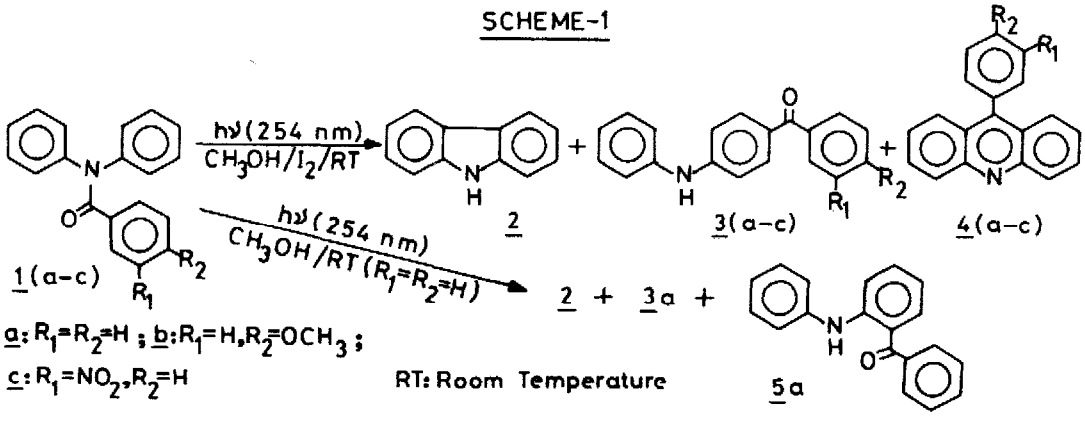
ABSTRACT: A unique synthesis of 9-arylacridines has been achieved by the photolysis of N-aroyldiphenylamines alongwith carbazole and photomigrated products.

The photochemical reaction of benzanilides, first reported by Cleveland and Chapman[2] in the sixties, has been extensively utilised for the synthesis of various heterocyclic compounds such as alkaloids and aza-steroids and several comprehensive reviews[3-5] have been published in the literature. In connection with our interest for the photochemical studies on enamides[1] and other heterocyclic systems[6], we wish to report here for the first time, our observations on the photolysis of N-aroyldiphenylamines, a potential class of dienamides which has not been studied so far[3-5], and the results obtained thereof may be useful for the synthesis of alkaloids[7-9].

Irradiation[10] of a methanolic solution (350 ml) of N-benzoyldiphenylamine (1a)(1.0 g; 3.7 mmol) with iodine as oxidant (Scheme-1) under nitrogen atmosphere at room temperature (32°) for 35 h neatly afforded, after usual workup and chromatography over silica gel, carbazole (2)(50 mg; 8%), the known[11] 4-benzoyldiphenylamine (3a)(571 mg; 59%) and notably, culminating in the first photochemical synthesis of 9-phenylacridine (4a)(200 mg; 22%), mp. 183°(acetone-petroleum ether, 60-80°)(lit.[12] mp. 184-5°), IR (KBr)ν_{max} 3060,1630,1610,1515,1440,755 and 710 cm^{-1}; ^1H NMR(200 MHz, $CDCl_3$)δ 7.48 (3H,m), 7.70(2H,d,J=10.5 Hz), 7.72(2H,d,J=10.5 Hz), 7.83(2H,dd,J=10.5, 2.0 Hz), 7.97 (2H,dd,J=8.0, 2.0 Hz), 8.22(2H,dd,J=9.0, 2.0 Hz); MS(70 eV) m/z 255($M^{\bullet+}$, 100%).

The photochemical reaction was found to be consistent for other substrates [1(b-c)] leading to the formation of 3(b-c) and 4(b-c) in varying yields (Table-1), thereby demonstrating the generality of the photochemical method for the synthesis of 9-arylacridines (4).

SCHEME-1



a: $R_1=R_2=H$; b: $R_1=H, R_2=OCH_3$;
c: $R_1=NO_2, R_2=H$ RT: Room Temperature

TABLE-1: RESULTS OF OXIDATIVE IRRADIATION (16W) OF N-AROYLDIPHENYLAMINES [1(a-c)]

N-Aroyldiphenylamine(1) MP.(solvent)[b]	Time (h)	4-Aroyldiphenylamine(3)[a] MP.(solvent)[b] Yield in mg(%)[c]	IR(KBr) (cm^{-1})	9-Arylacridine(4)[a] MP.(solvent)[b] Yield in mg(%)[c]	IR(KBr) (cm^{-1})
a: 180°(A-P) [lit.[13] mp.180°]	35	153°(A-P) [lit.[11] mp.154°] 571(59)	3300, 1630	183°(A-P) [lit.[12] mp.184-5°] 200(22)	1630, 1515, 755,710
b: 141°(A-P) [lit.[14] mp.143°]	31	164-5°(A-P) 451(54)	3310, 1635	212°(A-P) [lit.[15] mp.213°] 45(5)	1605, 1510, 760
c: 115°(A-P) [lit.[16] mp.118°]	44	153°(A-P) 79(15)	3315, 1640	261°(A-P) 75(15)	1630, 1530, 755,705

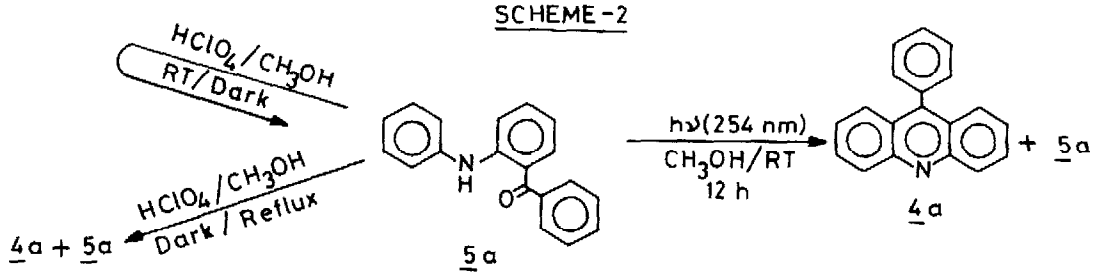
a : Compounds 3(b-c) and 4c are new and give satisfactory elemental analyses (C, ± 0.2%; H, ± 0.4% and N, ± 0.3%). ^{1}H NMR (200 MHz, $CDCl_3$) spectral data for 3(a-c) and 4(b-c) are given in Note 19.

b : Melting points are uncorrected and recorded in Köfler block apparatus and solvent abbreviations are: A - Acetone and P - Petroleum ether, 60-80°.

c : Yield refers to the combined amounts of first and second crop of crystallised product obtained after chromatography.

The irradiation of 1a in methanol at 254 nm (Scheme-1) for 17 h led only to the ortho- (5a) and para-migrated (3a) products alongwith carbazole (2). The absence of 9-phenylacridine (4a) in this reaction clearly indicates the catalytic role of iodine [and possibly hydroiodic acid generated in situ (Scheme-3)] in the formation of this compound.

SCHEME-2



In order to ascertain the mechanistic pathway for the conversion of 5a to 4a, we studied several photochemical and thermal experiments (Scheme-2) with 5a, whereby we could isolate 4a and 5a in varying proportions (Table-2). As evident from these results (Table-2) :

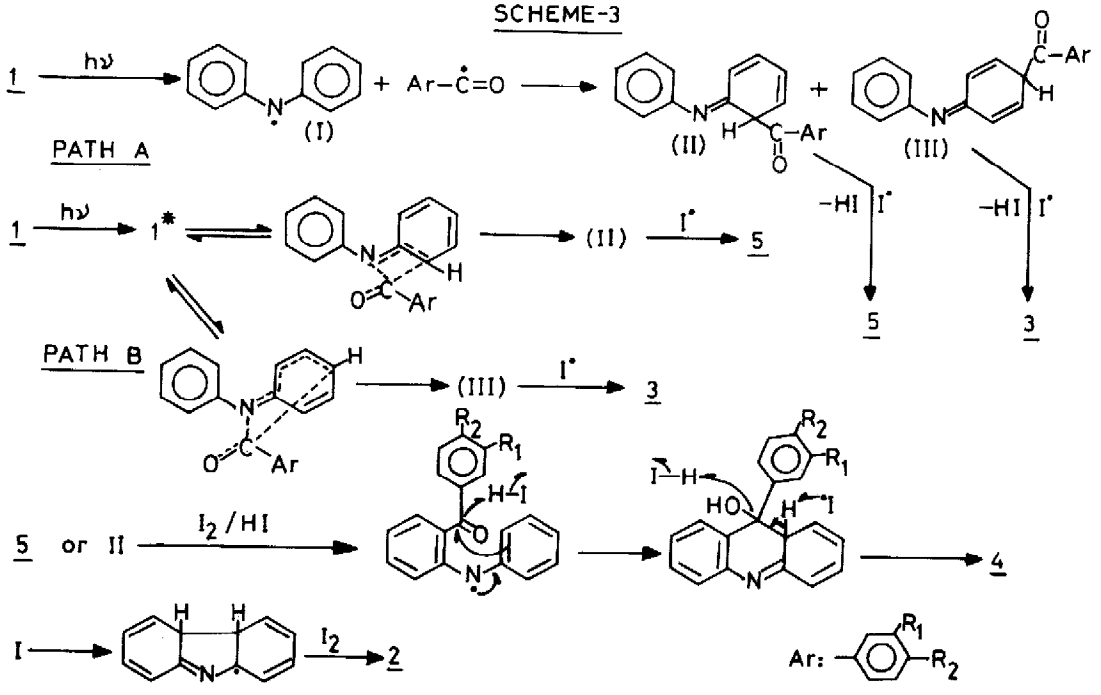
(i) the optimum condition for the efficient photochemical conversion of 5a to 4a requires the use of iodine and hydroiodic acid (entry 1); (ii) compared to a radical initiator (entries 4,5) or an acid catalyst alone (entries 3,6), a combination of both (entries 1,2) gave an optimum yield of the acridine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

TABLE-2: PHOTOCHEMICAL AND THERMAL REACTIONS OF 2-BENZOYLDIPHENYLAMINE (5a)

Entry	Method	2-Benzoyldiphenylamine(5a) mg	Recovered 5a mg(%)	Acridine(4a) 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)	-

Furthermore, 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 h (Scheme-2) no acridine could be isolated (Table-2, entry 9), confirming thereby the role of light in the transformation of 5a to 4a. Repeating the reaction under refluxing condition in dark for 2 h, acridine (4a) could be obtained in 25% yield (Table-2, entry 8), thereby unambiguously establishing a cationic pathway of the reaction under thermal

SCHEME-3



condition[12].

As is apparent from the foregoing results (Table-2), the major pathway for the formation of 9-arylacridines (4) from 2-aroyldiphenylamines (5) under photochemical condition may be depicted by a radical mechanism via the sequences shown in Scheme-3, in contrast to that of the thermal reaction process.

Finally, the genesis of the photomigrated products [3(a-c) and 5a] may be explained by a photo-Fries rearrangement[17] and that of carbazole (2), as reported earlier[18], by a photocyclisation of diphenylamine radical (I) (Scheme-3).

Thus, we conclude that the oxidative photolysis of N-aroyldiphenylamines leads to [1,3]- or [1,5]- aroyl migration from nitrogen to the ring depending on the condition of irradiation and offers an easy access to 9-arylacridines through a unique photocyclisation pathway.

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19. 4-Benzoyldiphenylamine(3a): δ 6.18(1H,s), 7.07(3H,m), 7.22(2H,dd,J=8.7, 1.3 Hz), 7.35(2H,m), 7.50(3H,m), 7.76(2H,dd,J=6.1, 1.8 Hz), 7.79(2H,dd,J=6.7, 1.7 Hz).

4-(4-Methoxybenzoyl)-diphenylamine(3b): δ 3.83(3H,s), 6.17(1H,s), 7.04(5H,m), 7.25 (2H,d,J=8.0 Hz), 7.38(2H,d,J=8.0 Hz), 7.79(2H,d,J=8.0 Hz), 7.83(2H,d,J=8.0 Hz).

4-(3-Nitrobenzoyl)-diphenylamine(3c): δ 7.26(5H,m), 7.38(4H,d,J=8.0 Hz), 7.45(1H, s), 7.50(1H,d,J=8.0 Hz), 7.86(1H,dd,J=8.0, 2.0 Hz), 8.22(1H,dd,J=8.0, 2.0 Hz), 8.35(1H,d,J=2.0 Hz).

9-(4-Methoxyphenyl)-acridine(4b): δ 3.96(3H,s), 7.19(2H,dd,J=8.5, 0.9 Hz), 7.42 (2H,dd,J=7.6, 0.9 Hz), 7.49(2H,dd,J=8.5, 1.9 Hz), 7.80(2H,dd,J=8.5, 1.9 Hz), 7.82 (2H,dd,J=8.5, 1.9 Hz), 8.32(2H,dd,J=8.5, 1.9 Hz).

9-(3-Nitrophenyl)-acridine(4c): δ 7.58(4H,m), 7.86(2H,dd,J=8.4, 1.7 Hz), 7.88(2H, dd,J=8.4, 1.7 Hz), 8.37(2H,dd,J=8.4,1.7 Hz), 8.41(1H,d,J=1.7 Hz), 8.54(1H,m).

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