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Photochemistry of *N*-acetyl and *N*-benzoyl carbazoles: photo-Fries rearrangement and photoinduced single electron transfer

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Abstract

The photochemistry of two *N*-acyl carbazoles, *N*-acetyl and *N*-benzoyl carbazole, in different pure and mixed organic solvents is studied. Depending on the properties of the medium, photo-Fries rearrangement and photoinduced single electron transfer (PSET) processes are observed yielding the former 1-acyl and 3-acyl carbazoles and the latter 3-chloro-*N*-acyl carbazole. k_{SV}, k_Q and ϕ for fluorescence emission, conversion of *N*-acyl carbazole and product formation yields have been measured as well as the properties of the *N*-acyl carbazole radical cations formed during the PSET process (laser flash photolysis experiments). The Rehm–Weller equation is used in order to evaluate the ΔG°_{ET} of the PSET processes. © 1997 Elsevier Science S.A.

Keywords: *N*-acyl carbazole; *N*-acetyl carbazole; *N*-benzoyl carbazole; Photo-Fries; Photo-rearrangement; Photoinduced single electron transfer (PSET)

1. Introduction

Although the photo-Fries rearrangement of *N*-acetyl carbazole had been previously studied, the results related with the dependence of the products molar ratio (1-acetyl to 3-acetyl carbazole molar ratio) on the solvent used [1] and on the initial *N*-acetyl carbazole concentration [2] were quite contradictory. In 1981, Zander [1] described briefly the photo-rearrangement of *N*-acetyl carbazole in cyclohexane claiming that 1-acetyl carbazole was the only product; the experiments were conducted with an *N*-acetyl carbazole concentration equal to 1.9×10^{-3} mol dm^{-3}. Some years ago, in 1970, Morita et al. [2] described the photo-Fries rearrangement of *N*-acetyl carbazole stating that: (a) 1-acetyl and 3-acetyl carbazole were obtained with higher quantum yield of the former than the latter; (b) the quantum yields for product formation were higher in cyclohexane than in EtOH; and (c) the photo-rearrangement did not show any dependence on irradiation time and on initial *N*-acetyl carbazole concentration; the authors apparently worked with the concentration range 0.5×10^{-3} to 3.0×10^{-3} mol dm^{-3}.

The photochemical behavior of *N*-benzoyl carbazole has also been described as quite contradictory. Thus, under oxidative conditions in organic media (organic solvents + I_2) the photo-Fries rearrangement was reported as wavelength and solvent dependent [3,4], while in the same organic media, without I_2, the *N*-benzoyl carbazole was described as totally photo-stable [5]. These authors did not pay any attention to the effect of the concentration on the photo-Fries rearrangement.

In a previous paper we described some aspects of our product study of the photolysis of *N*-acetyl carbazole in EtOH and in CH_2Cl_2 solution [6]. In this preliminary study we paid only attention to the isolation and characterization of the products obtained by photo-Fries rearrangement and in the effect of the concentration of *N*-acetyl carbazole on the photo-rearrangement process. As part of a program related with the study of the influence of the properties of the medium (electron affinity, proton and hydrogen donor character, polarity, dielectric constant, viscosity, etc.) on the photoreactivity of carbazoles [7–9] and aza-carbazoles (β-carbolines, [10–17]) we decided to study the photochemistry of *N*-acetyl carbazole (**1a**) in a wide range of organic solvents (cyclohexane, benzene, EtOH, CH_3CN, THF, DMF, CH_2Cl_2, $HCCl_3$, CCl_4, CCl_4–benzene, CCl_4–EtOH and CCl_4–CH_3CN) in different experimental conditions (different atmosphere, λ_{exc}, source intensity, irradiation time, concentration, presence of photosensitizers, photoquenchers, radical scavengers, etc), studying not only the photorearrangement but also the photoinduced single electron transfer (PSET) process which occurs when chloroalkanes are present in the

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reaction medium. Additionally in this work, we present a study of the UV photochemical irradiation of *N*-benzoyl carbazole (**1b**) in benzene, MeOH, EtOH, CH_3CN, CH_2Cl_2, $HCCl_3$, CCl_4 and benzene–CCl_4 and EtOH–CCl_4 mixtures and of the products thus formed. The photo-Fries rearrangement of **1b** to 1-benzoyl (**2b**) and 3-benzoyl carbazole (**3b**) (Scheme 1, reaction a) was observed in benzene, CH_2Cl_2 and EtOH without any wavelength dependence but with a strong *N*-benzoyl carbazole concentration dependence. The exciplex formation followed by a photoinduced single electron transfer process was observed in CCl_4 and in EtOH–CCl_4 mixtures yielding 3-chloro-*N*-benzoyl carbazole (**6b**) as stable photoproduct. The kinetic aspects of the reactions (k_Q, k_{obs} and *N*-acyl carbazole consumption and products quantum yield ϕ) as well as the spectral properties of the radical cation formed in the PSET process have been studied. Finally, in order to explain some results obtained, semiempirical calculations (computational chemistry; PM3 and ZINDO/S methods) were also attempted.

2. Experimental details

2.1. Materials

N-Acetyl carbazole (**1a**) [6] and *N*-benzoyl carbazole (**1b**) [18,19] were prepared and characterized (m.p., UV, IR, ^1H- and ^{13}C-NMR and MS) as reported elsewhere. Carbazole, 1-dodecylmercapthane (RSH) and tetramethyldiazetine dioxide (TMDD) were purchased from Aldrich Chemical Co. and were used without further purification. Xanthone and benzophenone were purchased from BDH Company and were recrystallized from EtOH. The purity of the samples were checked by comparing their m.p. and electronic absorption spectrum with published data [6,18–20]. Potassium ferrioxalate for Hatchard–Parker actinometer was prepared according to the literature [21], potassium hydrogen oxalate was purchased from BDH. *N*-Chlorobenzotriazole was prepared and characterized according to the procedure described by Rees and Storr [22].

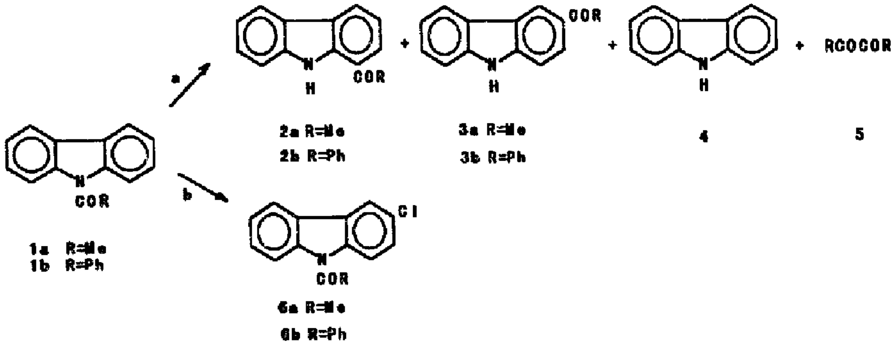
Spectrograde and HPLC grade hexane, benzene, MeOH, EtOH, i-PrOH, tert-BuOH, CH_3CN, EtOH, CH_2Cl_2, $HCCl_3$, CCl_4 were purchased from Mallincrodt.

Thin layer chromatography (TLC) analyses were best performed on silica gel plates (Merck, F254 nm). Column adsorption chromatography was performed with silica gel (Merck, Kieselgel 60, 70-230 mesh). Solvents for chromatography and recrystallization were carefully purified and dried before use [23].

2.2. Preparation of acyl carbazoles to be used as authentic samples

Compounds **2a** (1-acetyl carbazole), **2b** (1-benzoyl carbazole), **3a** (3-acetyl carbazole) and **3b** (3-benzoyl carbazole) were prepared according to procedures described elsewhere [6,18,19]. The chloro-*N*-acyl carbazoles **6a** and **6b** were prepared and purified according to the following procedure. To a stirred solution of *N*-acyl carbazole (3.25×10^{-3} mol dm^{-3}) in $HCCl_3$ (50 ml), containing silica gel (6 g), a solution of *N*-chloro benzotriazole (3.25×10^{-3} mol dm^{-3}) in $HCCl_3$ (50 ml) was added. The reaction mixture was refluxed under stirring in the dark during 6 h, until the TLC and GC analysis indicated that the conversion was completed. The reaction mixture was then filtered off and the silica washed with $HCCl_3$ (3 × 15 ml), the combined extracts were washed with water (100 ml) and the organic layer was dried over K_2CO_3, filtered off and evaporated under reduced pressure. The greenish solid residue obtained was separated by column adsorption chromatography (eluent: hexane and ethyl acetate–hexane mixtures). From the eluted fractions the products were isolated and characterized by their physical and spectroscopical properties:

3-Chloro-*N*-acetyl carbazole (**6a**): white plates from ethanol, mp 123–125°C [24]. ^1H-NMR (200 MHz, $DCCl_3$): δ (ppm), 8.15 (d, 1 H, 8-H, $J=9$ Hz), 8.07 (d, 1 H, 1-H, $J=8$ Hz), 7.89 (d, 1 H, 5-H, $J=8$ Hz), 7.86 (s, 1 H, 4-H) and 7.49 (m, 3-H, 2-, 6- and 7-H). ^{13}C-NMR (200 MHz, $DCCl_3$): δ (ppm) 169.7 (CO), 140 (9a-C), 138 (8a-C), 129.3 (3-C), 127.9 (2-C), 127.2 (7-C), 125.3 (4a-, 4b-C), 123.8 (6-C), 120.1 (4-C), 119.4 (5-C), 117.5 (1-C), 115.9 (8-C)



Scheme 1.

and 27.6 (CH3). MS (70 eV): *m/z* (%), 275 (18.2), 273 (51.5), 245 (9.1), 243 (M+, 27.3), 230 (12.1), 229 (33.3), 228 (45.5), 227 (100), 202 (12.1), 201 (21.2), 200 (39.4), 199 (20.8), 164 (42.2), 138 (6.1) and 44 (27.3).

3-Chloro-*N*-benzoyl carbazole (**6b**): white plates from ethanol, m.p. 221–222°C [24]. ^{1}H-NMR (200 MHz, $DCCl_3$): δ (ppm), 7.95 (d, 1H, $J=8.0$ Hz, 4-H), 7.89 (s, 1H, 5-H), 7.69 (m, 2H, $J=7.5$ Hz, 12-H and 16-H), 7.53 (m, 2H, $J=7.9$ Hz, 1-H and 8-H) and 7.31 (m, 6H, 2-H, 6-H, 7-H, 13-H, 14-H and 15-H). ^{13}C-NMR (200 MHz, $DCCl_3$): δ (ppm), 169.4 (CO), 139.9(9a-C), 137.8 (8a-C), 135.4 (11-C), 132.7 (14-C), 130.7 (3-C), 128.9 (12-C, 13-C, 15-C and 16-C), 127.3 (2-C), 126.7 (7-C), 126.1 (4a-C), 124.9 (4b-C), 123.5 (6-C), 119.9 (4-C), 119.7 (5-C), 116.8 (1-C) and 115.7 (8-C). MS (70 eV): *m/z* (%), 307 ($M^{+\cdot}$, 4), 305 (12), 271 (3), 203 (60), 201 (18), 166 (9), 164 (4), 105 (100) and 77 (43).

2.3. Equipment

UV absorption spectra were recorded using a Hewlett Packard HP 8451 A UV–visible diode array spectrophotometer; shoulder positions were identified with the first and the second derivatives of the absorbance data. All the measurements were made with 1 cm stoppered quartz cells at 298 K.

Fluorescence and phosphorescence measurements were performed on a Perkin–Elmer LS 5 spectrofluorometer whose output is automatically corrected for instrumental response by means of a Rhodamine B quantum counter and equipped with a Hamamatsu R928 photomultiplier tube. The excitation spectra were performed on the same spectrometer. The fluorescence emission and excitation spectra of the solvent blanks were run in each case, to check that they showed negligible emission over the wavelength range monitored for emission and excitation experiments. The measurements at room temperature were recorded with stoppered quartz cells of 1 cm using 90° mode. The spectra at 77 K were recorded in transparent matrices produced by freezing the EPA (ethyl ether:iso-pentane:EtOH, 5:5:2) solution contained in a round cell (2 mm pathlength) with liquid N_2. Using the front surface accessory (FSA), measurements of the intensity of the fluorescence from powdered carbazoles samples were made. The powdered samples were previously kept in a dried vacuum atmosphere for at least 24 h. FSA was also used to measure fluorescence from the adsorbed phase. Carbazoles were adsorbed by silica gel surfaces (TLC aluminium sheet and silica gel 60, layer thickness 0.2 mm). These surfaces were treated as follows: the sheets were eluted with MeOH, then irradiated with a 366 nm Hg lamp for 10 min, and were finally kept at 110°C for 10 min. The carbazoles were placed on the sheet. The dried strip of the sheet showing only one fluorescent spot was placed on the FSA and the fluorescence spectra were recorded. The emission and excitation fluorescence spectra at controlled temperatures were run on the same spectrometer as well as those spectra run using triangular fluorimetric cells, 45° mode.

Laser flash photolysis experiments were performed by using a pulsed frequency quadrupled Nd:YAG laser (J. K. Lasers HY750, 15 ns FWHM, maximum energy 750 mJ at 1.06 µm). the energy of a single 266 nm pulse was monitored by using a beam splitter and a pyroelectric energy meter (Laser Precision Corp.). Laser-induced transient transmission changes were monitored, perpendicular to the laser beam, by using a Xe arc lamp (ILC UV 33P). The analyzing light passed through a 2 mm wide section of the excited sample and was then focused at the entrance slit of a 0.25 m, double-grating monochromator (PTI f/4, spectral resolution 3 nm). A photomultiplier (Hamamatsu R936) and a Tektronix R-7912 transient digitizer interfaced to a PC IBM Asyst. Programs were used to acquire and process the signals. The sequence generators, lamp pulsing unit, and back-off system were home made.

Fluorescence lifetime values (τ_{fluo}) values were measured using an Edinburg OB900 fluorometer.

Gas chromatography (GC) analysis was performed with a Hewlett Packard research gas chromatograph 5890 A equipped with capillary column (Ultra-2, 25 m × 0.2 mm × 0.11 µm; carrier, helium, 10 ml min^{-1}; oven temperature program, 100–400°C; rate, 10°C min^{-1}; detector, flame ionization (FID)). The same apparatus was employed for quantitative analysis using internal standards and evaluating calibration coefficients for all compounds whose authentic samples had been previously prepared. The quantitative data for the other components of the complex reaction mixtures are based on the relative areas related with those of the added standards.

The mass spectra were run on a VG-MASS LAB-TRIO 2 apparatus at 70 eV, using the direct insertion technique at a source temperature of 230°C. The ratios *m/z* and the relative intensities are reported in this work. GC–MS data were obtained with the same apparatus employing the Ultra-2 capillary column described above.

IR spectra were recorded on neat samples, using the Nujol technique for solids, with a Perkin–Elmer M 710 B spectrophotometer.

Nuclear magnetic resonance spectra (^{1}H- and ^{13}C-NMR) were recorded with a Bruker AC 200 spectrometer at 200 MHz. Samples were spun in 5 mm tubes at approximately 27°C. Tetramethylsilane (TMS) was used as the internal standard. Data are reported as δ values in parts per million (ppm). Relative integral ratios are given in parentheses. $DCCl_3$ was used as the solvent in all the samples.

Melting points are uncorrected and were determined on a Kofler hot-plate apparatus.

2.4. Quantum yield

Quantum yields were determined using potassium ferrioxalate as an actinometer [21]. A 6×10^{-3} mol dm^{-3} solution of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ was prepared for measurements at about 366 nm. The *N*-acyl carbazole (3.69×10^{-3} mol dm^{-3}) was dissolved in the selected organic solvent, and irradiated simultaneously with the actinometer using a high-pressure Hg lamp (Hanau TQ 150) and glass filters or a low pressure Hg lamp (Hanau TNN 15/32). The conversion of the *N*-acyl carbazole and the formation of the photoproducts were monitored by GC. The quantum yields are shown in the tables.

2.5. *Determination of the oxidation potentials of N-acyl carbazoles and reduction potentials of chloromethanes*

All the electrochemical studies were carried out in CH_3CN (J. T. Baker, HPLC grade), dried over molecular sieves (4 Å) using tetraethyl ammonium perchlorate (TEAP, 0.1 mol dm^{-3}, Fluka, polarographic grade) as the supporting electrolyte. The cell used was of conventional design. The potentials were determined by cyclic voltammetry, with a sweep rate of 300 mV s^{-1}. The working electrode was a platinum wire, the auxiliary electrode was a coiled platinum wire and the reference electrode was a saturated calomel electrode (SCE). All potentials are reported vs. SCE. The experiments were performed in an Ar atmosphere. The substrates concentrations were 5.0×10^{-4} mol dm^{-3}.

2.6. *Photoirradiation*

2.6.1. *General method for photo-fries rearrangement studies*

Solutions of the *N*-acyl carbazoles **1a** and **1b** (10 mg) were prepared in different organic media (organic solvent; 10 ml). A 2 ml aliquot of a solution was placed in a 3 ml quartz stoppered cell and was bubbled with Ar (or dry N_2 or dry O_2) during 20 min. This cell was placed in an optical bench and was irradiated with a high pressure Hg lamp (450 W, Ealing Co.) whose radiation was collimated (quartz lens) and filtered with an interference filter (Schott, path band 5 nm) to give a nearly parallel beam at 313 nm. Irradiation time was 135 min or it is indicated in each experiment. Experiments using as lamp source a low pressure Hg lamp (Hanau Quartz lampen TNK 15/32) and a medium pressure Hg lamp (Hanau Quartz lampen TQ 150) were conducted following the same methodology.

The progress of the reaction was monitored by two different methods. Method 1: TLC (eluent, hexane–CH_3COOEt (7:3, v:v), spots were visualized with UV light (254 and 366 nm) and with I_2). Method 2: GC analysis (Ultra-2 capillary column).

The photoproducts obtained, present in the photolyzed solution were identified by comparison of their R_t (retention time in GC) and MS (GC–MS technique) with those of the authentic samples. The composition as a percentage of the photolyzed mixtures were determined by quantitative GC using internal standards.

In order to study the dependence of the photo-Fries rearrangement on the concentration of *N*-benzoyl carbazole, solutions of different concentration were irradiated according the protocol above described. The results obtained are shown and discussed in Section 3.

In order to isolate, purify and characterize the photoproducts obtained, preparative photolysis was conducted according to the following procedure. A solution of *N*-acyl carbazole (200 mg) in benzene (200 ml) was placed in a Pyrex Erlenmeyer flask and was irradiated with stirring under the selected atmosphere (Ar, O_2, N_2 or air) employing an external medium pressure Hg lamp and filters (Hanau-Quartz lampen, TQ 150, $\lambda_{exc} > 313$) which were placed 10 cm from the flask. The irradiation time was 24–30 h and the progress of the reaction was monitored by TLC and GC. When the conversion of the starting material was appropriate the photolyzed solution was evaporated carefully to dryness under reduced pressure. The yellowish solid residue obtained after the evaporation of the solvent was worked up by silica gel column chromatography (eluent: hexane and hexane–CH_3COOEt mixture). From the eluted fractions, the photoproducts were isolated and characterized by comparison with authentic samples (R_T, R_f, m.p., IR, UV and ^{1}H- and ^{13}C-NMR and MS).

Irradiations of *N*-acyl carbazoles **1a** and **1b** in benzene solution in the presence of (a) tetramethyldiazetine dioxide (TMDD), (b) xanthone, (c) 1-dodecylmecapthane (RSH) and (d) cyclohexene were conducted according to the method above described. The results obtained are presented in Section 3.

Irradiations of *N*-benzoyl carbazole in benzene and in MeOH solution in the presence of I_2 were performed according to the method above described and the results obtained are shown in Section 3.

2.6.2. *General method for irradiation of N-acyl carbazoles in the presence of CCl_4*

Several solutions of *N*-acyl carbazoles **1a** and **1b** (10 mg) were prepared in different organic media (organic solvent; 10 ml). A 2 ml aliquot of the solution was irradiated according to the methods described in Section 2.6.1 during 135 min. The progress of the reaction was monitored as usual by TLC and GC analysis, and simultaneously the pH values were measured on the corresponding aqueous extract obtained from small volumes of the photolyzed solution and the Cl^- concentrations were determined by using the $AgNO_3/HNO_3$ test on the photolyzed solution (organic medium) and on the corresponding aqueous extracts. The photoproducts obtained in the photolyzed solution were identified by comparison of their R_T (GC) and MS (GC–MS) with those of the authentic samples.

The yields of the identified photoproducts, the pH values measured and the presence of Cl^- ions are discussed in Section 3.

In order to isolate, purify and identify the photoproducts the preparative photolysis were carried out according to the procedure described in Section 2.6.1. The photolyzed solution was evaporated carefully to dryness under reduced pressure and a greenish solid residue was obtained. The solid residue was separated on silica gel column chromatography (eluent, hexane) and from the eluted fractions the photoproducts were isolated and characterized (R_T, R_f, m.p., IR, UV, ^{1}H- and ^{13}C-NMR and MS).

2.6.3. Irradiation of N-acetyl carbazole and N-benzoyl carbazole mixtures

Mixtures of *N*-acetyl carbazole and *N*-benzoyl carbazole (1:1, mol:mol) in benzene solution were irradiated following the methodology described in Section 2.6.1. The results obtained are presented in Section 3.

2.6.4. Irradiation of N-acetyl carbazole and carbazole mixtures

Mixtures of *N*-acetyl carbazole and carbazole (1:1, mol:mol) in benzene solution were irradiated following the methodology described in Section 2.6.1. The results obtained are presented in Section 3.

2.7. Calculations

The ground-state geometry and heat of formation as well as static charge distribution for predicting chemical reactivity of *N*-acyl carbazoles **1a** and **1b** and possible reaction intermediates, were calculated by using the semiempirical parametrized PM3 method as implemented in version of the hyperchem 5.0 program, which has proved to be effective in studies on molecules containing heteroatoms, compared with other methods such as MINDO/3 or MNDO [25].

3. Results and discussion

3.1. Photo-Fries rearrangement

When *N*-acetyl carbazole (**1a**) (4.78×10^{-3} mol dm^{-3}) in benzene, under an Ar atmosphere, was irradiated with $\lambda_{exc} = 313$ nm (high pressure Hg lamp, Ealing Co., 250 W, see Section 2), three main photoproducts were obtained. As was expected, 1-acetyl carbazole (**2a**), 3-acetyl carbazole (**3a**) and carbazole (**4**) were obtained together with small amounts of acetaldehyde and diacetyl (**5**) and unconverted *N*-acetyl carbazole (Scheme 1, reaction a). As is shown in Table 1, the *N*-acetyl carbazole conversion and the **2a** and **3a** product yields are slightly lower when irradiations were conducted in the presence of air or O_2. The minor effect would suggest that O_2 does not quench efficiently the electronic excited state which gives the photorearrangement being this reactive excited state the S_1 state. In agreement with this suggestion the effect of O_2 on *N*-acetyl carbazole conversion quantum yield (ϕ_1, see Table 1) is also minor. Similar results were obtained with *N*-benzoyl carbazole (**1b**) (Scheme 1, reaction a and Table 1).

Additionally, we conducted some experiments in order to check the S_1 character of the reactive excited state. Thus, taking into account the energy of the T_1 state of *N*-acetyl carbazole ($E_T = 68.9$ kcal mol^{-1}; phosphorescence at 77 K in EPA (5:5:2) solution, $\lambda_{exc} = 313$ nm, λ_{max}(em) = 415 nm, see Section 2) and of the T_1 state of *N*-benzoyl carbazole ($E_T = 68.5$ kcal mol^{-1}, phosphorescence at 77 K in EPA (5:5:2) solution, λexc = 310 nm, λmax = 416 nm), xanthone ($E_T = 74.0$ kcal mol^{-1} [20,26]) and tetramethyl-diazetine dioxide (TMDD; $E_T = 54.0$ kcal mol^{-1} [20,26]) were selected to be used as a triplet photosensitizer (the former) and as a triplet quencher (the latter) [20]. As a result, no reaction was observed in benzene solution when *N*-acetyl carbazole and *N*-benzoyl carbazole were irradiated in the presence of xanthone ($\lambda_{exc} = 365$ nm) while normal photo-Fries rearrangement was observed in the presence of TMDD.

Table 1
Irradiation of *N*-acyl carbazoles in benzene under different atmospheres [a]. Photoproducts obtained and quantum efficiency of **1a** and **1b** conversion

Atmosphere	Conversion (%)	ϕ_{1a} [c]	Photoproducts (%) [b]		
			N-acetyl carbazole		
			4	**2a**	**3a**
Ar	84.0	0.065	19.3	51.0	13.6
Air	76.0	0.065	19.1	44.4	11.8
O_2	73.5	0.063	18.9	44.4	10.2
			N-benzoyl carbazole		
		ϕ_{1b} [c]	**4**	**2b**	**3b**
Ar	42.5	0.034	10.1	22.7	8.4
Air	39.8	0.029	11.2	20.4	6.6
O_2	40.0	0.029	10.8	19.6	7.1

[a] Concentration: **1a**, 4.78 mol dm^{-3}; **1b**, 3.69×10^{-3} mol dm^{-3}; 313 nm; *T*, 298 K; irradiation time, 120 min.

[b] Calculated by GC.

[c] Quantum efficiency of **1** conversion, obtained at low conversion of **1**; I_0, 1.09×10^{-6} Einstein min^{-1}; actinometer, potassium ferrioxalate.

We also studied the photochemical behavior of both *N*-acyl carbazoles in solution at different λ_{exc} values (254 and 320 nm). In order to use $\lambda_{exc} = 254$ nm we needed to use EtOH as solvent. In these experiments we calculated k_{obs} from the slopes of *N*-acetyl carbazole conversion percentages versus time plots. In our hands, the photo-Fries rearrangement of **1a** and **1b** did not show any significant dependence on wavelength, contrary to the wavelength dependence for *N*-benzoyl carbazole photo-Fries rearrangement claimed by Gosh et al. [27,28].

Besides, we also studied the combined effect of the light intensity and wavelength on the photo-rearrangement but no noticeable difference was observed. Thus, we can conclude that the photo-absorption step would not be the limiting velocity step (slowest step) of the photo-Fries rearrangement.

In order to study the effect of the properties of the solvent on the photochemistry of *N*-acyl carbazoles we conducted irradiation of *N*-acetyl carbazole (4.78×10^{-3} mol dm^{-3}) in cyclohexane, THF, $HCCl_3$, CH_3CN, DMF as well as EtOH and CH_2Cl_2. As is shown in Table 2, an increase in the polarity of the solvent diminishes the conversion of *N*-acetyl carba-

Table 2
Irradiation of **1a** and **1b** in different solvents [a]. Yield [b] of the products obtained and k_{obs} [c]

Solvent	$E_T(30)$ [d] (kcal mol^{-1})	$k_{obs}(\times 10^{-3})$ (min^{-1})	Conversion (%)	Photoproducts (%) [b]		
				4	**2**	**3**
1a					**2a**	**3a**
Cyclohexane	30.9	16.28	70.5	12.7	49.0	8.6
Benzene	34.3	15.28	72.1	17.5	47.0	7.6
THF	37.4	11.30	57.2	10.5	44.3	8.2
$CHCl_3$	39.1	12.20	60.0	10.0	41.9	8.1
CH_2Cl_2	40.7	9.87	53.4	13.0	36.3	4.1
DMF	43.8	8.00	43.1	3.7	35.5	3.9
CH_3CN	45.6	5.00	31.3	13.0	16.5	1.8
EtOH	51.9	5.87	35.6	15.6	14.2	5.8
CCl_4	32.2	4.88	10.1 [e]		9.7	1.0
1b					**2b**	**3b**
Benzene	34.3	4.05	42.2	6.3	24.8	12.0
CH_2Cl_2	40.7	0.36	4.8	1.0	2.5	1.3
$CHCl_3$	39.1					
CCl_4	32.2					
EtOH	51.9	3.06	33.9	10.1	23.9	11.5

[a] Concentration: **1a**, 4.78×10^{-3} mol dm^{-3}; **1b**, 3.69×10^{-3} mol dm^{-3}; λ_{exc}, 313 nm; irradiation time, 75 min; T, 298 K; atmosphere, air.
[b] Calculated by GC.
[c] $k_{rel}(S) = k_{obs}(\text{cyclohexane})/k_{obs}(S)$; S, solvent. $K_{rel}(S)$, 1 (cyclohexane); 1.03 (benzene); 1.44 (THF); 1.33 ($HCCl_3$); 1.65 (CH_2Cl_2); 2.04 (DMF); 3.26 (CH_3CN) and 2.77 (EtOH).
[d] Ref. [29].
[e] 3-Chloro-*N*-acetyl carbazole (1.2%) was also detected as product.

zole. This effect is clearly shown in the value of k_{rel}, defined in the solvent (S) as $k_{rel}(S) = k_{obs}(\text{cyclohexane})/k_{obs}(S)$. This dependence of k_{obs} on the polarity of the medium is similar to the observed effect of the polarity of the solvent on the absorption and fluorescence spectra (Stokes' shifts, see Table 9 and Section 3.5.). The effect observed on carbazole yield (**4**) is a bit different; not only the polarity of the solvent but also its hydrogen donor character, expressed as an α value [29,30], would account for the carbazole yield. From the mechanistic point of view the carbazole would be originated by reaction of carbazolyl radical with the hydrogen donor solvent present in the solvent cage. Additionally irradiations of *N*-acetyl carbazole (4.78×10^{-3} mol dm^{-3}) and *N*-benzoyl carbazole (3.69×10^{-3} mol dm^{-3}) in benzene under Ar atmosphere in the presence of (a) 1.7 mol dm^{-3} of EtOH or (b) 0.1 mol dm^{-3} of 1-dodecylmercapthane (RSH) showed a drastic increase in the carbazole yield (Table 3). The presence of an hydrogen donor species in the reaction medium (benzene, $\alpha=0.00$; EtOH, $\alpha=0.86$ and RSH, $\alpha=0.90$ [26,30]) would account for the results obtained. In the same way can be explained the carbazole yield obtained in CH_2Cl_2 ($\alpha=0.13$ [26,29,30]), CH_3CN ($\alpha=0.19$ [26,29,30]) and $HCCl_3$ ($\alpha=0.20$ [13,16,17]) shown in Table 2.

Finally we can mention that the photo-rearrangement was not modified when cyclohexene, a radical scavenger, was added to the benzene solution (experiments conducted under Ar atmosphere) and that by irradiation of a 1:1 (mol: mol) mixture of *N*-acetyl carbazole and carbazole in benzene, any dimeric product (*N,N'*-bicarbazolyl [8,9] was observed. Both results suggest that the photo-Fries rearrangement takes place in the solvent cage and that the carbazolyl radicals do not diffuse freely in the medium, probably reacting with hydrogen donor species which are close to the solvent cage.

As can be seen in Tables 2 and 3, similar results were obtained for *N*-benzoyl carbazole. Besides, as shown in Table 4, the quantitative composition of photolysis products

Table 3
Irradiation of benzenic solution of **1a** and **1b** [a] in the presence of EtOH and 1-dodecylmercapthane (RSH). Yields [b] of the photoproducts obtained

Hydrogen donor	Concentration (mol dm^{-3})	Conversion (%)	Photoproducts (%) [b]		
			4	**2**	**3**
1a				**2b**	**3b**
		72.1	17.5	47.0	7.6
EtOH	1.7	66.6	23.8	35.5	6.2
RSH	0.1	79.0	34.4	35.8	6.3
1b				**2b**	**3b**
		42.2	6.3	24.8	12.0
EtOH	1.7	65.3	61.4	3.8	
RSH	0.1	66.3	62.6	4.0	

[a] Concentration: **1a**, 4.78×10^{-3} mol dm^{-3}; **1b**, 3.69×10^{-3} mol dm^{-3}; λ_{exc}, 313 nm; irradiation time, 75 min; T, 298 K.
[b] Calculated by GC.

Table 4
Effect of the concentration on the conversion of *N*-benzoyl carbazole in benzene [a]. Photoproducts yield (%) and conversion of **1b**

Concentration ($mol\ dm^{-3}$) **1b**	Conversion (%) **1b**	Photoproducts (%) [b] **4**	**2b**	**3b**
3.69×10^{-2}	3.7	2.5	0.5	0.7
1.85×10^{-2}	7.0	4.3	1.2	1.4
7.38×10^{-3}	16.9	11.2	2.7	2.9
3.69×10^{-3}	14.5	12.0	2.5	2.5
2.21×10^{-3}	77.0	68.2	4.0	4.0
1.48×10^{-4}	81.0	65.2	6.4	6.5
7.38×10^{-4}	89.7	64.0	9.6	9.9

[a] Experimental conditions, see footnotes Table 2.

[b] Measured by GC.

strongly depends on the *N*-benzoyl carbazole concentration. If the concentration of *N*-benzoyl carbazole is higher than 10^{-4} mol dm^{-3} (10^{-3} to 10^{-2} mol dm^{-3}), the non-converted *N*-benzoyl carbazole is recovered in high yield and 1-benzoyl and 3-benzoyl carbazole are obtained in low yield. Similar results had been previously obtained regarding the concentration effect on the photo-Fries rearrangement of *N*-acetyl carbazole [6,7].

It should be noted that, in 1989, Chakrabarti et al. [5] reported that *N*-benzoyl carbazole did not undergo photo-Fries rearrangement and no expected photo-rearranged products could be obtained although some carbazole was isolated. Irradiation were performed in benzene or MeOH at 254 or at 365 nm, in N_2 atmosphere at *N*-benzoyl carbazole concentration 1.2×10^{-2} mol dm^{-3}. Besides, Ghosh et al. [3,4] described the photochemical rearrangement of *N*-benzoyl carbazole. First [3], they described the oxidative irradiation of this substrate in MeOH (1.05×10^{-2} mol dm^{-3}) with I_2 as oxidant, at different wavelengths.

They conclude that the product ratio was wavelength dependent; at 254 nm, only 3-benzoyl carbazole was isolated meanwhile, at 365–366 nm, the 1-benzoyl carbazole was the predominant rearranged product in the reaction mixture (1-benzoyl (15%) and 3-benzoyl carbazole (5%)). Second [4], they described the photolysis of *N*-benzoyl carbazole in MeOH, MeOH + I_2 and benzene, with different wavelength (254 and 365–366 nm) and the additional conclusion was that in benzene without I_2, at both wavelengths, only 1-benzoyl carbazole was obtained (yield < 10%). In our hands, when a 10^{-2} mol dm^{-3} solution of *N*-benzoyl carbazole in MeOH with I_2 (5.6×10^{-3} mol dm^{-3}) was irradiated at 254 nm during 24 h, no photo-rearranged product was obtained. On the contrary, when a 10^{-3} mol dm^{-3} solution was irradiated, in the presence of I_2 (1×10^{-3} mol dm^{-3}) during 24 h, we obtained both at 254 and 366 nm a similar product distribution as those obtained in simultaneous irradiations of *N*-benzoyl carbazole in MeOH without I_2. According to our results, the 1-benzoyl to 3-benzoyl carbazole molar ratio obtained by irradiation in the presence of I_2 is not wavelength dependent, although it is concentration dependent. Additionally, as can be seen in Table 2, in benzene solution without I_2, 1-benzoyl carbazole was obtained together with 3-benzoyl carbazole in a 2:1 molar ratio.

3.2. Photo-Fries rearrangement: kinetics

The kinetic aspects of the photolysis of *N*-acyl carbazoles **1a** and **1b** were studied and from the plots of conversion of carbazole versus irradiation time was concluded that the conversion follows the equation $C = C_o\exp(-k_{obs}t)$ (pseudo-first-order kinetics). Thus, the plots of $\ln(C_o/C)$ versus time (min) were lineal and from the slopes we obtained the corresponding k_{obs}. These values together with the conversion quantum yield of **1a** (ϕ_{1a}), the formation quantum yield of products ($\phi_p = \phi_{2a} + \phi_{3a}$), the formation quantum yield of carbazole (ϕ_4) and R, defined as $R = (\phi_{2a} + \phi_{3a})/\phi_4$, are shown in Table 5. In agreement with the results presented in Table 2, the ϕ_{1a} and the k_{obs} are lower at higher solvent polarity while ϕ_p keeps anomalous high values because it includes the ϕ_4 value which, as we commented, depends on the hydrogen donor character of the solvent. This apparently anomalous behavior of ϕ_p and ϕ_4 is clearly shown in the values of R. Finally, the ϕ obtained for products **2a** and **3a** are shown in Table 6 and it can be seen that there is no clear quenching effect of $HCCl_3$ and CH_2Cl_2 in the photo-formation of the rearranged products and, as we describe later in the present paper, even in CCl_4 we observed to some extent photo-Fries rearrangement. These results are quite different

Table 5
Irradiation of **1a** in different organic solvents [a]. k_{obs} and ϕ_p

Solvent	$E_T(30)$ (kcal mol^{-1})	k_{obs} (min^{-1})	ϕ_{1a} [b]	ϕ_p [c]	ϕ_4	$\phi_{2a}+\phi_{3a}$	R [d]
Cyclohexane	30.9	1.63×10^{-2}	0.137	0.0107	0.0019	0.0088	4.6
CH_2Cl_2	40.7	9.87×10^{-3}	0.080	0.0040	0.0010	0.0028	2.8
CH_3CN	45.6	5.00×10^{-3}	0.043	0.0033	0.0013	0.0018	1.4
EtOH	51.9	5.87×10^{-3}	0.050	0.0043	0.0019	0.0027	1.3

[a] Concentration of **1a**, 4.78×10^{-3} mol dm^{-3}; λ_{exc}, 313 nm; T, 298 K.

[b] Calculated by GC; I_o, 1.09×10^{-6} Einstein min^{-1}; actinometer, potassium ferrioxalate; conversion of **1a** < 10%.

[c] Calculated from ϕ_{1a}.

[d] Calculated as $R = (\phi_{2a} + \phi_{3a})/\phi_4$.

Table 6
Irradiations of **1a** in different organic solvents [a]. Quantum efficiency of formation of the products **2a** and **3a**

Solvent	ϕ_{3a} [b]	ϕ_{2a} [b]	ϕ_{2a}/ϕ_{3a}
Cyclohexane	0.0074	0.0014	5.2
Benzene	0.0066	0.0011	6.0
THF	0.0048	0.0008	6.0
$CHCl_3$	0.0044	0.0008	5.5
CH_2Cl_2	0.0026	0.0005	5.0
DMF	0.0018	0.0003	6.0
CH_3CN	0.0016	0.0003	6.2
EtOH	0.0017	0.0003	4.9

[a] Concentration of **1a**, 4.78×10^{-3} mol dm^{-3}; λ_{exc}, 313 nm; atmosphere, Ar; *T*, 298 K.
[b] Calculated by GC.

than those we show in Table 4 for *N*-benzoyl carbazole, which in CH_2Cl_2 showed a conversion ten times lower than those in benzene and in EtOH, while no photo-rearrangement was observed in $HCCl_3$ and in CCl_4 solution. A lower *N*-benzoyl carbazole S_1 population would account for the high efficient quenching of the *N*-benzoyl photo-Fries rearrangement by CCl_4, $HCCl_3$ and also CH_2Cl_2 [7].

3.3. Irradiations in the presence of chloroalkanes

In our laboratory we have been studying the photochemical behavior of several nitrogen organic compounds in the presence of CCl_4 [6,7,10–17] as part of a program related with the study of photoinduced electron transfer processes and the applications of Rehm–Weller–Gibbs [31,32] and Marcus–Hush [31,32] equations. Thus, we decided to investigate the photochemistry of *N*-acetyl carbazole in CCl_4 solution.

When *N*-acetyl carbazole (4.78×10^{-3} mol dm^{-3}) in CCl_4 (Ar atmosphere, irradiation time 75 min) was irradiated according to the general method described in Section 2, the formation of 1-acetyl carbazole (**2a**, 9.7%), 3-acetyl carbazole (**3a**, 1%) and 3-chloro-*N*-acetyl carbazole (**6a**, 1.2%) was observed together with a low conversion of the *N*-acetyl carbazole (10.9%) (Scheme 1, reactions a and b). Also the kinetic parameters obtained, $k_{obs} = 4.88 \times 10^{-3}$ min^{-1} and $\phi_{1a} = 0.0127$, compared with those presented in Tables 2 and 5 showed a lower efficiency for the photo-Fries rearrangement of compound **1a** in CCl_4 medium. By comparing these results with those obtained in cyclohexane, benzene, EtOH and other organic solvents (see Table 2) and taking into account the fluorescence quenching experiments described in this work, we can conclude that the electronic excited state responsible for the photo-Fries rearrangement, the S_1 state, is efficiently quenched by CCl_4, probably giving an exciplex, as follows:

$$^{1}N{-}AcCA^{*} + CCl_4 \rightarrow [N{-}AcCA^{\delta+} \ldots CCl_4^{\delta-}]^{*} \quad (E_2^{*})$$

$$E_2^{*} \rightarrow N{-}AcCA + CCl_4 + \text{heat}$$

from which an emissive fluorescence process was not observed

$$E2^{*} \rightarrow N{-}AcCA + CCl_4 + h\nu_{EXP}$$

Additionally, in some extent an enhanced intersystem crossing process must be taking into account in the presence of CCl_4 (heavy atom effect or external spin–orbital coupling [20,33])

$$^{1}N{-}AcCA^{*} + CCl_4 \rightarrow {}^{3}N{-}AcCA^{*} + CCl_4$$

The yield of 3-chloro-*N*-acetyl carbazole (**6a**) (Scheme 1, reaction b) as photoproduct backs up the suggestion of an exciplex formation followed by an electron transfer process and the nucleophilic substitution by Cl^- at *N*-acetyl carbazole cation radical present in the solvent cage, to give the chloroderivative **6a**.

$$[N{-}AcCA^{\delta+} \ldots CCl_4^{\delta-}]^{*} \rightarrow [N{-}AcCA^{+\cdot}\ {}^{\cdot}CCl_3 \ldots {}^{-}Cl]$$

$$[N{-}AcCA^{+} \ldots {}^{\cdot}CCl_3 \ldots {}^{-}Cl] \rightarrow \underset{(6a)}{N{-}AcCA{-}Cl} + HCCl_3$$

The charge density values calculated for *N*-acetyl carbazole as radical cation species would account for this nucleophilic substitution proposed.

The *N*-acetyl carbazole cation radical was characterized by its absorption spectrum (λ_{max}(abs) = 500 nm) and its life-

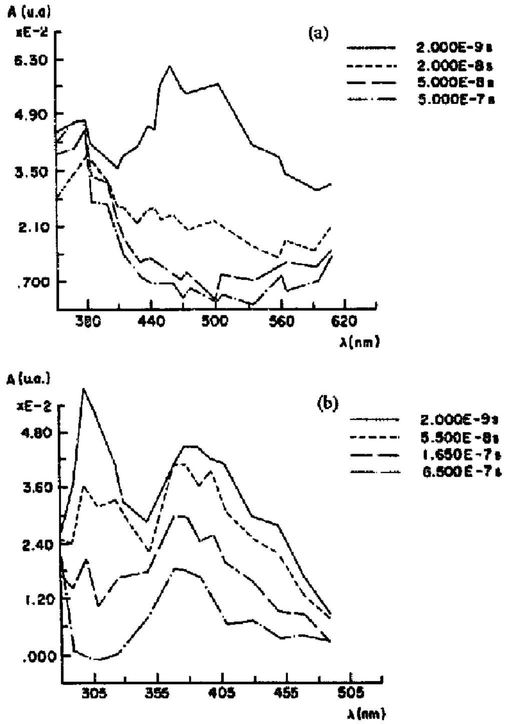


Fig. 1. Time evolution of the absorption spectrum of the *N*-acetyl carbazole cation radical **1a** and *N*-benzoyl carbazol cation radical **1b**. Laser flash photolysis experiments: solvent, CCl_4; λ_{exc}, 266 nm; *T*, 298 K.

time (τ = 15.19 ns) when a 5.20×10^{-5} mol dm^{-3} solution of *N*-acetyl carbazole in CCl_4 was used in laser flash photolysis experiments (see Fig. 1 and Section 2).

Besides, the absence of carbazole (**4**) in the reaction mixture as well as of dimeric products such as bicarbazolyl compounds that we had described elsewhere [8,9] suggested that in CCl_4 medium the carbazolyl radical would not be formed in high yields and, additionally, if it were formed it would not escape from the solvent cage.

Additionally we studied the photochemical behavior of *N*-acetyl carbazole in CCl_4–benzene, CCl_4–CH_3CN and CCl_4–EtOH mixtures. As can be seen in Table 7, the electron transfer process would be the only process in all the CCl_4–EtOH mixtures studied, while in benzene even at the highest CCl_4 concentrations (1.024 and 5.024 mol dm^{-3}) the main process would be the photo-Fries rearrangement and in CCl_4–CH_3CN mixtures both photo-processes would have similar efficiency.

It is interesting to note the results obtained when *N*-benzoyl carbazole (3.60×10^{-3} mol dm^{-3}) was irradiated in benzene and in EtOH, in the presence of CCl_4 (5.024 mol dm^{-3}, Ar atmosphere). No reaction was observed in benzene–CCl_4 media while in EtOH–CCl_4 media *N*-benzoyl carbazole was partially converted into carbazole (**4**, 3.0% yield) and 3-chloro-*N*-benzoyl carbazole (**6b**, 15% yield). At the end of the latter experiment Cl^- was detected ($AgNO_3/HNO_3$ test) and pH 4 was measured. The UV, fluorescence excitation and emission spectra together with the photochemical behavior of *N*-benzoyl carbazole in benzene–CCl_4 and in EtOH–CCl_4 let us suggest that, although the absorption spectra do not substantiate the existence of a CTC of *N*-benzoyl carbazole with CCl_4, both in the ground state, it can be assumed that an electron transfer proceeds in the exciplex $[A^{\delta+}\ldots CCl4^{\delta-}]^*$ in polar protic media. In benzene medium the dissipation of the singlet excitation energy of the exciplex by radiative and non-radiative processes are the main stabilization pathways. In EtOH medium the additional stabilization by solvatation of the polar exciplex and the ionic radical species formed in the solvent cage $[A^{+}\ldots{}^{\cdot}CCl_3\ldots Cl^{-}]$ would explain the photochemical behavior observed. By using laser flash-photolysis spectroscopy the *N*-benzoyl carbazol cation radical ($A^{+\cdot}$) was characterized in CCl_4 medium, by its absorption spectrum (λ_{max} = 395 nm) and by its τ_0 = 168.3 ns (Fig. 1).

In conclusion, the simultaneous presence of CCl_4, as an efficient electron acceptor, and a solvent of high polarity and hydrogen donor character are necessary to yield and to stabilize the primary cation radical, anion radical and radical formed in the solvent cage. In these environmental conditions the back electron transfer process is not important and the photo-induced electron transfer process can compete efficiently with the photo-Fries rearrangement.

3.4. *Irradiations in the presence of chloroalkanes: kinetics*

In order to study the kinetic aspects of the photolysis of *N*-acetyl carbazole in the presence of CCl_4 we used a set-up that provided λ_{exc} 313 nm (see Section 2) and CCl_4 concentrations lower than or equal to 9 mol dm^{-3} because in these experimental conditions the only species that absorbs radiation is the *N*-acetyl carbazole. Thus, our experimental conditions correlate with those of the Rehm–Weller [31,32] expression that we used in order to evaluate the possibility of an electron transfer process from *N*-acetyl carbazole electronic excited to CCl_4 in the ground state. Besides, in this way we reproduce the conditions used in the fluorescence quenching experiments (λ_{exc} 310 nm).

Thus, when a 4.78×10^{-3} mol dm^{-3} solution of *N*-acetyl carbazole under Ar atmosphere was irradiated in the presence of different concentrations of CCl_4 (1.0–9.0 mol dm^{-3}) we observed that the rate of *N*-acetyl carbazole conversion is high at higher CCl_4 concentration, so the photoconversion is a bimolecular process. Additionally, from the plots of ln(C_0/C) versus time (min) the corresponding k_{obs} values were

Table 7
Irradiation of **1a** in different organic solvents in the presence of CCl_4 [a]

Solvent	CCl_4 (mol dm^{-3})	Conversion (%)	ϕ_{1a} [c]	Photoproducts (%) [b]				pH
				4	**2a**	**3a**	**6a**	
Benzene		70.5	0.134	17.5	47.0	7.6		neutral
Benzene	0.048	65.3	0.044	11.8	49.2	7.3		neutral
Benzene	0.502	50.0	0.034	4.6	44.2	7.8		neutral
Benzene	1.024	38.2	0.037	2.6	23.5	5.0	0.1	6
Benzene	5.024	33.3	0.019	1.6	27.9	>0.1	0.4	5
CH_3CN		31.3	0.043	3.7	35.5	3.9		neutral
CH_3CN	5.024	10.7	0.007	0.6	2.4	>0.1	4.5	1
EtOH		35.6	0.050	15.6	14.2	5.8		neutral
EtOH	0.212	2.0	0.015	3.2	2.9		1.0	5
EtOH	1.024	10.0	0.055	1.2			8.5	2
EtOH [d]	5.024	12.0	0.066	1.4			10.3	2

[a] Concentration of **1a**, 4.78×10^{-3} mol dm^{-3}; λ_{exc}, 313 nm; irradiation time, 75 min; atmosphere, Ar; T, 298 K.

[b] Calculated by GC.

[c] Quantum efficiency of **1a** with **1a** conversion = 19%; $I_0 = 1.09 \times 10^{-6}$ Einstein min^{-1}; actinometer, potassium ferrioxalate.

[d] Irradiation time, 17 min.

obtained: k_{obs} (min^{-1}) (CCl_4 concentrations; mol dm^{-3}), 1.66×10^{-3} (1.0), 3.78×10^{-3} (3.0), 6.06×10^{-3} (5.0), 6.80×10^{-3} (7.9) and 7.20×10^{-3} (9.0). A linear relation between k_{obs} and CCl_4 concentration was observed until $[CCl_4] < 4$ mol dm^{-3}. At higher CCl_4 concentration the ratio between both variables is not linear and k_{obs} tends to the k_{obs} limit value which is aproximately 7.50×10^{-3} min^{-1}. This results suggests that at CCl_4 concentrations higher than 5 mol dm^{-3}, the quenching sphere [20] of *N*-acetyl carbazole has on average one (or more) molecule of CCl_4. As a consequence, the system is less sensitive to the additional CCl_4 molecules added to the medium and at these high concentrations the environmental conditions of the *N*-acetyl carbazole molecules are similar to those in the so-called static quenching conditions [20,33].

Additionally, in the same experiments the *N*-acetyl carbazole consumption quantum yield (ϕ_{1a}) was measured in conditions that the *N*-acetyl carbazole conversion was not higher than 10%. According to these results we can suggest that during the first 45 min of irradiation the process follows pseudo-first-order kinetics but at longer irradiation time periods the *N*-acetyl carbazole consumption occurs at higher velocities. Considering an irradiation period of 135 min, we simulate theoretically the plot of consumption of *N*-acetyl carbazole (%) versus time, considering that *N*-acetyl carbazole consumption follows the equation $C = C_0\exp(-k_{obs}t)$. After 45 min the experimental data obtained do not match the theoretical curve (values) calculated. The simultaneous consumption of *N*-acetyl carbazole through a parallel process is obvious. As we know that the pH of the solution was diminishing during the irradiation of *N*-acetyl carbazole in the presence of CCl_4 in benzene, CH_3CN and EtOH media, we ran some experiments in order to study the stability of *N*-acetyl carbazole in organic acid medium. Thus, a 4.28×10^{-3} mol dm^{-3} solution of *N*-acetyl carbazole in EtOH was bubbled with HCl(g) until pH 2 was reached, and to a 4.78×10^{-3} mol dm^{-3} solution of *N*-acetyl carbazole in EtOH the buffer potassium hydrogen oxalate–NaOH was added in order to keep pH 4. Both solutions were kept in the dark during 4 h. At pH 2 the *N*-acetyl carbazole hydrolysis follows pseudo-first-order kinetics while at pH 4 the hydrolysis process is minor. In agreement with our experimental results, when during the photolysis in organic media in the presence of CCl_4 the pH reaches a value near by 3, the acid hydrolysis of *N*-acetyl carbazole begins to compete with the photo-induced electron transfer and as consequence more acetyl carbazole is consumed.

Table 8
Effect of organic solvents on the λ_{max}(abs) of *N*-acyl carbazoles [a]

Solvent	$E_T(30)$ [b]	λ_{max}(abs) (nm)	
		N-acetyl carbazole	*N*-benzoyl carbazole
Hexane	30.9	314	316
CCl_4	32.5	316	316
Benzene	34.5	316	316
p-Dioxane	36.0	316	316
$CHCl_3$	39.1	314	316
CH_2Cl_2	41.1	314	316
Acetone	42.2	314	316
tert-BuOH	43.9	312	314
CH_3CN	45.6	314	314
i-PrOH	48.6	312	314
n-PrOH	50.7	312	314
EtOH	51.9	312	314
MeOH	55.5	312	314

[a] Concentration, 4.78×10^{-5} mol dm^{-3}; *T*, 298 K.
[b] Ref. [29].

Besides, as has been discussed previously (see the results shown in Table 7) from the electronic excited state *N*-acetyl carbazole can also give the photo-Fries rearrangement, this

Table 9
Effect of the solvent on the electronic spectrum of *N*-acyl carbazoles **1a** and **1b** [a]

Solvent	λ_{abs} (0,0) (nm)	ν_{abs} (0,0) (cm^{-1})	$\Delta\nu_{abs}$ [a] (cm^{-1})	λ_{fluo} (0,0) (nm)	ν_{fluo} (0,0) (cm^{-1})	$\Delta\nu_{fluo}$ [b] (cm^{-1})	ΔStokes [c] (cm^{-1})	E_{abs} (S_1) (kcal mol^{-1})	E_{fluo} (S_1) (kcal mol^{-1})	ϕ_{fluo}	τ_{fluo} [e] (ns)
1a											
Hexane	312	32051		337	29674		2377	91.7	84.9	0.093	
CH_2Cl_2	314	31847	204	338	29586	88	2261	91.1	84.6	0.049	8.2
EtOH	315	31746	305	342	29240	434	2506	90.8	83.6	0.053	10.3
CH_3CN	316	31646	405	343	29155	348	2491	90.5	83.4	0.051	
1b											
Hexane	312	32051		341	29326		2725	91.7	83.7	0.034	
CH_2Cl_2	314	31847	204	343	29155	171	2692	90.8	83.4	0.047	
EtOH	315	31746	305	344	29070	256	2676	90.2	82.2	0.010	12.6
MeCN	317	31153	898	345	28986	340	2167	89.2	82.9	0.008	

[a] Concentration, 10^{-5} mol dm^{-3}; λ_{exc}, 310 nm; *T*, 298 K;
[b] $\Delta\nu_{abs} = \nu_{abs}(0,0)$ [hex] $- \nu_{abs}(0,0)$ [solv.].
[c] $\Delta\nu_{fluo} = \nu_{fluo}(0,0)$ [hex] $- \nu_{fluo}(0,0)$ [solv.].
[d] $\Delta = \nu_{abs}(0,0) - \nu_{fluo}(0,0)$.
[e] Fluorescence lifetime measured in the present work.

fact depending on the environmental properties where the electronic excited state is created.

3.5. Spectroscopic studies: UV absorption and fluorescence

To shed some light on the mechanism of the interaction of *N*-acyl carbazoles **1a** and **1b** with halomethanes and especially with CCl_4, the electronic absorption spectra in halomethane solutions as well as the quenching of *N*-acetyl carbazole fluorescence emission by halomethanes was investigated.

Thus, in Table 8 the effect of solvents of different polarity, expressed as $E_T(30)$ [29] and the λ_{max}(abs) is shown. As can be seen, although the shifts are small they are the typical minor bathochromic shifts of the π,π^* transitions because of the high polar character of the solvents. In order to quantify this solvent effect simultaneously on *N*-acyl carbazole absorption and on fluorescence emission spectra, we calculated the Stokes' shifts [33] (ΔStokes $= \nu_{abs}(0,0) - \nu_{fluo}(0,0)$) from the absorption ($\nu_{abs}(0,0)$) and emission fluorescence ($\nu_{fluo}(0,0)$) spectra. By combining this equation with the one that includes the Lippert parameter (ΔL) for each solvent, $\Delta\text{Stokes} = 2(\mu_e - \mu_f)2\Delta L/hcr^3$ [33] where the Lippert parameter can be calculated as $\Delta L = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$ [33], we could calculate the $\Delta\mu = \mu_e - \mu_f$ value (difference between the ground state and S_1 state dipolar moment) and compared it with that obtained by semiempirical calculations (PM3 and ZINDO/S methods as they are implemented in hyperchem 5.0) [25]. As is shown in Table 9, in which also the *N*-acetyl and *N*-benzoyl carbazoles fluorescence quantum yields (ϕ_{fluo}) and their fluorescence lifetimes (τ_{fluo}) in different solvents are included, the Stokes' shifts for *N*-acetyl carbazole are almost similar, just slightly smaller, than the *N*-benzoyl carbazole Stokes' shifts but they are quite different from that corresponding to carbazole [7] (ΔStokes carbazole < 1000). The presence of the polarizable carbonyl group in the *N*-acyl carbazole derivatives and the higher $\Delta\mu$ values theoretically and experimentally calculated ($\Delta\mu$ (Debye), carbazole 2.39, *N*-acetyl-carbazole 4.45 and *N*-benzoyl carbazole 6.40) would account for these results. The same fact would explain the dependence on the polarity of the solvent shown by the relative intensity (RI) of the fluorescence emission and the ϕ_{fluo} of the *N*-acetyl carbazole (Table 9). Besides, the ϕ_{fluo} for *N*-acetyl and *N*-benzoyl carbazole are ten times minor that those for carbazole; owing to the presence of the carbonyl group, the S_1 to T_1 process (intersystem crossing) is more efficient making, as a consequence, the *N*-acyl carbazole phosphorescence quantum yield higher.

We also studied the fluorescence of **1a** and **1b** in halomethane solutions. As expected, with an increasing number of chlorine atoms in the halomethane molecule, the intensity of the *N*-acetyl carbazole fluorescence decreases ($EtOH > CH_2Cl_2 > HCCl_3$) disappearing completely in CCl_4 medium (external spin–orbital coupling or heavy atom effect [20]). Although halomethanes showed a similar effect on *N*-benzoyl carbazole fluorescence, the presence of a new fluorescence species (exciplex) was observed in *N*-benzoyl carbazole–CCl_4 systems.

Although no emissive exciplex could be detected in *N*-acetyl carbazole–halomethane solutions, as shown in Fig. 2, the Stern–Volmer dependence for the fluorescence quenching of *N*-acetyl carbazole is linear. The values of K_{SV} obtained (see Table 10) indicates that in each organic medium used the fluorescence quenching of *N*-acetyl carbazole can be related with the electron affinity of the halomethane, expressed as the reductive potential value (E_{red}) and as the ΔE(LUMO − HOMO) of each halomethane (see Table 11), which also indicates that the halomethane acts as electron acceptor.

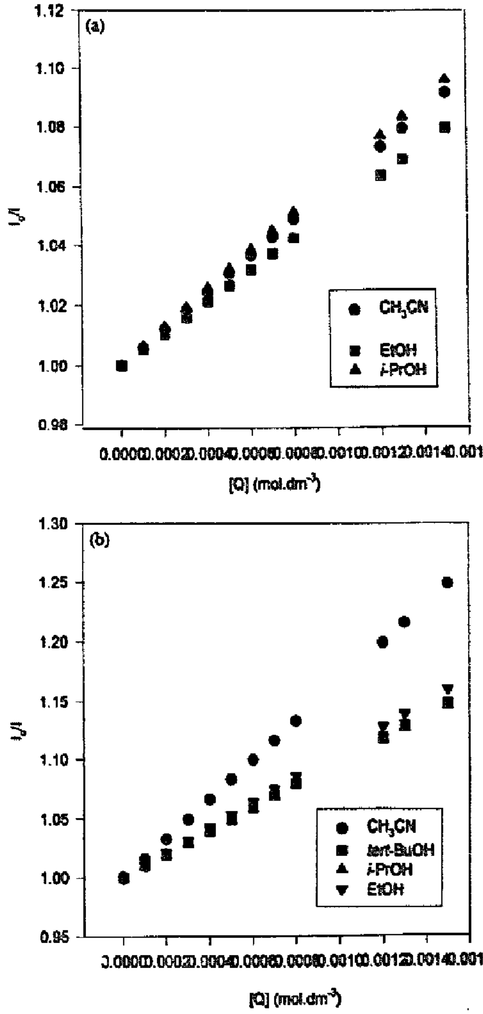


Fig. 2. Plots of I_0/I vs. [Q] (Q, quencher). (a) Q, $HCCl_3$; solvent, CH_3CN (●), EtOH (■), i-PrOH (▲); and (b) Q, CCl_4; solvent, CH_3CN (●), EtOH (▼), i-PrOH (▲) and tert-BuOH (■). Concentration of **1a**; 2.40×10^{-5} mol dm^{-3}; λ_{exc}, 310 nm; *T*, 298 K.

Table 10
Stern–Volmer constants (k_{sv}) for *N*-acetyl carbazole in different organic media using chloroalkanes as quenchers

Quenchers	k_{SV} (M^{-1}) [a]			
	CH_3CN 3.45×10^{-3} [b]	EtOH 1.08×10^{-3} [b]	i-PrOH 2.86×10^{-2} [b]	tert-BuOH 3.32×10^{-2} [b]
CH_2Cl_2	17	15		
$CHCl_3$	61	53	64	
CCl_4	165.6	106.5	97	98.6

[a] T, 298 K.
[b] Viscosity of the solvent (η) from Ref. [29].

Doubtless, the quenching produced by all the quenchers used involves an electron transfer process. The anomalous values obtained in i-PrOH and in tert-BuOH agree with their lower ϵ value (see Table 11: 18.3 and 4.3 respectively), their low capability to stabilize by solvation the dipolar exciplex formed, their higher viscosity and their molecular volume. As it is known [15,34–36], the anomalous behavior shown by nitrogen organic compounds in quenching studies done in i-PrOH and in tert-BuOH solution can be explained by taking into account the Swain–Grunwald mechanism. It has been suggested that the rate of dissociation of pre-existing amine–alcohol complexes is primarily determined by the energy required to create a cavity prior to dissociation and that this energy increases with the size of the solvent (tert-BuOH > i-PrOH > EtOH) and, of course, with bigger size of the quenching molecule.

According to the proposed diffusion quenching model, we observed a mild but clear increase in the k_Q values with the temperature for the CCl_4 quenching in EtOH solution.

$K_Q\times10^{10}$ (M^{-1} seg^{-1})	0.57	0.75	1.03	1.41
T (K)	283	288	298	308

4. Summary

As a conclusion, the photophysical and photochemical processes for *N*-acyl carbazoles **1a** and **1b** in organic diluted solutions can be represented as follows:

$$A+h\nu\rightarrow{}^1A^* \quad (1)$$

$$^1A^*\rightarrow A+h\nu_f \quad (2)$$

$$^1A^*\rightarrow{}^3A^* \quad (3)$$

$$^3A^*\rightarrow A+h\nu_p \quad (4)$$

$$^1A^*\rightarrow \text{products } \mathit{2, 3, 4} \quad (5)$$

$$^1A^*+RCl\rightarrow{}^3A^*+RCl \quad (6)$$

$$^1A^*+RCl\rightarrow{}^1[A^{\delta+}\ldots RCl^{\delta-}]^* \quad (7)$$

$$^1[A^{\delta+}\ldots RCl^{\delta-}]^*\rightarrow A+RCl+h\nu_{exc} \quad (8)$$

$$^1[A^{\delta+}\ldots RCl^{\delta-}]^*\rightarrow[A^{+\cdot}\ldots{}^{\cdot}R\ldots Cl^-] \quad (9)$$

$$[A^{+\cdot}\ldots{}^{\cdot}R\ldots Cl^-]\rightarrow \text{product } \mathit{6}\ \mathrm{l} \quad (10)$$

$$A+H\rightarrow \mathit{4} \quad (11)$$

Which process predominates, photo-Fries rearrangement (step 5), exciplex formation (step 7), exciplex emission (step 8), photo-induced single electron transfer (step 9) and/or acid hydrolysis (step 11) depends on each *N*-acyl carbazole and simultaneously on the electron affinity, proton and hydrogen donor character, viscosity and polarity of the medium.

Thus, for *N*-benzoyl carbazole when irradiations are conducted in the presence of halomethanes such as CH_2Cl_2, $HCCl_3$ and CCl_4, steps 6, 7, 8, 9 and 10 are high efficient, the photo-rearrangement (step 5) not being observed at all in CCl_4.

On the contrary, for *N*-acetyl carbazole we observed that when the irradiations were conducted in the presence of hal-

Table 11
k_Q obtained for *N*-acyl carbazoles **1a** and **1b** in organic media by using chlorinated quenchers

Quenchers	E_{red} (V vs. SCE)	LUMO [c] (eV)	HOMO [c] (eV)	k_Q (M^{-1} s^{-1}) [a]			
				CH_3CN 37.5 [d]	EtOH 26.0 [d]	i-PrOH 18.3 [d]	tert-BuOH 4.3 [d]
1a							
CH_2Cl_2	−2.33	+0.5209	−10.5821	1.57×10^8	1.45×10^8		
$CHCl_3$	−1.67	−0.1170	−10.8384	5.92×10^8	5.15×10^8	6.21×10^8	
CCl_4	−0.78	−0.6283	−10.9871	1.61×10^{10}	1.03×10^{10}	$9.42.10^9$	9.57×10^9
1b							
H_2Cl_2	−2.33	+0.5209	−10.5821	1.71×10^8	6.67×10^7	4.18×10^7	
$CHCl_3$	−1.67	−0.1170	−10.8384	5.97×10^9	4.57×10^9	4.39×10^9	7.79×10^9
CCl_4	−0.78	−0.6283	−10.9871	3.23×10^{10}	1.66×10^{10}	1.28×10^{10}	

[a] Values calculated in the present work.
[b] Reductive potential energy vs. CSE for the quenchers.
[c] Values calculated in the present work. Geometries optimized by semiempirial PM3 method [25].
[d] Dielectric constant (ϵ, 298 K). k_{diff} ($\times10^{-10}$ M^{-1} s^{-1}) [26] (solvent; η, Poise [29]): 1.87 (CH_3CN, 3.45×10^{-3}), 5.98 (EtOH, 1.08×10^{-3}), 2.25 (*i*PrOH, 2.86×10^{-2}), 1.94 (tert-BuOH, 3.32×10^{-2}).

Table 12
ΔG°_{ET} for *N*-acyl carbazoles **1a** and **1b** [a]

Solvent	Quencher	$-E_{red}(A)$ (V vs. CSE)	$\Delta E_{exc}(0,0)(D)$ (kcal mol^{-1})		ΔG°_{ET} (Kcal mol^{-1})		$\log(k_Q)$ [b]	
			1a	**1b**	**1a**	**1b**	**1a**	**1b**
CH_3CN	CH_2Cl_2	2.33	83.4	82.9	−7.2	+8.64		8.23
	$CHCl_3$	1.67			−8.0	−6.5[illegible]	8.77	9.77
	CCl_4	0.78			−28.[illegible]	[illegible]	[illegible]	10.50
EtOH	CH_2Cl_2		83.6	82.2	+7.0	+9.35		7.82
	$CHCl_3$				−8.2	−5.87	8.71	9.65
	CCl_4				−28.7	−26.3	10.01	10.20
i-PrOH [c]	CH_2Cl_2	2.33	83.7	81.9	+6.9	+9.64		7.62
	$CHCl_3$	1.67			−8.3	−5.57	8.79	9.64
	CCl_4	0.78			−28.8	−26.09	9.97	10.11

[a] Calculated from Rehm–Weller equation [31,32]; $E_{ox}(D)$ 1.16 V vs. CSE.
[b] Measured in the present work.
[c] Similar results are obtained in tert-BuOH.

omethanes both photoreactions, photo-Fries rearrangement (step 5) and photo-induced single electron transfer (steps 9 and 10), occur simultaneously, predominating clearly the latter only in EtOH–CCl_4 medium.

It is interesting to mention that, for both *N*-acyl carbazoles, only the photo-Fries rearrangement was observed in the absence of halomethanes.

We wish to add that the proposed electron transfer (step 9 and Table 12) from singlet excited *N*-acyl carbazole to haloalkanes in the transient excited exciplex would be the main primary photochemical process which initiates a chemical reaction through the formation of an intermolecular pair $[A^{+\cdot}...RCl^{-\cdot}]$, which gives $[A^{+\cdot}...{}^{\cdot}R...Cl^{-}]$ via the well-known $RCl + e^{-} \rightarrow {}^{\cdot}R + Cl^{-}$ concerted electron transfer bond-breaking process [37]; the probability of the back electron transfer decrease and thermodinamically stable photoproducts are formed.

Finally, by using semiempirical methods [25], we calculated the charge density on each carbon atom in order to compare the reactivity of *N*-acyl carbazoles as neutral and as cation radical species with Cl−. According to the values obtained, the nucleophilic substitution would occur preferentially on the latter moiety at the 3-C position in agreement with the experimental results obtained (yield of 3-chloro-*N*-acyl carbazoles **6a** and **6b**).

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