rivative of **6** and various impurities. The 120-mg fraction was crystallized from 5 mL of water chilled to 5 °C [yield 93 mg (32%); mp 235–250 °C] plus a second crop of 18 mg: total yield 37%; UV λ_{max} (MeOH) 238–239 nm (ϵ 13 800), 293–294 (4400), 363 (15 600), λ_{max} (0.1 N HCl) 239 (10 700), 259–261 (6100), 340 (16 400), λ_{max} (pH7) 232–233 (14 100), 293–294 (5400), 356–358 (12 800); λ_{max} (0.1 N NaOH) 231–232 (18 800), 280–281 (7300), 347–348 (12 000); IR 3.0–3.1 (NH, OH), 6.13 and 6.31 μm (heterocyclic C=N); ^{1}H NMR (slurried in D_2O, evaporated, and redissolved in CD_3OD) δ 5.43 (dd, H-1′, $J_{1',2'A} = 6.0$ Hz, $J_{1',2'B} = 10.5$ Hz), 4.47 (rough dt, H-3′, presumably ddd), 4.04 (m, H-4′), 3.85 (dd, H-5′A, $J_{4',5'A} = 3.6$ Hz), 3.65 (dd, H-5′B, $J_{4',5'B} = 3.3$ Hz, $J_{gem} = 12$ Hz), 2.5 (ddd, H-2′A, $J_{2'A,3'} = 6.0$ Hz, $J_{1',2'A} = 1.05$ Hz), 2.3 (ddd, H-2′B, $J_{2'B,3'} = 1.5$ Hz, $J_{1',2'B} = 6.0$ Hz, $J_{gem} = 13.3$ Hz). Anal. Calcd for $C_{10}H_{13}N_5O_3\cdot{}^2/_3H_2O$: C, 40.67; H, 4.89; N, 23.71; S, 10.85. Found: C, 40.76; H, 5.02; N, 23.35; S, 10.63.

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Registry No. **4**, 88287-89-2; **5**, 88287-90-5; **6**, 88287-91-6; **7**, 50908-41-3; **8**·HCl, 88287-61-0; **9**, 88287-60-9; **10**, 88287-62-1; 11, 88287-63-2; **12**, 88287-64-3; **13**, 88287-65-4; **14a**, 88287-67-6; **14c**, 88287-66-5; **15a**, 88335-33-5; **15b**, 52646-33-0; **15c**, 88287-68-7; **16a**, 88287-69-8; **16b**, 88287-70-1; **16c**, 88287-71-2; **17a**, 88287-72-3; **17b**, 88287-73-4; **17c**, 88287-74-5; **18a**, 88295-39-0; **18b**, 88287-75-6; **18c**, 88287-76-7; **19a**, 88287-77-8; **19c**, 88287-78-9; **20b**, 88287-79-0; **21a**, 88287-80-3; **21b**, 88287-82-5; **21c**, 88287-81-4; **22a**, 88287-84-7; **23a**, 88287-85-8; **24a**, 80523-94-0; **24b**, 88287-87-0; **24c**, 88287-88-1; **26**, 3911-55-5; **27**, 88287-83-6; **30a**, 88287-86-9; dimethyl acetylenedicarboxylate, 762-42-5; benzyl mercaptan, 100-53-8.

Control of Regiochemistry in Photodimerization through Micellar Preorientational Effect: 2-Substituted Naphthalenes[†]

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Photodimerization of 2-substituted naphthalenes in organic solvents has been well explored. In contrast to their behavior in organic solvents, in anionic and cationic micellar media enhanced reactivity and pronounced regioselectivity are observed. Reactivity enhancement in micellar media is attributed to the local concentration effect. Enhanced reactivity in CTAC and DTAC compared to CTAB micelles is attributed to the counterion effect, and the regioselective photodimerization observed in anionic and cationic micelles leading exclusively to the cis dimer or the products derived therefrom is rationalized on the basis of the preorientational effect of micelles.

Control of stereo- and regiochemistry in photochemical reactions through the use of constrained systems such as molecular and liquid crystals, monolayers, and micellar assemblies has opened new vistas in photochemistry.[1] In particular the photocycloaddition reactions of cyclopentenones,[2] cyclohexenones,[3] pyridones,[4] and 9-(hydroxymethyl)anthracene[5] in micellar media have demonstrated the potential use of micellar effects in controlling the regiochemistry of photodimerization reactions. The ability of micelles to organize reactants in a specific geometry (preorientational effect) and the polar nature of the micellar interface are the two features that could affect the regiochemistry of photodimerization. Studies on photodimerization of coumarin[6] and 9-methylanthracene[7] in micellar media have revealed that in such systems the polarity effect is predominant in effecting a regioselective dimerization. During the photodimerization of 7-alkoxy- and 4-methyl-7-alkoxycoumarins[8] in micellar media, a failure to control the regiochemistry of the photodimerization was observed, thus suggesting limitations of micellar effects. A study of 2-substituted naphthalenes **1**–**6** (Scheme I) in micellar media was undertaken in order to understand the extent of micellar effects on regiochemical control of photodimerization reactions.

The photodimerization of 2-substituted naphthalenes in organic solvents has been well explored.[9–19] In organic solvents the trans dimer **7** is the major and the cis dimer **8** (or products derived therefrom) the minor product (Figure 1).[14] It has been established that the dimerization process is polarity independent,[9,12] hence the polarity effect of micelles can be excluded. Further, the 2-substituents—alkoxy, carbomethoxy, and nitrile—being hy-

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[†] Respectfully dedicated to Prof. P. de Mayo on the occasion of his 60th birthday.

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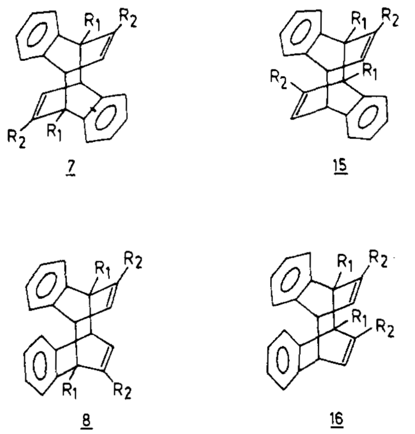


Figure 1. Four possible (4 + 4) photodimers of 2-substituted naphthalenes.

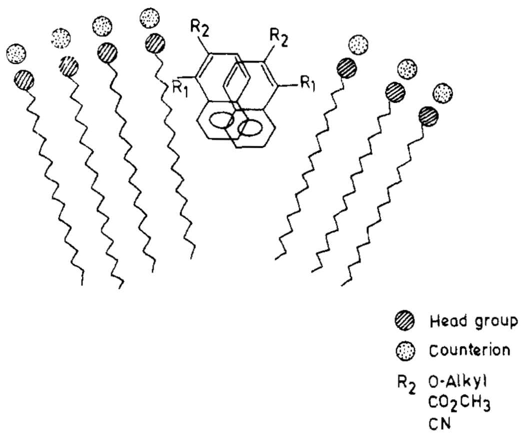
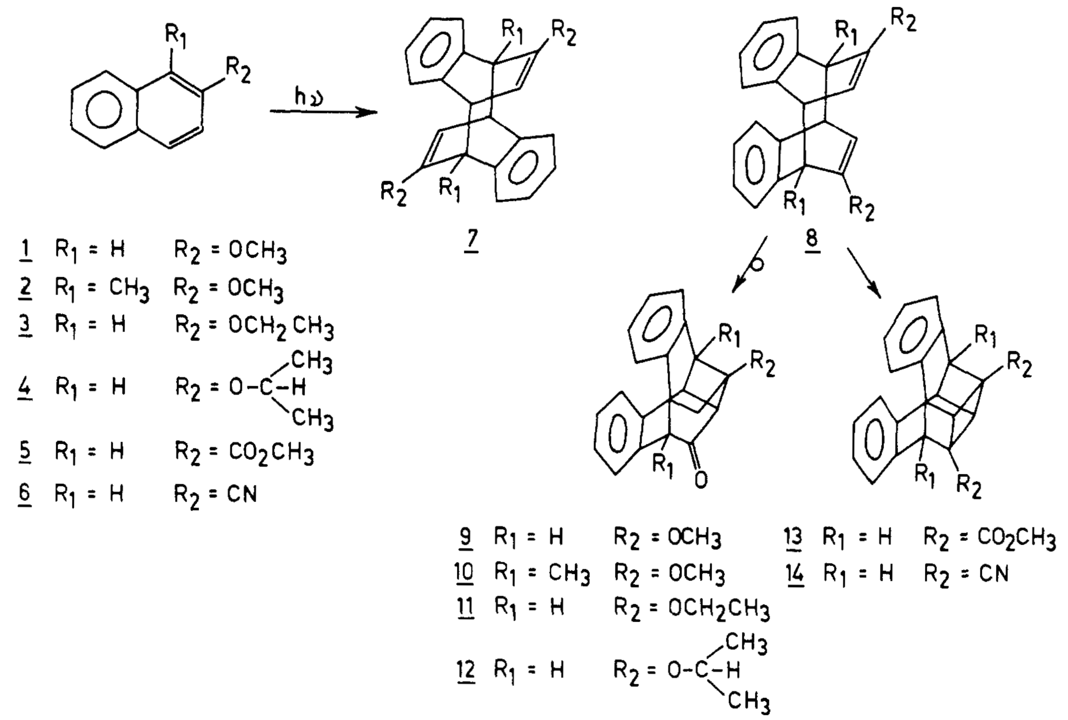


Figure 2. Expected orientation of 2-substituted naphthalenes in micelles.

Scheme I



drophilic in nature serves to orient the molecules at the interface with the substituent group directed toward the polar exterior (Figure 2). This molecular orientation should lead to the cis dimer. Results presented here bear out the above expectation. The cis dimers of 2-alkoxynaphthalenes **1**–**4** rearrange to the corresponding ketones **9**–**12**[17] while the cis dimers of 2-carbomethoxy- and 2-cyanonaphthalenes (**5** and **6**)[15,16] give the corresponding cage products **13** and **14**[18] (Scheme I).

Results

The details of irradiation conditions and products formed are summarized in Table I. Physical and spectral data of products isolated in this study are in perfect agreement with literature reports.[13,14,17] 2-Substituted naphthalenes **1**–**6** were irradiated in organic solvents under a nitrogen atmosphere alongside the micellar solutions in order to afford a comparison. Present results on the irradiation in organic solvents (Table I) are in fair agreement with literature reports.[13-15] While no cis dimer was isolable in any case, for **1**–**4** the trans dimer was the major and the corresponding ketone from the cis dimer the minor product. The conversion percentages were exceedingly low, revealing the low reactivity of these substrates in organic solvents.

Irradiation of **1**–**4** in SDS, CTAB, CTAC, and DTAC micelles gave as the sole product the ketones **9**–**12** derived from the corresponding cis dimers. In the case of 2-ethoxynaphthalene (**3**), a copious precipitation of the cis dimer **8** ($R_1 = H$, $R^2 = OCH_2CH_3$) occurred during photolysis in CTAC. In CTAB the precipitation was faint, and in SDS and DTAC no precipitation occurred. 2-Alkoxynaphthalenes **1**, **2**, and **4** did not precipitate out any cis dimers. After workup of the photolyzed micellar solutions as indicated in Experimental Section, the corresponding ketones were isolated together with unreacted substrates. Neither the trans dimer nor any rearranged products therefrom were isolated. 2-Carbomethoxy- and 2-cyanonaphthalenes were irradiated in SDS and CTAC micelles, and the corresponding cage products **13** and **14**, respectively, were the only products isolated.

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Table I. Photodimerization of 2-Substituted Naphthalenes in Organic Solvent and in Micellar Media

compound	surfactant/solvent	amount solubilized, M ($\langle S \rangle$)[a]	time of photolysis,[b] h	% conv	product yields,[c] %: trans, dimer	ketone	cis, dimer
2-methoxynaphthalene (**1**)	benzene[d]	0.32	720	2.5	80		
	SDS (0.1 M)	0.010 (5)	100	20		60	
	CTAB (0.05 M)	0.007 (12)	100	33		30	
	CTAC (0.025 M)	0.007 (22)	20	72		71	
	DTAC (0.1 M)	0.007	24	55		67	
1-methyl-2-methoxynaphthalene (**2**)	cyclohexane	0.58	143	5.0	50	45	
	SDS (0.1 M)	0.019 (12)	80	40		45	
	CTAB (0.05 M)	0.017 (19)	80	50		12	
	CTAC (0.025 M)	0.008 (23)	36	70		61	
	DTAC (0.1 M)	0.007	36	66		65	
2-ethoxynaphthalene (**3**)	benzene	0.30	480	6.0	40	10	
	SDS (0.1 M)	0.010 (7)	45	31		51	
	CTAB (0.05 M)	0.017 (28)	45	26		16	4
	CTAC (0.025 M)	0.017 (22)	40	58		56	18
	DTAC (0.1 M)	0.012	45	40		60	
2-isopropoxynaphthalene (**4**)	cyclohexane	1.14	240	1.0	52	20	
	SDS (0.1 M)	0.010 (7)	20	15		20	
	CTAB (0.05 M)	0.015 (24)	28	14		15	
	CTAC (0.025 M)	0.008 (23)	28	25		45	
	DTAC (0.1 M)	0.008	28	25		45	
2-carbomethoxynaphthalene (**5**)	benzene:isopropyl alcohol (1:1)	0.19	168	2.0	25 (cage product **13**)		
	SDS (0.1 M)	0.011 (7)	50	11	57 (cage product **13**)		
	CTAC (0.025 M)	0.001 (30)	60	28	36 (cage product)		
2-cyanonaphthalene (**6**)	benzene:*n*-hexene (1:2)	0.10	240	15	**15** (cage product)		
	CTAC (0.025 M)	0.004 (17)	192	73	38 (cage product)		

[a] $\langle S \rangle$, the mean occupancy number of a micelle was calculated by using aggregation numbers 60, 80, and 82 for SDS, CTAB, and CTAC, respectively. [b] Irradiation was carried out in Pyrex tubes by using a Hanovia 450-W medium-pressure mercury arc lamp. [c] Yields presented correspond to TLC isolated yields; average of at least two independent runs. [d] Irradiations in benzene:isopropyl alcohol (1:1), dioxane:water (1:1), and tetrahydrofuran have been reported to yield only the trans dimer (ref 9).

In micellar media compared to organic solvents, enhanced percentages of conversion in shorter durations of irradiation were observed (Table I). Further, the efficiency of the photodimerization was higher in cationic micelles having chloride counterions when compared to those having bromide as counterions. No attempt was made to measure the quantum yield as the reactions required long irradiation times.

Discussion

Distinct features of the micellar irradiations of 2-substituted naphthalenes **1**–**6** are (i) reactivity enhancement compared to organic solvent media, (ii) pronounced regioselectivity in the formation of products, and (iii) reactivity enhancement in cationic micelles due to change of counterion from bromide to chloride.[20,21]

Enhancement of reactivity in micellar media compared to that in organic solvent media is the characteristic micellar catalysis arising due to an increased local concentration of the reactants. Such reactivity enhancements in photodimerization processes have been observed earlier.[2-8,22]

Since polarity of the medium is not an important factor during the photodimerization of 2-substituted naphthalenes,[9,12] the pronounced regioselectivity observed in micellar media can be attributed to the preorientational effect. Unlike aqueous or nonaqueous solvent media, in biphasic systems such as micelles the site of solubilization and the nature of orientation of the reactants are important factors that influence reactivity. Likely sites of solubilization for benzene, naphthalene, and pyrene and the nature of orientation of aromatics bearing hydrophilic groups in micellar media have been investigated.[23-29] On the basis of these reports and the observation of decreased reactivity due to counterion quenching in CTAB micelles, we believe that 2-substituted naphthalenes **1**–**6** are oriented in micelles at the interface as shown in Figure 1. This preorientation, we believe, dictates the regiochemistry of the photodimerization process, and this is expected to lead to cis dimers. The cis dimer rearranges to the ketone in case of 2-alkoxynaphthalenes and gives cage products in the case of **5** and **6**. Photodimerization of 2-substituted naphthalenes in micellar media is the first example where the polarity effect is clearly excluded and the preorientational effect is predominantly operative in effecting the control of regiochemistry.

Comparison of the photodimerization of 2-substituted naphthalenes with 7-alkoxy- and 4-methyl-7-alkoxycoumarins in micellar media[8] reveals the probable extent to which the preorientational effect can be utilized in controlling regiochemistry. Like 2-substituted naphthalenes, 7-alkoxy- and 4-methyl-7-alkoxycoumarins exhibit medium polarity independent photodimerization in organic solvent media;[30] however, a failure to control the regio-

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chemistry through micellar preorientational effect was observed. This observation compared with the above results on 2-substituted naphthalenes suggests that the micellar preorientational effect could perhaps be utilized for only those systems wherein the hydrophobic interaction leading to preorientation is stronger than the interaction involved in the photodimerization process.

The observation of reactivity enhancement in cationic micelles due to a change of counterion from bromide to chloride lends support to the belief that the 2-substituted naphthalenes are solubilized at the interface. The quenching of the excited singlet states of these substrates by bromide counterions in CTAB leads to a decreased reactivity as compared to that in CTAC. Such counterion effects on the fluorescence quenching of excited singlet states of micelle-solubilized naphthalene, pyrene, and anthracene derivatives have been observed previously.[20,21] Our observations are in agreement with those reports and imply that in effecting an efficient photochemical reaction in micellar media counterion effects will have to be taken into consideration.

Experimental Section

Sodium dodecylsulfate (SDS), cetyltrimethylammonium bromide (CTAB), cetyltrimethylamonium chloride (CTAC), and dodecyltrimethylammonium chloride (DTAC) of Eastman Kodak were used after repeated recrystallization from 95% ethanol and methanol. Double distilled water was used to make up micellar solutions. Distilled organic solvents were used. 2-Substituted naphthalenes **1** and **6** were commercial samples (Aldrich) while **2–5** were synthesized by following reported procedures.[31]

Solubilization of Reactants in Micellar Solutions. 2-Substituted naphthalenes **1–6** (100–200 mg) were stirred for 12 h with 100 mL of surfactant solutions (SDS, 0.1 M; CTAB, 0.05 M; CTAC, 0.025 M; DTAC, 0.1 M) of concentrations well above their cmc. The micellar solutions were filtered through Whatman No. 1 filter paper to remove insoluble material, if any, into Pyrex irradiation tubes.

Irradiation and Workup Procedures. Transparent micellar solutions were irradiated at room temperature in Pyrex tubes with a 450-W medium-pressure mercury arc lamp for time intervals indicated in Table I. Nitrogen was bubbled through the solutions for 45 min prior to photolysis, and the irradiation tubes were tightly stoppered. In case of 2-ethoxynaphthalene (**3**), copious precipitation of the cis dimer occurred in CTAC and a light precipitation in CTAB. The precipitate was filtered off following every 10 h of photolysis and air-dried. No precipitation occurred during other irradiations, requiring, therefore, the following workup procedure.

In the case of SDS, workup involved the addition of sodium chloride to the irradiated solution to "salt out" SDS, unreacted substrate, and the products. The "salted out" precipitate was filtered, dried at 45 °C, and washed repeatedly with chloroform. The chloroform extract was washed repeatedly with water, and dried, and the solvent was evaporated. The crude product was subjected to preparative TLC (silica gel/chloroform). For **1–4** the corresponding ketones **9–12** and for **5** and **6** the corresponding cage products **13** and **14** were the only products isolated in addition to unreacted substrates. For cationic detergents (CTAB, CTAC, and DTAC), workup involved dilution of the photolyzed solutions to well below their cmc's and extraction with chloroform or ether.

Irradiation in organic solvents was carried out in nitrogen-purged solution in Pyrex tubes at room temperature under identical conditions as micellar irradiations. Reported workup procedures were adopted.[14]

Identification of Products. The ketones **9–12** and the cage products **13** and **14** were identified by their melting points, UV, IR, ^{1}H NMR, and mass spectra. The spectra obtained for products in this study are in perfect agreement with literature reports.[14-16]

The cis dimer of 2-ethoxynaphthalene, not isolated previously, is a white crystalline solid melting in the range 175–177 °C and has the following spectral features: UV ($CHCl_3$) λ_{max} 274 nm (ϵ 11 600), 283 (11 300); IR (Nujol) ν 1650 cm^{-1}; 1H NMR ($CDCl_3$) δ 1.49 (t, 6 H, J = 8 Hz), 3.88–4.07 (4 H), 4.16 (q, 4 H, J = 8 Hz), 5.67 (2 H), 6.95–7.46 (m, 8 H); mass spectrum, m/e (relative percent) 344 (M^+, 4), 172 (100).

Upon refluxing in benzene containing a catalytic quantity of *p*-toluenesulfonic acid, the cis dimer gave **11** quantitatively.

Control Experiments. A 20-mg sample of the trans dimer of each of the 2-substituted naphthalenes **1–4** was stirred in 100-mL surfactant solutions for 12 h. The trans dimers were found to be insoluble and recovered quantitatively upon filtration of the stirred solution. Because of the insolubility of the trans dimers, the possible photodegradtion of these dimers in micellar media could not be verified. However, if formed, these dimers are expected to precipitate out of the micellar solutions. Even upon dilution of the photolyzed micellar solution well below their cmc's, no precipitation was observed.

Acknowledgment. The Council of Scientific and Industrial Research, Government of India, is thanked for financial support.

Registry No. **1**, 93-04-9; **2**, 1130-80-9; **3**, 93-18-5; **4**, 15052-09-2; **5**, 2459-25-8; **6**, 613-46-7; **8** (R_1 = H; R_2 = OCH_2CH_3), 87935-90-8.

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