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Photo-Fries rearrangement of aryl acetamides: regioselectivity induced by the aqueous micellar green environment†

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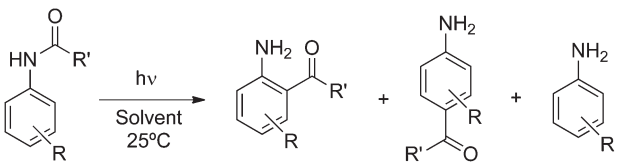
Photochemical reactions tend to give more than one photoproduct. However, such a reaction can be a powerful synthetic tool when it is possible to conduct it in regioselective conditions yielding a single photoproduct. Water–surfactant solutions as reaction media can be considered as an approach in this context because they show products with different features than those from isotropic solutions. Here we describe results obtained from studying the effect on the prototypical photoreaction, known as the photo-Fries reaction of several substituted acetanilides and α-naphthyl acetamide within surfactant micelles (ionic and non-ionic micelles). This reaction involves homolytic cleavage of a C–N bond to yield a singlet radical pair. The surfactant micelles control the rotational and translational mobility of the radical pair, resulting in noticeable photoproduct selectivity.

Introduction

Generally, photochemical reactions tend to give more than one product. For such reactions to be useful in synthesis it is necessary to be able to control the experimental conditions to yield a single product. Therefore, product selectivity in reactions is a great challenge in synthetic organic photochemistry, especially when radical pairs or radical–ion pairs are formed as primary intermediate species. The use of confined assemblies, such as zeolites, micelles, polyolefin films, cavitands, dendrimers, *etc.*, can be considered as strategies devised to control product distributions in photochemical reactions.[1] The restricted mobility within the hydrophobic cores of these confined assemblies limits the tendency of radicals, radical cations, or other reactive intermediates to undergo radical-destroying bimolecular reactions and prevents the access to adventitious reagents (*i.e.* water and oxygen) that would cause their decay in solution. In the present article we describe the results of our studies on the use of cationic, anionic and neutral surfactant micelles, which are capable of solubilizing organic molecules (hydrophobic molecules) in water, as the media in achieving product selectivity in the prototypical photoreaction, the photo-Fries reactions of several substituted aryl acetanilides.

The photo-Fries rearrangement reaction was discovered by Anderson and Reese[2] and involves the homolytic cleavage of a carbon–heteroatom bond, *i.e.*, C–O, C–S and C–N, of esters, thioesters and amides, respectively.[3] The radical mechanism of the photo-Fries rearrangement is well established and it is known that this rearrangement occurs mainly through the excited singlet state.[1i,4] Previous studies on the product distribution of the photo-Fries rearrangement reaction of (hetero) aryl amides in isotropic media afforded *ortho*- and *para*-rearranged photoproducts as well as the corresponding aryl amine (Scheme 1).[5]

Surfactants, which are amphiphilic molecules, aggregate in solution to form micelles when their concentration is above the critical micellar concentration (cmc). Under these conditions, the micelles enhance the solubility of hydrophobic compounds in water. In fact, the most important property of micelles is that they have the ability to concentrate guest molecules into relatively small effective volumes and then to promote the interaction of such molecules.[1c,6] The model of a micelle usually presented is such that the interior contains the hydrophobic chain part of the amphiphilic moiety while the



Scheme 1 The photo-Fries rearrangement of acetanilides.

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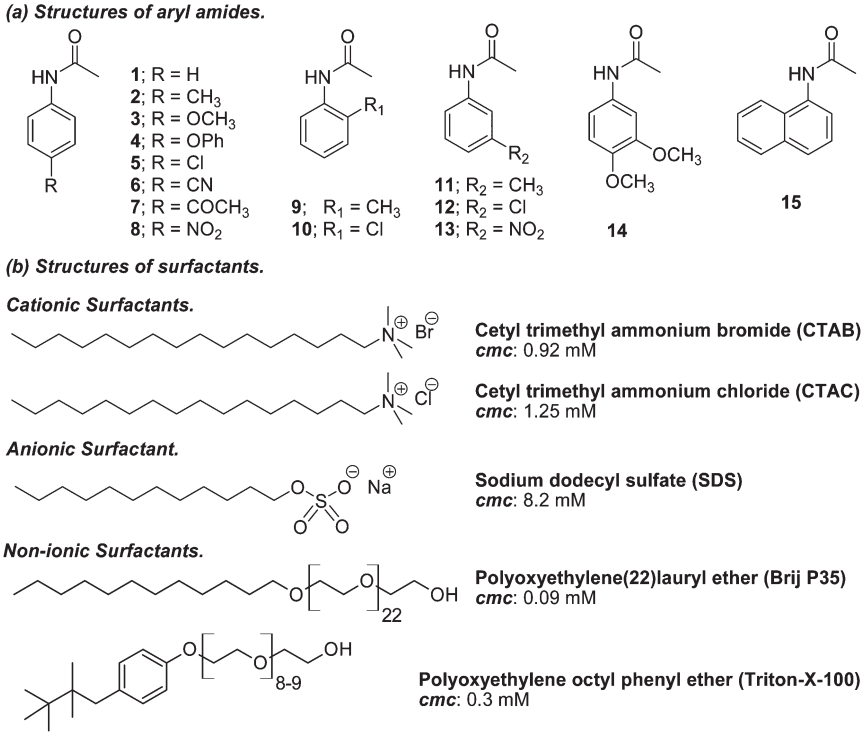


Scheme 2 Structures of the aryl acetamides and the surfactants studied.

polar head group (charged or neutral head) is located at the surface, forming a double layer in contact with the surrounding water. Micelles are not a static species but rather exist in a dynamic equilibrium with the surfactant monomers, they can be employed to organize organic substrates.[7] In micelles, large cage effects are observed relative to homogeneous solvents whose magnitude cannot be explained by the microviscosity inside the micelle. The main reason for this observation is that the hydrophobicity of the solutes inhibits diffusion into the aqueous phase, thereby increasing the time spent by the reaction intermediates in the restricted space of the micelle. If the intermediates are geminate radical pairs, which are produced photochemically, the rotational and translational mobility of these species are constrained inside the micelles. Therefore, the product distribution and the relative chemical yield of the products observed in micellar solution can be significantly different relative to homogeneous solution.[1m,7]

There have been a lot of studies on controlling the reactivity of radicals generated within the micelle supercage where polarity, viscosity, electrostatic, and hydrophobic interactions as well as hydrogen-bonding solvation may play critical roles in determining their reactivities.[8] In addition, several studies designed to analyze and quantify micellar cage effects (reactivity, selectivity and efficiency) on photochemical reactions in water have been performed. Because the photo-Fries rearrangement involves in-cage recombination *versus* diffusion of radicals, aryl esters have been chosen as model substrates to study the non-homogeneous environments.[9] In these studies, SDS was also the preferred surfactant among other ionic surfactants for carrying out the photoreactions. However, some examples in the literature show that the photo-Fries rearrangement reaction of benzamides in SDS micellar solution and acetanilides in water–cyclodextrin systems have also been studied.[9f,g] Since 2-amino arylketones are key synthons in the preparation of 4-quinolones and their derivatives, with demonstrated biological and pharmaceutical properties,[10] we decided to study the photo-Fries rearrangement of a series of substituted aryl and polycyclic aryl amides in micellar solution in order to evaluate if this provides high selectivity for 2-amino phenone formation within the micelle assembly. The structures of the aryl acetamides and surfactants employed in this study are shown in Scheme 2.

Experimental

Materials and equipment

Acetanilide, *ortho*-, *meta* and *para*-substituted anilines, 3,4-dimethoxyaniline and α-naphthylacetamide were purchased from Aldrich and were used without further purification. Surfactants (SDS, Brij, CTAC, CTAB, Triton X-100 and Tween 80) were purchased from Fluka and Sigma Aldrich. Spectrograde solvents were obtained from J. T. Baker and were used as received. Pyridine was distilled and stored over KOH pellets. Melting points were determined using a Fisher Jones apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were registered using a Bruker AC-200 spectrometer in $CDCl_3$; chemical shifts (δ) are reported in parts per million (ppm), relative to

internal tetramethylsilane. 2D NOESY spectra were registered using a Bruker AC-500 spectrometer in D_2O; chemical shifts (δ) are reported in parts per million (ppm), relative to internal trimethylsilylpropionic acid. Coupling constant (J) values are given in Hz. The measurements were carried out using standard pulse sequences. GC analysis was carried out using a Hewlett Packard 5890 gas chromatograph using an Ultra 2 capillary chromatographic column. For amides **1–14**, the chromatograms were recorded with the following program: initial temperature: 100 °C, 2 minutes; rate: 10 °C min^{-1}; final temperature: 250 °C, 10 minutes. For amide **15**, the chromatograms were recorded as follows: initial temperature: 150 °C, 2 minutes; rate: 10 °C min^{-1}; final temperature: 250 °C, 15 minutes. Reverse phase HPLC analysis was carried out using a JASCO PU 1580 with a UV detector PU 1575 using a RP–18 reverse chromatographic column (Supelco; eluent: MeCN–H_2O mixtures; flow: 1 mL min^{-1}; detector: UV, λ 230 and 260 nm). The UV-visible spectra were measured using a Shimadzu UV-1203 spectrophotometer. All the measurements were made using 1 cm stoppered quartz cells at 298 K.

Determination of the constants of binding (K_b) of acetanilides in micellar media

Solutions of acetanilides **4**, **11**, **12** and **13** were prepared in deionized water (MilliQ) and their concentration varied between 5.5×10^{-5} M and 1.0×10^{-4} M. An aliquot (2 mL) of the acetanilide solution was placed in a two-faced stoppered quartz cuvette provided with a stir bar and the UV-visible spectrum was registered, then the A_0 value at the maximum wavelength was read. Next, aliquots of concentrated surfactant solution (10 μL) were added successively and the UV-visible spectra were registered taking for each solution the A value at the maximum wavelength. After each addition of surfactant solution the resulting solution was stirred for 20 minutes. With the values of A_0 and A in hand, plots of $(A_0/(A - A_0))$ *versus* the reciprocal of the concentration of the surfactants were created and the data were fitted with a linear regression program provided by SigmaPlot version 11.0. From the ratio of the slope and the origin it was easy to calculate the K_b values.

Synthesis of acetanilides 2–15

To a solution of the acetanilides (0.010 mol) in pyridine (10 mL) chilled in an ice-bath was added dropwise acetyl chloride (0.012 mol) for 10 minutes under stirring. The reaction mixture stood for an additional 45 minutes under stirring. Once tlc confirmed total consumption of the starting material, the reaction mixture was extracted with dichloromethane (10 mL) and washed with a solution of diluted HCl (10 mL). The organic phase was then washed with water, dried with Na_2SO_4, filtrated and evaporated under pressure. The acetanilides were purified from the solid residue using column chromatography with hexane and ethyl acetate mixtures giving the corresponding acetanilides in excellent yields (>90%). The acetanilides **2–14** were characterized by comparison with the physical constant (m.p.) and spectroscopical data (^{1}H-NMR and ^{13}C-NMR) reported in the literature. These data and the corresponding references are listed in ESI.†

Photoirradiations

General procedure

Photoirradiations of acetanilides in homogeneous media. Stock solutions of amides 1–15 (0.106 mmol) in cyclohexane (100 mL) were prepared. An aliquot (65 mL) was placed in a stoppered Erlenmeyer quartz flask (100 mL) and was degassed with argon for 30 min. The flask was placed in a home made optical bench which provided the possibility to use two or four lamps. The solutions of the amides were stirred during the irradiation process. Irradiations with λ_{exc} = 313 nm were carried out with four phosphorous–coated lamps (HelioQuartz, each of 18 Watts, purchased in Italy) that give a nearly parallel beam at 313 nm. Irradiations with λ_{exc} = 254 nm were carried with four germicidal lamps (Philips, each of 20 Watts, purchased in Argentina). The progress of the reaction was monitored using TLC [eluent: hexane–ethyl acetate (8 : 2 v/v); spots were visualized with UV light (254 and 366 nm) and with I_2] and by GC analysis (Ultra 2 capillary column) following the programs above mentioned depending on the amide analyzed. When the conversion of the starting material was higher than 90%, the photolyzed solution was evaporated carefully to dryness under reduced pressure. The yellowish solid residue obtained was worked up by silica gel column chromatography (eluent: hexane 100% followed by hexane–ethyl acetate mixtures). From the eluted fractions, the photoproducts were isolated and characterized by means of physical and spectroscopic methods.

Photoirradiations of acetanilides in micellar media. Stock solutions of surfactants in deionized water were freshly prepared and the concentrations of these solutions were: SDS 0.10 M; CTAC 0.02 M; CTAB 0.02 M; Brij-P35 0.05 M; Triton-X-100 0.05 M and Tween 80 0.10% (v/v). The acetanilide (5 mg) was placed in a stoppered quartz cell provided with a stir bar (3 ml) and the surfactant stock solution (2 mL) was added. Then, the solution was vigorously stirred for one hour and degassed with argon for an additional 20 min. The quartz cell was placed in a homemade optical bench equipped with two germicidal lamps (Philips, each of 20 Watts, purchased in Argentina). The progress of the photoreaction was monitored using two different methods, UV-visible spectroscopy and GC analysis (Ultra 2 capillary column). The conversion of the amides was kept below 20% to avoid secondary reactions and the formation of by-products. Prior to injection into the GC apparatus, the micellar solutions were treated as follows. The photolyzed solutions were diluted with 2 mL of an aqueous solution of NaCl and then extracted with ethyl acetate (3 × 2 mL) while the system was carefully shaken. The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness under vacuum. The yellowish solid residue was dissolved using dicloromethane (2.00 mL) and this new solution was injected into the GC for chromatographic analysis. The products were characterized by comparison with the physical constant (m.p.) and spectroscopical data (^{1}H-NMR and ^{13}C-NMR) reported in

the literature. These data and the corresponding references are listed in ESI.† The substituted anilines **1c–15c** were identified by comparison of their chromatographic characteristics with those of authentic commercial samples.

Results and discussion

The use of micelles of ionic and neutral surfactants to carry out photoreactions requires knowledge of the location of the reactants in the system. We conducted UV-visible and ^{1}H NMR studies of guest molecules (acetanilides) within micelles to gain an understanding of the reactants' positioning. Our first approach was to determine the binding constant (K_b) between acetanilides and micelles using UV-visible spectroscopy. Among the guest acetanilides investigated, we selected acetanilides **4**, **11**, **12** and **13** which were soluble enough in water to record the UV-visible spectrum and then, to determine the K_b. The UV-visible spectra of **4** and **13** in water in the presence and absence of the surfactants Brij-P35 and CTAC, respectively, are presented in Fig. 1. Addition of increasing amounts of surfactant produced both bathochromic and hyperchromic shifts of the lower energy band. This spectroscopic behaviour demonstrates that the **4** and **13** acetanilides bind to the micelle and we propose that this molecular interaction takes place with the hydrophobic core of the micelle. A similar behaviour was observed for acetanilides **11** and **12** and the UV-visible spectra are shown in Fig. 1S (see ESI†).

Furthermore, if the binding of the guest to the micelle can be described as an equilibrium, K_b can be written according to eqn (1) where S is the acetanilide, Surf is the surfactant and [S-Surf] is the acetanilide surfactant complex.

$$[S] + [Surf] \overset{K_b}{\rightleftharpoons} [S\text{-}Surf] \quad K_b = \frac{[S\text{-}Surf]}{[S][Surf]} \tag{1}$$

The application of the Lambert–Beer law to eqn (1) gives eqn (2) where A and A_0 are the absorbance at the maxima wavelength in the presence and absence of surfactant, respectively, and ε_S and ε_C are the molar absorptivity of the acetanilides and the complex. Rearranging eqn (2) provides eqn (3) where a linear relationship is observed between $(A - A_0)^{-1}$ and the reciprocal of the concentration of the surfactant.

$$\frac{(A - A_0)}{A_0} = \frac{\varepsilon_C \cdot K_b \cdot [Surf]}{\varepsilon_S \cdot (1 + K_b \cdot [Surf])} \tag{2}$$

$$\frac{A_0}{(A - A_0)} = \frac{\varepsilon_S}{\varepsilon_C} + \frac{\varepsilon_S}{\varepsilon_C \cdot K_b}\frac{1}{[Surf]} = A_0\frac{1}{\Delta A} \tag{3}$$

Fig. 2 shows the experimental data obtained for the acetanilide **4**-Brij-P35 and acetanilide **13**-CTAC systems and also shows the best linear regression curves. The plots for the other surfactants are shown in Fig. 2S (see ESI†).

From the ratio of the slope and the origin it was easy to calculate the K_b values which are collected in Table 1 for acetanilides **4**, **11**, **12** and **13** with different surfactants. These data show that the acetanilides bind to the micelles and those that have a hydrophobic character, *i.e.* acetanilide **4**, show high values.

Savelli and co-workers have estimated a K_b value $\leq$100 M^{-1} for substrates that are not very hydrophobic in SDS, CTAC and CTAB such as phenyl chloroformate.[11] Furthermore, Quina, Treiner and co-workers pointed out that these values of K_b are typical of organic solutes with aryl moieties.[12] This is the case for acetanilides **11**, **12** and **13** whose K_b values are lower than 100 M^{-1}. This behaviour can be attributed to the fact that these acetanilides are soluble enough in water at the concentration ($\approx 1 \times 10^{-5}$ M) that the UV-visible experiments were carried out at. Noteworthy is the case of acetanilide **11** where the K_b values in SDS, CATC and CTAB are much lower which is attributed to the high solubility of the acetanilide in water.

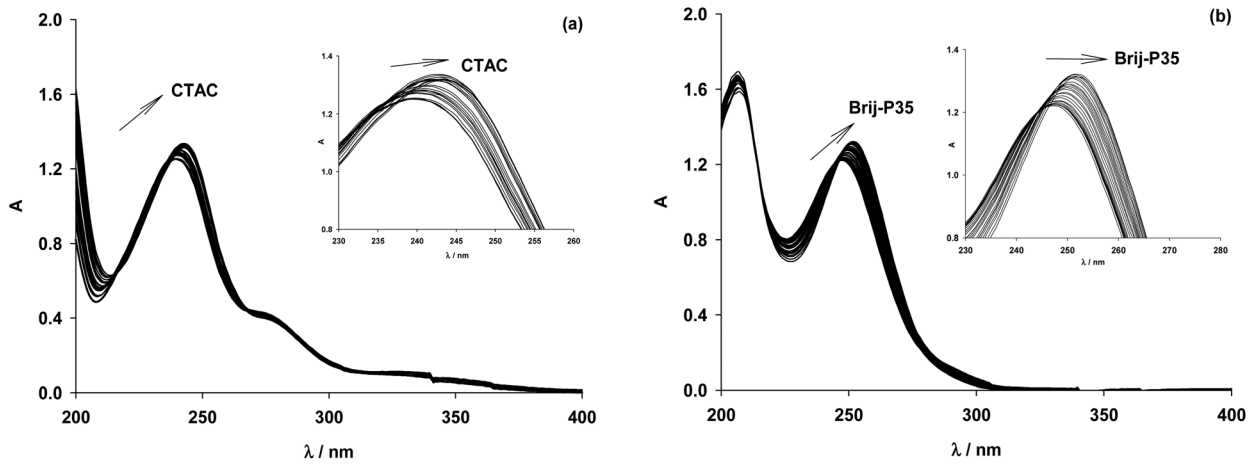


Fig. 1 UV-visible spectra of acetanilides. Effect of addition of surfactants in the acetanilide water solution (room temperature): (a) acetanilide **13** with increasing concentration of CTAC and (b) acetanilide **4** with increasing concentration of Brij-P35. Insets: partial spectrum magnification showing the hyperchromic and bathochromic shifts for acetanilide **13** around 240 nm (plot (a)) and for acetanilide **4** around 247 nm (plot (b)).

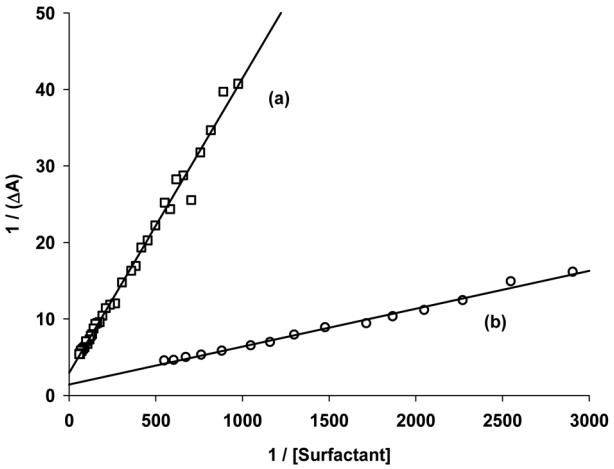


Fig. 2 Plot of reciprocal of ΔA *vs.* reciprocal of concentration of surfactants in water at room temperature: (a) acetanilide **13** with CTAC and (b) acetanilide **4** with Brij-P35.

Table 1 Binding constant (K_b) in water of acetanilides **4**, **11**, **12** and **13** in the presence of different surfactants at room temperature

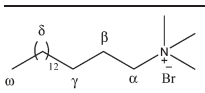
	K_b/M^{-1}			
Acetanilides	SDS	CTAC	CTAB	Brij-P35
4	109	552	459	214
11	7	11	32	63
12	17	135	113	58
13	81	76	70	33

Acetanilide **4** is an example of a hydrophobic amide. It does not demonstrate much solubility in water at the concentration used in the UV-visible experiments and the K_b values are near or greater than 100 M^{-1}. Cabaleiro Lago and co-workers have estimated the K_b values between a series of substituted benzoyl chlorides and the Brij-P35 surfactant and found that these values are higher than those obtained for CTAC and SDS.[13] A minimum value of K_b for the Brij-P35 surfactant was estimated around 190 M^{-1} which accounts for a more apolar environment using pyrene as a micropolarity probe. Therefore, the data collected in Table 1 for acetanilides **4**, **11–13** in this non-ionic surfactant show a similar trend to that which was observed for the ionic surfactants.

With the aim of searching for the location of the acetanilides within the hydrophobic core of the micelles, we conducted ^{1}H NMR studies of guest molecules within surfactant micelles to gain an understanding of the reactants' positioning. NMR spectroscopy has been employed previously to assess the location of a solute within the micellar assembly.[14] Among the fifteen guests investigated, we selected acetanilides **1**, **3**, **5**, **7**, **8** and **11** and the surfactants CTAB, SDS and Brij-P35 for the 1D and 2D ^{1}H NMR spectroscopy study. ^{1}H NMR of the surfactants in D_2O in the presence and absence of acetanilides showed differential effects on the various protons of the surfactants, causing slightly upfield and downfield shifts (~0.1–0.01 ppm). The magnitudes of the change in the shifts are much above the value for typical errors in the chemical shifts equal to 0.002 ppm.[14c] Table 2 shows the differential chemical shifts for CTAB in the presence of several acetanilides. Similar spectroscopic behaviours were also observed for the surfactants SDS and Brij-P35 and the results are shown in Table 2S (see ESI†). The intimate interaction between the acetanilides and the hydrocarbon chains of the surfactants has a significant role in the surfactant proton shift. Thus, the differential chemical shifts shown in Tables 2 and 2S† suggest that the acetanilides could be located in the shell as well as the hydrophobic core of the surfactant micelles. This behaviour can be ascribed to the high concentration of acetanilide solutes used in our NMR experiments that are preferentially solubilized at the core/shell interface but spread further into the shell and the core of the micelle.[14a]

Additional ^{1}H NMR studies were carried out in order to confirm qualitatively the location of the acetanilides within the micelle assembly. 2D NOESY experiments were performed in D_2O mixing a surfactant with an acetanilide in a *ca.* 1 : 1 molar ratio. Fig. 3 shows a 2D NOESY NMR spectrum for a solution of Brij-P35 (7 mM) in the presence of acetanilide **1** (10 mM) in D_2O. The inset green frames identify the Nuclear Overhauser Effect (NOE) between the signals of the aromatic protons (H-2, H-3 and H-4) and the methyl protons (H-7) of acetanilide **1** and the signals of the surfactant (H-1, H-2, H-5 and H-6). The numbering of the protons of the surfactant Brij-P35 and acetanilide **1** are shown in Fig. 3. Similar results were obtained for solutions of SDS and CTAB in D_2O in the presence of acetanilides **1**, **7** and **11** and the corresponding 2D

Table 2 Differential chemical shift ($\Delta\delta$) of CTAB (70 mM) in the presence of acetanilides (10 mM) in D_2O at room temperature



			$\Delta\delta$/ppm			
Acetanilides	$N^+(CH_3)_3$	α-CH_2	β-CH_2	γ-CH_2	δ-CH_2	ω-CH_3
1	0.05	0.12	0.11	—	−0.05	0.08
3	0.04	0.08	0.06	—	−0.01	−0.03
5	0.03	0.08	0.08	—	−0.04	−0.06
8	−0.01	0.004	−0.001	0.01	0.01	−0.02

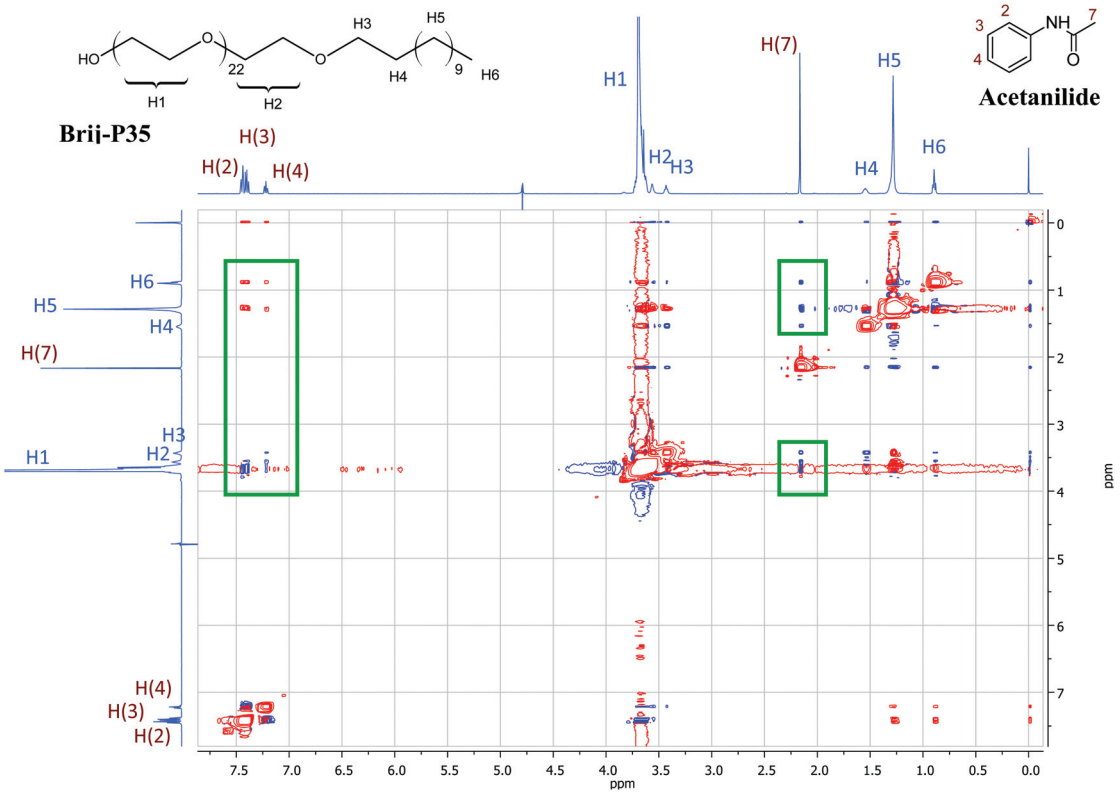


Fig. 3 2D NOESY spectrum of a solution of Brij-P35 (7 mM) and **1** (10 mM) in D_2O at room temperature.

NOESY NMR spectra are shown in Fig. 3S (see ESI†). The intermolecular NOEs connecting the resonances of the acetanilide and surfactant are clearly visible in the figures confirming the results described with 1D NMR spectroscopy. Although a precise positioning cannot be estimated with certainty, we can suggest that the acetanilides are located in the shell as well as the hydrophobic core of the surfactant micelles taking into account that the aromatic protons as well as the methyl protons of the acetanilides correlate nicely with the different protons of the surfactants.

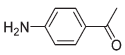
The NMR spectroscopic results encouraged us to study the photochemical reactions of substituted acetanilides in water–surfactant solutions as reaction media because working with acetanilide concentrations around or higher than 5.0×10^{-3} M means that the substrates are spread within the shell/hydrophobic core of the micelle and the photoreaction is expected to take place within the micelle.

To examine the capability of neutral and ionic micelles as a reaction medium to induce photoproduct regio-selectivity from aryl amides, the unimolecular photochemical reaction, specifically the photo-Fries rearrangement of several substituted aryl acetamides and α-naphthyl acetamide (see Scheme 4) was investigated. In this reaction, upon irradiation, a molecule from its singlet excited state fragments to form a radical pair. Depending upon the mobility and confinement provided by the medium, the primary intermediates can yield various products as discussed below.

Irradiation of acetanilide (**1**) in cyclohexane, an isotropic medium that represents the behavior of a guest in an unrestricted environment, resulted in the formation of 45% **1a** and 38% **1b** (Table 3). A small amount of cage escape product (**1c**) was also observed. Irradiation of acetanilide **1** in an aqueous solution in the presence of neutral and ionic surfactants yields 2-acetyl aniline (**1a**) with noticeable selectivity and in high yield which is a quite different behavior compared to that in cyclohexane (Table 3). The selectivity obtained with the Brij-P35 surfactant is better (quantitative) than that obtained with micelles from classical surfactants such as SDS, CTAC, CTAB, Tween 80, and Triton-X100 where a significant amount of compound **1b** (13–27%) was obtained. Furthermore, no aniline was observed when the irradiations of **1** were carried out in water in the presence of surfactants which evidences the suppression of products arising from cage escape. In all the experiments performed in water in the presence of surfactants, the concentration of the surfactants was 100 times higher than the cmc (see Table 3). Note that all photochemical reactions were kept at about 20% conversion, which is a standard operating procedure in mechanistic photochemistry.[15] This avoids complications in analysis due to secondary photoreactions from the products of the reaction under investigation.

The results presented above clearly demonstrate that the singlet radical pair **A**, *i.e.*, anilinium radical and acetyl radical (see Scheme 3), generated in the shell/core of the micellar assembly is restrained within the cage eliminating diffusion

Table 3 Irradiation of acetanilide (**1**) in cyclohexane and micellar media

		Yield[a] (%)		
				
Solvent	Surfactant	**1a**	**1b**	**1c**
Cyclohexane	—	45	38	15
H_2O	SDS (0.10 M)	73	17	
H_2O	Brij-P35 (0.05 M)	>99		
H_2O	CTAC (0.02 M)	66	27	
H_2O	CTAB (0.02 M)	68	22	
H_2O	Tween 80 [b]	72	23	
H_2O	Triton X-100 (0.05 M)	85	13	

[a] λ_{exc}: 254 nm; atmosphere: Ar; [acetanilide]: 0.010 M; Δt: 360 min; T: 25 °C. [b] [Tween 80]: 0.10% v/v; Δt: 180 min.

into the aqueous phase, and thereby no aniline (**1c**) was obtained. Another important aspect, namely the higher ratio of the products **1a** : **1b** in the micellar systems than in cyclohexane implies suppression of the rotational freedom of the encapsulated molecules in the micro-heterogeneous medium. Therefore, we can conclude that the lack of cage escape products and the selectivity of the photoreaction are due to a significant rigidity and confinement of the micellar assembly. However, there exists some amount of rotation for the radical pair **A** within the long chain micelles, resulting in the formation of **1b**.

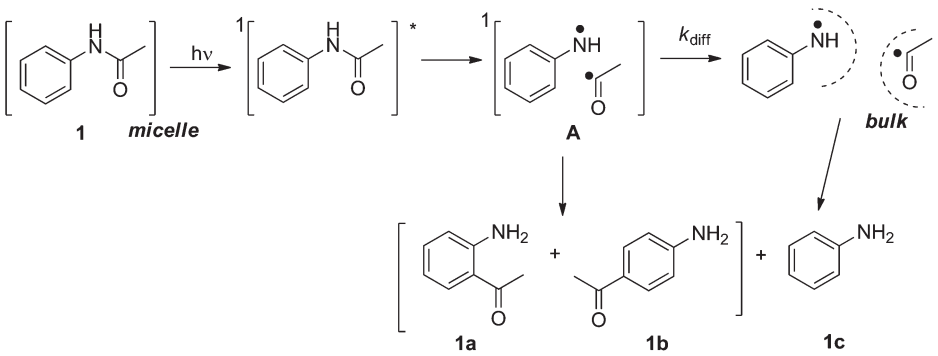
Next, we studied the photo-Fries rearrangement of several mono *ortho*- and *para*- and also disubstituted acetanilides bearing electron donor and electron withdrawing groups in homogeneous (cyclohexane) and micellar media. In Scheme 4 are shown the photoreactions of the acetanilides (**2–15**) together with the corresponding product distribution. The chemical yields of the photoproducts are collected in Table 4.

The acetanilides **2–14** upon irradiation in cyclohexane afforded the migrated photoproducts and the corresponding substituted anilines (Table 4). No selectivity was observed in the homogeneous media. However, when the photoreactions were performed in water–surfactant media noticeable selectivity was observed. Irradiation of the *para*-substituted acetanilides bearing electron donor and electron withdrawing substituents (**2–5** and **7**) afforded the *ortho*-migrated products (**2a–5a** and **7a**) in high to quantitative yields. However, in some few cases *para*-substituted anilines were detected in very low yields (≤9%) showing again a significant inhibition of the out-of-cage escape of the radical intermediates formed within the micelle.

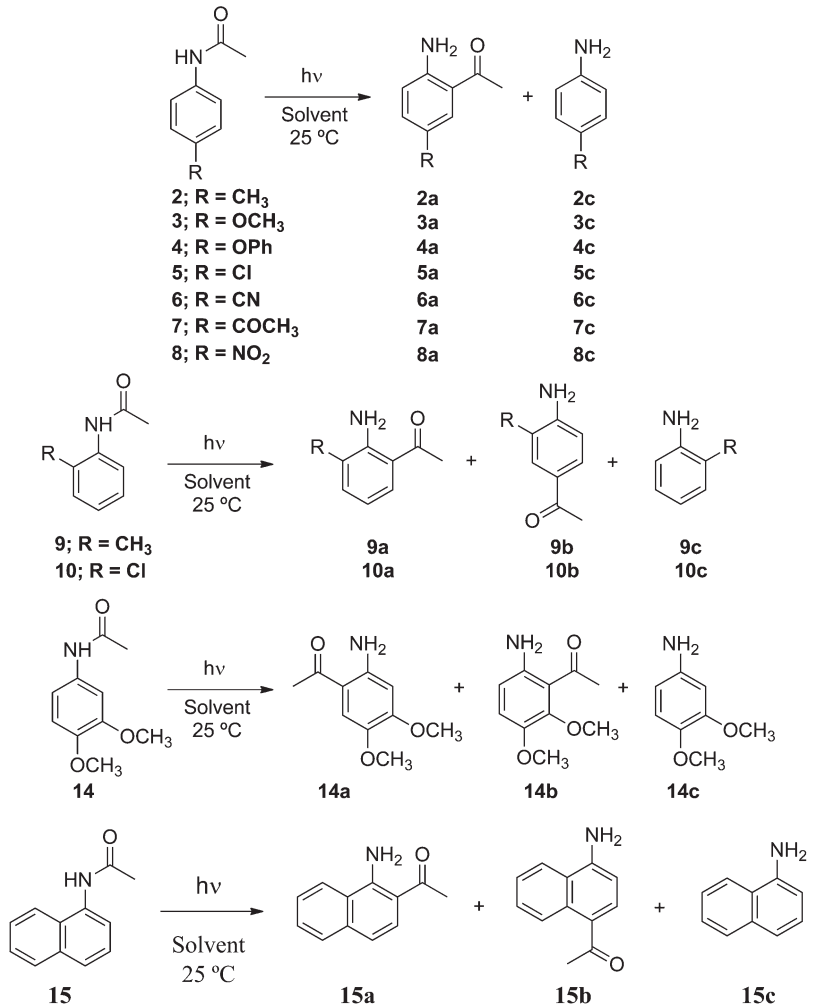
Irradiation of compound **6** in all micellar media gives the desired *ortho*-migrated photoproduct (**6a**) in good yields together with significant amounts (22–37%) of *p*-cyanoaniline **6c**. When surfactant Brij-P35 was used the photochemical reaction gave **6a** in quantitative yield (Table 4). We attributed the formation of **6c** to the partial solubility of acetanilide **6** in water where the photoreaction takes place simultaneously within the micellar assembly and in the bulk.

When 4-nitro acetanilide (**8**) was irradiated in isotropic and anisotropic media for 12 h no photo-Fries rearrangement took place, and the starting material was recovered quantitatively. This behavior can be explained by nitroarenes showing a high intersystem-crossing quantum yield (ϕ_{ISC} = *ca.* 0.50) and hence, a change in the multiplicity of the excited state from a singlet to triplet excited state is promoted.[16] Therefore, we propose that a population of the triplet excited state of acetanilide **8** is favored because the photo-Fries reaction of acetanilides takes place from the singlet excited state,[3] and no reaction occurs from the triplet excited state of acetanilide **8**.

The irradiation of the *ortho*-substituted acetanilides **9** and **10** in micellar solution showed a noticeable selectivity (see Table 4). No substituted anilines (**9c** and **10c**) were formed while the migrated photoproducts were obtained in fairly good yield. The migration of the acetyl group to the *ortho* position of the phenyl moiety is favored over the *para* position giving an *ortho* : *para* ratio of *ca.* 2 : 1. It is worth noting that the irradiation of compound **10** in water–Triton X-100 media gives product **10a** in quantitative yield. A similar behavior was observed for the irradiation of 3,4-dimethoxy acetanilide (**14**) in micellar media. The photoproducts **14a** and **14b** were formed exclusively, where **14a** was always formed in yields



Scheme 3 Photochemical reaction of acetanilide in micellar media.



Scheme 4 Photoreaction of acetanilides **2–15**.

higher than **14b**; aniline **14c** was not detected in the reaction mixture (see Table 4). This selectivity arises from the fact that because of steric hindrance the acetyl radical migrates preferentially to C-6 rather than to C-2 of the aromatic moiety.

Finally, a polycyclic aryl amide such as α-naphthyl acetamide (**15**) was also irradiated in cyclohexane at λ_{exc} 310 nm rendering the expected photoproducts **15a**, **15b** and **15c** (see Table 4). When the photo-Fries reaction of **15** occurred in micellar solutions, compound **15a** was formed in excellent yields independent of the nature of the surfactant employed. In few cases, photoproducts **15b** and **15c** were detected in the reaction mixture in very low yields.

It is worth noting that the irradiation of acetanilides **1**, **9** and **10** does not provide the *ortho* rearranged photoproducts with high selectivity as was observed for the case of the *p*-substituted acetanilides (**2–5** and **7**). This behaviour can be attributed to the lower rigidity and confinement of conventional small molecule surfactant micelles when compared to more rigid and confined environments such as amphiphilic homopolymer nanopockets, capsules formed by a deep cavity cavitand and bile salt micelles.[11,m,n] Therefore, the loss of rigidity of the micelles favoured the mobility of the singlet radical pairs inside the micelle rendering the corresponding *para* rearranged photoproducts (**1b**, **9b** and **10b**) in significant amounts (see Table 4). Thus, the flexibility of the micelles allows the acetyl radical to reach the *para* position of the anilinium radical formed during the irradiation. Similar conclusions have been reached by Ramamurthy and co-workers when studying the photo-Fries rearrangement of naphthyl esters in amphiphilic homopolymers and conventional surfactant micelle–water solutions.

The photochemical reaction of the acetanilides **1–7** and **9–15** within the micellar assembly showed a noticeable selectivity favouring the formation of the *ortho* regioisomers over the escape photoproducts, *viz*. the anilines. However, significant amounts of the *para* regioisomers were obtained for acetanilides **1**, **9** and **10**. The photoreaction proceeded efficiently with a variety of electron donor and electron withdrawing substituents at the *para* and *ortho* positions of the aryl moiety. Also, α-naphthyl acetamide, a polycyclic aryl moiety, rearranged

Table 4 Irradiation of acetanilides (**2–7** and **9–15**) in cyclohexane and water–surfactant media

Acetanilides	**2**		**3**		**4**		**5**		**6**		**7**	
	Yield[a] (%)											
Medium[b]	**2a**	**2c**	**3a**	**3c**	**4a**	**4c**	**5a**	**5c**	**6a**	**6c**	**7a**	**7c**
Cyclohexane	48	28	49	26	62	28	42	25	64	35	48	41
SDS	88	9	95	2	93	6	98		88	22	>99	
Brij	95	2	>99		>99		97		>99		—	
CTAC	>99		>99		>99		>99		73	27	>99	
CTAB	>99		>99		>99		>99		80	20	>99	
Triton X-100	90	7	>99		90	5	>99		63	37	>99	

Acetanilides	**9**			**10**			**14**			**15**		
	Yield[a,c] (%)											
Medium[b]	**9a**	**9b**	**9c**	**10a**	**10b**	**10c**	**14a**	**14b**	**14c**	**15a**	**15b**	**15c**
Cyclohexane	42	30	15	39	27	16	51	17	15	40	35	15
SDS	67	33		66	34		63	25		94		5
Brij	73	27		69	31		73	17		97		
CTAC	64	36		54	46		70	14		98		
CTAB	70	30		61	36		51	17	15	95	1	2
Triton X-100	70	30		>99			63	25		93		

[a] λ_{exc}: 254 nm; atmosphere: Ar; [acetanilides]: 0.010 M; *T*: 25 °C. [b] Concentration of the surfactants in water as indicated in Table 3. [c] Irradiation of compound **15** (0.010 M) with λ_{exc}: 310 nm.

with selectivity and high efficiency. These results showed the applicability of the sustainable water surfactant media in the preparation of *ortho*-amino phenones as an alternative and efficient methodology in organic synthesis.

Conclusions

The photo-Fries reaction of the included photoactive acetanilides has helped establish surfactant micelle assemblies as being capable of affecting the selectivity of this reaction by restricting the freedom of the reactive intermediates. Inclusion of the substrates in the shell as well as in the hydrophobic core of the micelles has been established and confirmed by 1D and 2D ^{1}H-NMR spectroscopies. A noticeable selectivity in product distribution was observed in anisotropic media affording the *ortho*-migrated photoproducts with good to excellent yields. In all cases it is clear that inhibition of out-of-cage products, *viz.* anilines, occurs efficiently which means that the micelle assembly is rigid enough to prevent radical escape and/or to behave as a free radical scavenger. Another interesting feature of the micelle assembly is its effectiveness in dictating the behavior of singlet radical pairs suggesting that the micelles are able to constrict the mobility of short-lived radical pairs to some extent. However, significant amounts of the *para* regioisomers are obtained from acetanilides **1**, **9** and **10**. From a synthetic viewpoint, micellar media is a sustainable and alternative media that provides 2-acetyl anilines in excellent yields which are useful synthons in the preparation of quinolones.

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