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PHOTO-FRIES REARRANGEMENTS IN N-SULPHONYL CARBAZOLES

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Abstract:-When photo-Fries rearrangements in N-sulphonyl carbazoles 1 in benzene or methanol smoothly afforded 1- and 3-sulphonylcarbazoles 2 and 3 respectively in 29-55% yield, N-benzoylcarbazole 1d did not undergo similar rearrangements to give the expected products.

Though photochemical Fries rearrangements in phenolic esters and aromatic amides[1,2] have been extensively studied, very little attention has been given to sulphonamide photochemistry. In consideration of almost unexplored photochemical behaviour of carbazoles in relation to sulphonamides, we were interdsted in studying the photochemical behaviour of N-sulphonylcarbazoles. In present report we will discuss the results.

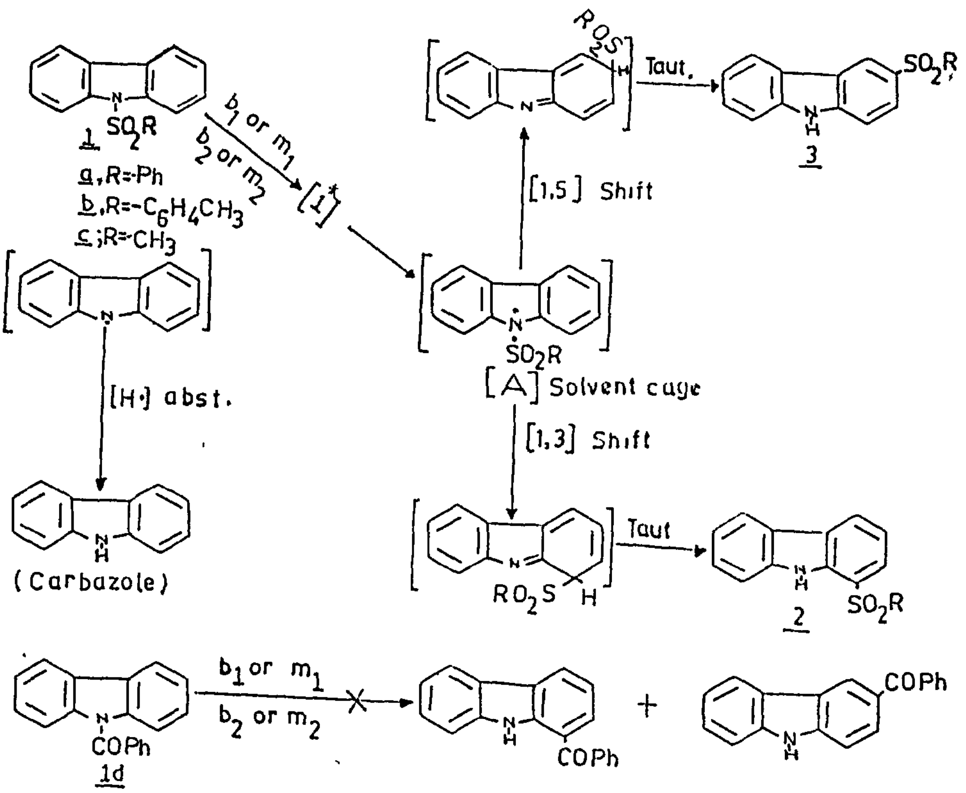
Irradiation of N-sulphonylcarbazoles 1(a-c) in benzene or methanol (Scheme, Experimental) at 254 or 365nm in nitrogen atmosphere(room temperature) clearly afforded the [1, 3] and [1, 5] migrated photoproducts 2(a-c) and 3(a-c) respectively (Table). In all cases formation of photo-rearranged 1- and 3-sulphonylcarbazoles from respective N-sulphonylcarbazoles accompanied carbazole and small amount of unreacted starting material.

Similar experiment with N-benzoylcarbazole 1d remained unsuccessful (Scheme, Experimental) and no expected photo-rearranged products could be isolated from the photolysate of 1d.

Photochemically excited $[1^*]$ underwent a fast homolytic cleavage of nitrogen-sulphur covalant bond in N-sulphonylcarbazole thereby generating the solvent-caged intermediate [A] (Scheme). Formation of photo-products 2 and 3 from [A] could be rationalised by the intramolecular [1, 3] and [1,5] migratation of the sulphonyl radical, $RSO_2^{\bullet}$,(Scheme). Part of [A] may undergo cage recombination to 1 and carbazole radicals which leak from the solvent-cage abstract hydrogen(H•) from neighbour molecules thereby producing carbazole.

Since photo-Fries rearrangements have been found to occur only in presence of light and in absence of any catalytic reagent[3], formation of [1, 3] and [1, 5] migrated sulphonylcarbazoles 2(a-c) and 3(a-c) respectively from N-sulphonylcarbazoles 1(a-c) constitute the examples of true photo-Fries rearrangement, hitherto not investigated in carbazole system. Interestingly such photochemical rearrangements in N-sulphonylcarbazoles 1(a-c) provide us with an easy access to the synthesis of 1- and 3-sulphonylcarbazoles which have been found difficult to synthesise by conventional synthetic stratagem.

SCHEME-1



b_1 or m_1 : irradiation at 254 nm in benzene or methanol

b_2 or m_2 : irradiation at 365 nm in benzene or methanol

TABLE-1

RESULTS OF IRRADIATION OF N-SULPHONYLCARBAZOLES

Entry	1[a]	Wavelength	Solvent	Time	Product (% yield)[b]		
					2	3	Car.
1.	a	254 nm	Benzene	20 hr	a(35),	a(45)	(10)
		254 nm	Methanol	20 hr	a(30),	a(45)	(7)
		365 nm	Benzene	7 hr	a(32),	a(40)	(7)
		365 nm	Methanol	7 hr	a(35),	a(50)	(3)
2.	b	254 nm	Benzene	20 hr	b(38),	b(45)	(6)
		254 nm	Methanol	20 hr	b(29),	b(40)	(15)
		365 nm	Benzene	7 hr	b(37),	b(48)	(5)
		365 nm	Methanol	7 hr	b(38),	b(46)	(6)
3.	c	254 nm	Benzene	20 hr	c(48),	c(30)	(5)
		254 nm	Methanol	20 hr	c(40),	c(25)	(10)
		365 nm	Benzene	7 hr	c(55),	c(35)	(2)
		365 nm	Methanol	7 hr	c(45),	c(37)	(7)

a: Compounds 1(a-c) were prepared by methods described in the experimental

b: Yields are referred to the amount of crystallised products obtained by chromatography. Compounds 2(a-c) and 3(a-c) are all new. Satisfactory microanalytical data were obtained for new compounds 2(a-c) and 3(a-c).

c: Car. = Carbazole.

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EXPERIMENTAL

Spectroscopic grade (Merck) benzene and methanol were used as solvents in the photolysis experiments. Irradiation was carried out in a quartz immersion well photochemical reactor (Applied Photophysics Ltd., England) with a 16-W, 254 nm medium pressure and 400-W, 365 nm medium pressure mercury vapour lamps fitted with protector quartz tubes. Melting points were determined on a Toshniwal melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker CXP (300 MHz) instrument. IR (KBr discs) were obtained using a Perkin Elmer 782 instrument. MS (70 ev) were obtained with a AEIMS 30 spectrometer.

Synthesis of starting compounds 1(a-d):

Carbazole [1.0g; 5.9 m mole] in 50 ml DMF-benzene (1:1) in 150 ml round bottom flask was treated with sodium hydride (0.168g; 7.0 m mole) at $0-5^{\circ}C$ under mechanical stirring. To the cold stirred solution benzenesulphonylchloride (0.8 ml; 6 m mole), p-toluenesulphonylchloride (1.12g; 5.9 m mole), methanesulphonylchloride (0.4 ml; 6.0 m mole) and benzoylchloride (0.69 ml; 6.0 m mole) were added in four separate experimental set up under similar experimental conditions. The reaction mixtures were stirred at room temperature for about 4 hrs. Excess sodiumhydride was then decomposed with 7% sulphuric acid solution and the reaction products were extracted with benzene (100 ml in each experiment). After drying the benzene extracts over anhydrous sodium sulphate, filtration and concentration, the extracts were chromatographed over columns of silica gel (60-120 mesh; Merck). On elution the columns with n-hexane-ethyl acetate (9:1) and subsequent work up afforded crystalline starting compounds 1(a-d) as follows :

N-benzenesulphonylcarbazole (1a):

(0.95g; 95%), m.p.:180°C; IR (KBr):1600, 1590, 1390, 1335, 1140, 1125, 1100 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) (ppm) : 7.19 (1H, d, J = 8.6 Hz), 7.39 (6H, m), 7.51 (4H, m), 7.80 (1H, d, J = 7.9 Hz), 7.95 (1H, d, J = 8.5 Hz), 8.41 (1H, d, J = 7.6 Hz); Ms: 307 (M$^+$).

N-p-toluenesulphonylcarbazole (1b):

(0.90g; 90%), m.p. : 120°C; IR (KBr) : 1595, 1400, 1330, 1300, 1150, 1130, 1110 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): 2.34 (3H, s), 7.15 (1H, d, J = 8.0 Hz), 7.42 (5H, m), 7.53 (4H, m), 7.78 (1H, d, J = 7.6 Hz), 7.96 (1H, d, J = 8.2 Hz), 8.39 (1H, d, J = 7.9 Hz); Ms : m/z 321 (M$^+$).

N-methanesulphonylcarbazole (1c):

(0.89g; 89%), m.p.: 101°C; IR (KBr):1600, 1410, 1331, 1290, 1140, 1127, 1120 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) (ppm) : 2.36 (3H, s), 7.10 (1H, d, J = 8.8 Hz), 7.46 (4H, m), 7.81 (1H, d, J = 8.0 Hz), 7.88 (1H, d, J = 7.7 Hz), 8.16 (1H, d, J = 8.1 Hz); MS : m/z 245 (M$^+$).

N-benzoylcarbazole (1d):

(0.90g; 90%), m.p. : 98°C (Lit[4]. m.p. 98°C)

Irradiation of compounds 1(a-d) at 254 nm as well as at 365 nm in benzene or methanol

Compounds 1(a-d) (1.0g of each) were dissolved in benzene or methanol (300 ml) and were irradiated separately at 254 nm as well as at 365 nm for the same period (same time of irradiation was maintained under a fixed wave length Table - 1) under N$_2$ atmosphere at room temperature. The photochemical reactions were monitored by T.L.C. After completion of irradiation the solvent was removed under vacuo. The red oily photolysates thus obtained in each run were subjected to chromatography over columns of silica gel (60-120 mesh) using n-hexane-ethyl acetate as the eluent.

Photoproducts obtained by irradiation of compounds (1a–1c, separately) at 254 nm as well as at 365 in benzene or methanol were found identical by work up under similar experimental condition. The variation in the time of irradiation under two different wave lengths (254 and 365 nm respecttively) as well as the yields of the products under different experimental conditions have been shown in Table – 1.

Photoproducts obtained by irradiation of 1a at 254 nm as well as at 365 nm in benzene or methanol:

Carbazole (n-hexane-ethyl acetate 9:1) : m.p. 241°C (Lit m.p. 245°C).

1-benzenesulphonylcarbazole (2a): (N-hexane-ethyl acetate:9:1):crystalline solid:m.p. 172°C; IR (KBr):3390, 1620, 1600, 1580, 1430, 1340, 1350, 1280, 1150, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (ppm);7.38 (3H, m), 7.57 (5H, m) 7.97 (1H, d, J = 8.0 Hz), 8.11 (2H, m), 8.34 (1H, d, J = 7.9 Hz) and 9.86 (1H, bs, D_2O exchangible); MS:m/z 307 (M^+).

3-benzenesulphonylcarbazole (3a): (n-hexane-ethyl acetate:7:3):crystalline solid:m.p. 205°C;IR (KBr) :3320, 1630, 1600, 1580, 1400, 1330, 1300, 1270, 1150, 1130 cm^{-1}; ^1H NMR (300 MHz, $CDCl_2$) (ppm):7.30 (3H, m), 7.54 (5H, m), 8.02 (2H, m), 8.18 (1H, d, J = 8.0 Hz), 8.77 (1H, bs) and 9.95 (1H, s, D_2O exchangible); MS:m/z 307 (M^+).

Photoproducts obtained by irradiation of 1b at 254 nm as well as at 365 nm in benzene or methanol : Carbazole (n-hexane-ethyl acetate:9:1)

1-p-toluenesulphonylcarbazole (2b): (n-hexane-ethyl acetate:9:1) crystalline solid; m.p. 200°C; IR (KBr):3385, 1620, 1585, 1435, 1340, 1310, 1145, 1135, 1100; ^1H NMR (300 MHz, $CDCl_3$) (ppm):2.37 (3H, s), 7.34 (3H, m); 7.53 (4H, m) 7.87 (1H, d, J = 8.6 Hz), 7.94 (2H, m), 8.28 (1H, d, J = 7.9 Hz) and 9.90 (1H, s, D_2O exchangible); MS:m/z 321 (M^+).

3-p-toluenesulphonylcarbazole (3b): (n-hexane-ethyl acetate:7:3):crystalline solid; m.p. 228°C; IR (KBr):3390, 1630, 1600, 1595, 1427, 1345, 1300, 1140, 1130, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (ppm):2.35 (3H, s), 7.37 (3H, m), 7.52 (4H, m), 7.97 (2H, m), 8.16 (1H, d, J = 8.0 Hz), 8.65 (1H, s) and 9.91 (1H, S, D_2O exchangible); MS:m/z 321 (M^+).

Photoproducts obtained by irradiation of 1c at 254 nm as well as at 365 nm in benzene or methanol:

Carbazole (n-hexane-ethyl acetate:9:1)

1-methanesulphonylcarbazole (2c): (n-hexane ethyl acetate:9:1) crystalline solid; m.p. 98°C; IR (KBr):3395, 1600, 1420, 1340, 1229, 1300, 1140, 1132, 1110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (ppm) 2.31 (3H, s), 7.28 (3H, m), 7.72

(1H, d, J = 8.0 Hz), 7.78 (2H, m), 8.07 (1H, d, J = 8.0 Hz) and 9.86 (1H, bs, D_2O exchingible); MS:m/z 245 (M^+).

3-methanesulphonylcarbazole (3c): (n-hexane-ethyl acetate:8:2):crystalline solid; m.p. 118°C; IR (KBr):3385, 1600, 1420, 1345, 1331, 1290, 1140, 1128, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (ppm):2.30 (3H, s), 7.29 (3H, m), 7.82 (2H, m), 7.95 (1H, d, J = 8.2 Hz), 8.45 (1H, s) and 9.84 (1H, s, D_2O exchingible); MS:m/z 245 (M^+).

No [1, 3] and/or [1, 5] benzoyl migrated photoproducts were obtained by irradiation of N-benzoylcarbazole (1d) in benzene or methanol at 254 nm as well as at 365 nm under N_2 atmosphere at room temperature. Some carbazole was however isolated.

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