provide 1 mol of trifluoromethyl radicals at roughly $^1/_{40}$ of the cost required to obtain them from iodotrifluoromethane,[6] while enough sulfur tetrafluoride to produce 1 mol of trifluoromethyl groups[7] costs at least 15 times as much as 1 mol of 1. Thus even a 10–15% conversion of 1 to a readily isolated trifluoromethylated product may sometimes represent the most economical and perhaps also the least cumbersome procedure. This is illustrated by the work reported here, which shows that electrolysis of solutions of 1 and undecylenic acid (2) produces mixtures from which pure 12,12,12-trifluorododecanoic acid (3) can be easily prepared with a yield of 12.4% based on 1.

Electrolysis of 1 in the presence of linear 1-alkenes was described in some detail in ref 4. When 0.1 or 0.2 mol of alkene dissolved in 40 mL of acetonitrile and 5.6 mL of water was used, the principal trifluoromethylated product was dimeric, but fractions containing the corresponding (trifluoromethyl)alkane, several isomeric 1-(trifluoromethyl)alkenes, and sometimes the 1,2-bis(trifluoromethyl)alkane were also obtained. The information given is not sufficient to allow the relative amounts of these products to be calculated, but they appear not to change greatly with the molecular weight of the alkene or the relative amounts of 1 and alkene taken. Attempts made here to effect larger changes in the product distribution by modifying the reaction conditions also met little success, though it seems that dimer formation could be somewhat reduced by using acetone/water and working at lower alkene concentrations. With 2, as with the simple alkenes, pouring the reaction mixture into water gave an oil from which it was not readily possible to isolate a single component by distillation. However, it is a great advantage that now the desired ultimate product 3 is solid at room temperature. A preliminary distillation gave a fraction containing unreacted 2 and the mixed monomeric products, which was catalytically hydrogenated to convert 2 to undecanoic acid and the isomeric (trifluoromethyl)undecenoic acids to 3. On distilling again, a fraction rich in 3 was collected from which the pure product was obtained by recrystallization from acetonitrile. The major impurity, undecanoic acid, is quite soluble in this solvent[8] even at 0 °C, while 3, like dodecanoic acid,[8] is very soluble at room temperature but only sparingly soluble at 0 °C.

Compound 3 was previously prepared in this laboratory several times by the reaction of dodecanedioic acid with sulfur tetrafluoride.[9] The electrochemical synthesis is without question the easier one, especially when fairly large amounts of the product are needed. Other acids in the series $CH_2{=}CH(CH_2)_nCOOH$ should react analogously but are considerably more difficult to obtain.

Experimental Section

Commercial samples of the starting materials and solvent were used as received. Each reaction mixture consisted of 30 mL (389 mmol) of 1, 60.6 mL (300 mmol) of 2, 144 mL of acetone, and 36 mL of water. The customary step of partially neutralizing the solution with a little sodium hydroxide was omitted because this was found not to affect the course of the reaction significantly. The electrolysis cell was as described before.[5] Fluorine NMR spectra of aliquots withdrawn at various times indicated that the monomeric products reached optimal concentrations when about 0.48 Faraday had passed through the cell, which was achieved by using an approximately constant current of 0.54 A for 24 h. The mixture was then poured into 700 mL of water, the dense oil isolated, and the water layer extracted with 2 × 50 mL of methylene chloride. The combined nonaqueous layers from five identical runs were distilled at 1 atm to remove volatile solvents and then at about 1 torr, with all the material boiling below 140 °C (mostly 105–130 °C) being collected as a single fraction weighing 170 g. This was diluted with 100 mL of glacial acetic acid and hydrogenated at low pressure over 5% Pd/C catalyst until hydrogen absorption ceased and the NMR spectrum no longer showed signals characteristic of the unsaturated products. After removal of the catalyst the mixture was distilled again at 1 torr by using a short Vigreux column and an air-cooled condenser. The boiling point rose more or less steadily during this distillation, and the distillate was collected in four fractions weighing 45, 32, 75, and 6 g and corresponding to boiling ranges of 95–106 °C, 106–110 °C, 110–116 °C, and 116–124 °C, respectively. This first of these consisted mostly of undecanoic acid, while 3 was most concentrated in the large third fraction, which partially sodified during the distillation. This was dissolved in 300 mL of acetonitrile and stored in the refrigerator overnight, and 43.4 g of 3 slightly contaminated with undecanoic acid were isolated. The filtrate and washings were distilled to remove acetonitrile and then vacuum distilled with the smaller fractions to obtain more product-rich material, which on treatment with acetonitrile yielded a further 17.1 g of solid. Repetition of this procedure produced another 4.1 g. On further recrystallization from acetonitrile the combined solids gave 57.6 g of pure 3. This material did not show the methyl triplet of undecanoic acid in its ^{1}H NMR spectrum, and its spectra and melting point agreed with those of 3 prepared by the sulfur tetrafluoride procedure.[9] A second crop of somewhat lower purity weighed 3.6 g, bringing the total yield to 12.4% based on 1 or 16.0% based on 2. The yield can be slightly improved if the remaining product-containing residues are worked up with crude material from a subsequent preparation.

Registry No. 1, 76-05-1; 2, 112-38-9; 3, 90584-39-7.

(6) Hudlicky, M. "Chemistry of Organic Fluorine Compounds", 2nd ed.; Ellis Horwood: Chichester, England, 1976; p 421.
(7) Reference 6, p 153.
(8) Hoerr, C. W.; Ralston, A. W. *J. Org. Chem.* **1944**, *9*, 329.
(9) Muller, N.; Birkhahn, R. H. *J. Phys. Chem.* **1967**, *71*, 957.

Photochemical Reactions in Constrained Systems: Changes in Mode of Solubilization due to Long-Chain Hydrophobic Groups

N. Ramnath and V. Ramamurthy*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

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The usefulness of organized media to bring about regioselectivity in photocycloadditions by surfactant aggregates has been demonstrated.[1-5] In general, hydrophilic groups such as carbonyl or hydroxyl have been used to orient these molecules at the micelle–water interface. Recently we have shown that micellar-induced preorientations have limitations.[6] The dimerization of 7-alkoxycoumarins in SDS and CTAB micelles was expected to lead to syn and/or anti head–head dimer by virtue of the aggregation of coumarin molecules at the interface in which carbonyl groups would face the aqueous exterior while the anchoring alkoxy groups held the coumarin solubilizates in an ordered row. Such an expectation however was not borne out. Since chain lengths up to C_{12} failed to bring

(1) Lee, K. H.; de Mayo, P. *J. Chem. Soc. Chem. Commun.* **1979**, 493. de Mayo, P.; Sydnes, L. K. *Ibid.* **1980**, 994. Berenjian, N.; de Mayo, P.; Sturgeon, M.; Sydnes, L. K.; Weedon, A. C. *Can. J. Chem.* **1982**, *60*, 425.
(2) Fargnes, R.; Maurette, M. T.; Oliveros, E.; Riviere, M.; Lattes, A. *Nouv. J. Chim.* **1979**, *3*, 487.
(3) Nakamura, Y.; Kato, T.; Morita, Y. *Tetrahedron Lett.* **1981**, *22*, 1025.
(4) Wolff, T. *J. Photochem.* **1981**, *16*, 343.
(5) Ramesh, V.; Ramamurthy, V. *J. Org. Chem.* **1984**, *49*, 536.
(6) (a) Muthuramu, K.; Ramnath, N.; Ramamurthy, V. *J. Org. Chem.* **1983**, *48*, 1872. (b) Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1982**, *41*, 3976.

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Table I. Photodimerization of 7-Alkoxycoumarins in Organic, Aqueous, and Micellar Media

coumarin	media (M)	concn of coumarin, M	duration of irradn,[a] h	products formed[b]	yield,[c] %
7-*O*-heptyl (**4**)[d]	chloroform-*d*	0.25	50	syn HT	54
	water	not soluble			
	SDS (0.05)	6×10^{-3}	50	syn HT	50
	CTAB (0.025)	6×10^{-3}	50	syn HT	6
	chloroform-*d*/ benzophenone (0.2)	0.23	50	no reaction	
7-*O*-dodecyl (**6**)[d]	chloroform-*d*	0.25	50	syn HT	17
	water	not soluble			
	SDS (0.05)	5×10^{-3}	50	syn HT	15
	CTAB (0.025)	5×10^{-3}	50	syn HT	5
	chloroform-*d*/ benzophenone (0.2)	0.25	50	no reaction	
7-*O*-tetradecyl (**7**)	chloroform-*d*	0.25	45	syn HT	17
	water	not soluble			
	SDS (0.1)	1×10^{-3}	110	syn HT	15
	CTAB (0.05)	not soluble			
7-*O*-hexadecyl (**8**)	chloroform-*d*	0.25	75	syn HT	30
	water not soluble				
	SDS (0.1)	0.8×10^{-3}	100	syn HT	10
	CTAB (0.05)	not soluble			
7-*O*-octadecyl (**9**)	chloroform-*d*	0.25	50	syn HT	25
	water	not soluble			
	SDS (0.1)	0.7×10^{-3}	100	syn HT	3
				anti HT	6
	CTAB (0.05)	not soluble			

[a] All irradiations were conducted in Pyrex vessels by using a 450-W medium pressure mercury lamp. [b] Structures of the dimers were identified by their spectral properties. [c] Yields presented correspond to TLC isolated yields. [d] Muthuramu, K.; Ramnath, N.; Ramamurthy, V. *J. Org. Chem.* **1983**, *48*, 1872.

Table II. Photodimerization of 4-Methoxy-7-alkoxycoumarins in Organic, Aqueous, and Micellar Media

coumarin	media (M)	concn of coumarin, M	duration of irradn,[a] h	products formed[b]	yield,[c] %
4-methyl-7-*O*-hexyl (**12**)[d]	chloroform	0.5	30	syn HT	54
	water	1×10^{-5}			
	SDS (0.05)	2.23×10^{-2}	72	syn HT	65
	CTAB (0.025)	1.62×10^{-2}	72	syn HT	22
	chloroform/ benzophenone (0.25)	0.38	72	no reaction	
4-methyl-7-*O*-dodecyl (**15**)[d]	chloroform	0.25	80	syn HT	35
	water	not soluble			
	SDS (0.05)	0.3×10^{-2}	100	syn HT	35
	CTAB (0.025)	0.3×10^{-2}	100	syn HT	10
4-methyl-7-*O*-octadecyl (**16**)	chloroform	0.25	75	syn HT	64
	water	not soluble			
	SDS (0.1)	0.6×10^{-3}	100	syn HT	4
	CTAB (0.05)	not soluble		syn HT	

[a] All irradiations were conducted in Pyrex vessels by using a 450-W medium pressure mercury lamp. [b] Structures of the dimers were identified by their spectral properties. [c] Yields presented correspond to TLC isolated yields. [d] Muthuramu, K.; Ramnath, N.; Ramamurthy, V. *J. Org. Chem.* **1983**, *48*, 1872.

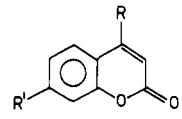
about preorientation of the coumarin molecules, it was of interest to know whether chains longer than C_{12} could provide a greater degree of hydrophobic association that can overcome the forces governing regioselectivity. This note presents the results of photodimerization of long-chain alkoxycoumarins with chain lengths C_{14}, C_{16}, and C_{18}.

Results

Coumarins **7–9** (Figure 1) dimerized in organic solvents to give a single dimer syn-head-tail. The dimers were characterized by comparison of their ^1H NMR spectra with those derived from 7-methoxycoumarin.[7] The photodimerization of coumarins **1–6** and **10–15** have already been reported[6a] and a few of them are included in Table I for comparison. 7-Alkoxycoumarins are insoluble in water; solubility of **7–9** and **16** in SDS is limited. Since **7–9** are only very sparingly soluble in CTAB and CTAC, micellar irradiations of these coumarins were conducted only in SDS.

Irradiations of **7** and **8** in SDS gave the corresponding syn head–tail dimer (Table I). Surprisingly, irradiation of **9** in SDS resulted in the precipitation of a mixture of two dimers in the ratio 2:1 as revealed by a 270-MHz ^1H NMR spectrum. The dimer formed in lower yield corresponded to the syn head–tail dimer. A 400-MHz ^1H NMR spectrum of the other dimer revealed it to have anti head–tail configuration. Formation of this dimer was unexpected. The anti dimers of coumarins are generally characteristic of triplet state reactions. However, triplet sensitization of **7–9** did not give anti head–tail dimers. A

(7) Ramasubbu, N.; Guru Row, T. N.; Venkatesan, K.; Ramamurthy, V.; Rao, C.N.R. *J. Chem. Soc., Chem. Commun.* **1982**, 178.



1 R = H; R' = OCH_3
2 R = H; R' = $O(CH_2)_3CH_3$
3 R = H; R' = $O(CH_2)_5CH_3$
4 R = H; R' = $O(CH_2)_6CH_3$
5 R = H; R' = $O(CH_2)_7CH_3$
6 R = H; R' = $O(CH_2)_{11}CH_3$
7 R = H; R' = $O(CH_2)_{13}CH_3$
8 R = H; R' = $O(CH_2)_{15}CH_3$
9 R = H; R' = $O(CH_2)_{17}CH_3$
10 R = CH_3; R' = OCH_3
11 R = CH_3; R' = $O(CH_2)_3CH_3$
12 R = CH_3; R' = $O(CH_2)_5CH_3$
13 R = CH_3; R' = $O(CH_2)_6CH_3$
14 R = CH_3; R' = $O(CH_2)_7CH_3$
15 R = CH_3; R' = $O(CH_2)_{11}CH_3$
16 R = CH_3; R' = $O(CH_2)_{17}CH_3$

Figure 1. 7-Alkoxy- and 4-methyl-7-alkoxycoumarins investigated.

surprising observation was the absence of syn dimers expected on the basis of the preorientation of 7-alkoxycoumarins in micelles.

Irradiation of 4-methyl-7-alkoxycoumarins **10–16** (Figure 1) gave only the syn head–tail dimers (Table II). In contrast to its counterpart, **16** gave only the syn head–tail dimer. Irradiation of **1–6** and **10–14** in CTAC revealed a significant increase in reactivity compared to CTAB (Table III). The role of counterions appears to be significant in this context.

Discussion

(A) Structure of Dimers. One of the dimers obtained from **9** has been established to have syn head–tail configuration by comparison of its spectral data with the syn head–tail dimer of 7-methoxycoumarin whose structure has been established through X-ray investigation.[7] The syn head–tail dimers formed upon irradiation of **7–9** and **10–16** show a closely similar pattern for the aromatic protons (H_5, H_6, and H_8) in their NMR spectra. These protons can be described as part of an AMX system. In comparison with the same protons of the monomer, H_5 and H_6 are shifted slightly upfield while H_8 is shifted to a higher field by over 0.6 ppm. This strong shielding effect on H_8 caused by diamagnetic anisotropy of a phenyl nucleus situated in front of the proton is possible only in the syn head–tail configuration. H_5 which appears as a doublet is only slightly affected. In general, the cyclobutyl protons of syn dimers resonate around δ 4.0–4.2 whereas those of anti isomers resonate below δ 3.90.[8,9] In the syn head–tail dimers of **7–9**, the cyclobutyl protons form part of a AA'BB' system and are split symmetrically about δ 4.16 with $J_{AB} = J_{A'B'} = 8$ Hz. This tallies well with the coupling constants for cis protons in similar systems.[10] The dimer identified as anti head–tail of **9**, importantly, shows a different absorption for the cyclobutyl protons. These absorb at two different regions as two sets of protons corresponding to four protons and are centered at δ 4.16 and 3.56. The coupling constants of 8 and 4 Hz agree well with the reported cis and trans couplings, respectively. On the basis of the splitting pattern of cyclobutyl protons, the dimer has been identified to have anti head–tail configuration. Similar splitting of cyclobutyl protons in the anti head–head dimer would not be expected. That it is the anti head–tail dimer was concluded by comparison of the splitting patterns in the anti head–head and anti head–tail dimers in similar systems.[8,9]

Table III. Photodimerization of 7-Alkoxy- and 4-Methyl-7-alkoxycoumarins in CTAB and CTAC Micelles

no.	concentrations of coumarin in CTAB (CTAC), M	duration of irradn, h	yield (%) of syn HT dimer in CTAB (0.025 M)	yield (%) of syn HT dimer in CTAC (0.025 M)
1	0.006 (0.008)	72	10	25
2	0.011 (0.008)	30	5	30
3	0.016 (0.007)	45	5	33
4	0.006 (0.006)	50	6	40
5	0.006 (0.008)	50	5	5
6	0.006 (0.008)	50	5	6
10	0.004 (0.004)	72	5	25
11	0.0075 (0.0115)	60	40	58
12	0.016 (0.007)	72	22	62
14	0.075 (0.0115)	100	40	50
15	0.003 (0.0035)	100	10	33

(B) Changes in the Mode of Solubilization due to Long-Chain Hydrophobic Groups. Since chain lengths up to C_{12} failed to bring about preorientation of the coumarin molecules, it was of interest to know whether chains longer than C_{12} could provide a greater degree of hydrophobic association that can overcome the forces governing regioselectivity. In this connection, the photodimerization of 7-alkoxycoumarins with chain lengths C_{14}, C_{16}, and C_{18} **7–9** and **16** in micelles was studied. Chain lengths upto C_{18} have been used to induce hydrophobicity.[11] Present results surprisingly show that not only are the long chains unsuccessful in bringing about the expected regioselectivity but that another feature, namely, the appearance of the hitherto unobserved anti head–tail dimer, lends a new dimension to the overall situation. The appearance of this new dimer is suggested to be a reflection of a change in the nature of solubilization of the substrates from small to moderately long-chain alkoxycoumarins to long-chain coumarins. With very large chain lengths such as in **9**, the C_{18} chain which is longer than the surfactant chain length (C_{12}) probably changes the mode of solubilization. Our conjecture is that for large chains the coumarin moiety is merely adsorbed on the micellar surface with the alkoxy chains curling up within the micellar core. Although there is no direct evidence for adsorption of the long-chain coumarins on the micellar surface, fluorescence offers a potential method to ascertain the site of solubilization.

The fluorescence properties of 7-alkoxycoumarins have been used in our laboratory to determine their site of solubilization.[12] Comparison of the solvent-dependent fluorescence emission intensities of alkoxycoumarins **1–5** and **10–12** in SDS and CTAB with that in organic solvents show that the fluorescence of these coumarins in micelles is greater than that in apolar organic solvents but less than that in water. The above results are interpreted to suggest that the site of solubilization of these coumarins is micelle–water interface. However, we have not been able to provide any experimental evidence for the adsorbed state owing to the poor solubility of these long-chain coumarins **7–9** in the low surfactant concentration required for such experimentation.

Under the conditions of solubility of **9** in SDS micelles, not more than two molecules/micelle could possibly be solubilized. Due to adsorption of the molecule, the mobility of the coumarin molecules may be greatly reduced as compared to the coumarins with shorter chains. It is

(8) Muthuramu, K. Ph.D. Thesis, Indian Institute of Science, Bangalore, 1983. Muthuramu, K.; Ramamurthy, V. *Ind. J. Chem.*, in press.
(9) Leenders, L. H.; Schouteden, E.; de Schryver, F. C. *J. Org. Chem.* **1973**, *38*, 957.
(10) Fleming, I.; Williams, D. H. *Tetrahedron* **1967**, *23*, 2747.
(11) Schmehl, R.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1938.
(12) Muthuramu, K.; Ramamurthy, V. *J. Photochem.*, in press.

conceivable that in the adsorbed state, two adjacently adsorbed molecules will dimerize to give the anti dimer. Formation of a syn dimer would require an overlap of two coumarin molecules which seems less conceivable in the adsorbed state. It may be argued that the low population of micelles, which in effect is a low concentration of coumarin molecules, may lead to intersystem crossing before an encounter, leading to the triplet-derived anti dimer. However, when **6** was irradiated at such low occupation numbers as for **9**, the product was still only the syn head–tail dimer. Further, triplet sensitization of **9** both in organic solvent and micellar media did not give anti dimer.

In the case of **8** which gives only the syn head–tail dimer, formation of the corresponding anti head–tail dimer could be expected since the chain has only two methylene units lesser than **9**. However reasons for this are not quite obvious. Since anomaly occurs only with C_{18}, we thought that it would be interesting to study the behavior of C_{20}-alkoxycoumarin. However disappointingly it was not soluble in an SDS micelle. 4-Methyl-7-alkoxycoumarins give the syn head–tail dimer, irrespective of the chain length. Although **16**, the counterpart of **9**, could also give the anti head–tail dimer, only the syn head–tail dimer was formed. Drieding models of this coumarin show steric interactions between the carbonyl group of one monomer with the methyl group of the other during such encounters. It is likely that this crowding is responsible for the nonformation of the anti head–tail dimer.

(C) Counterion Effect. Alkoxycoumarins **1–6** and **10–19** show a high degree of reactivity in CTAC compared to CTAB micelle (Table III). The observed large increase indicates a significant counterion effect. We attribute low reactivity in CTAB to the bromide ion quenching of excited singlet state of coumarin, thereby resulting in poor S_1 reactivity in CTAB. Since heavy atom induced intersystem crossing would be negligible in the presence of chloride ions, photodimerization of the coumarins (Table III) from S_1 competes favorably with intersystem crossing. Similar counterion effects have been observed during the fluorescence quenching and phosphorescent enhancement of naphthalene and pyrene in CTAB.[13] Decrease in phosphorescence quantum yield of anthracenes, indenes, and diphenyl amine in CTAC and a concomitant increase in CTAB have also been attributed to counterion effects.[14] Reactivity differences in CTAB and CTAC of anthracenes,[15] naphthalenes,[5] and acenaphthalenes[16] also confirm the counterion effects in micellar systems.

Results presented above show that irrespective of the magnitude of induced hydrophobic associations, micellar preorientational effects operate only if the inherent forces controlling regioselectivity are weak. The role of counterions in micellar reactivity is also important.

Experimental Section

SDS and CTAB (Sigma) and CTAC (Eastman Kodak) were recrystallized twice from 95% EtOH and methanol–ether mixture respectively. Double distilled water was used for micellization. All solvents were distilled before use. Coumarins **1–16** were prepared by condensation of 7-hydroxycoumarins with the corresponding alkyl bromide.[6] The solubilization method for SDS and CTAB have been described earlier.[6] Solubilization in CTAC was done in an identical manner.

Irradiation and Workup Procedure. The micellar solutions were irradiated in Pyrex tubes with a 450-W medium pressure mercury arc lamp for durations indicated in Tables I and II. For coumarins **1–5** and **10–13**, the corresponding dimer precipitated out during the course of the reaction. These dimers were recovered by filtration. The dimer retained back in the filtrate in the case of the above-mentioned coumarins and the dimers in the other cases **6–8** and **14** and **15** where they did not precipitate out were recovered as follows. For SDS reactions, the irradiated mixture (or filtrate) was saturated with sodium chloride to salt out the surfactant along with the monomer and dimer. Precipitated material was filtered out and dried at 45° after which it was washed repeatedly with chloroform. The chloroform extract was washed with water and dried, and the organic residue was separated by preparative TLC to obtain the pure syn head–tail dimer. For CTAB and CTAC reactions, the filtrate was diluted below its cmc and extracted with (50 × 10 mL) ether. The organic extract upon washing and drying yielded the pure dimer after preparative TLC.

Separation and Identification of Syn HT and Anti HT Dimers of 9. The solids obtained from irradiation of **9** in SDS contained a mixture of the two dimers in the ratio of 1:2 (syn:anti). The dried solids were dissolved in hexane with heating. On cooling, the solids precipitated out. These solids were separated from the mother liquor and again subjected to the same treatment. The more soluble syn dimer remains in the hexane layer. Repeated dissolutions in hexane yields the pure anti HT dimer. The spectral properties of the two dimers follow.

Syn head–tail dimer (syn HT) of 9: mp 96–98 °C; UV ($CHCl_3$) λ_{max} 279 (ϵ 2600), 244 (5000) nm; IR (Nujol) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, 6 H, 6 Hz), 1.2–1.4 (m, 64 H), 3.9 (t, 4 H, 6 Hz), 4.18 (t, 2 H, 8 Hz), 4.20 (t, 2 H, 8 Hz), 6.18 (d, 2 H, 2 Hz), 6.66 (d × d, 2 H, 2 Hz, 8 Hz), 7.02 (d, 2 H, 2 Hz); mass spectrum (70 eV), *m/e* 828, 800, 414, 386, 162.

Anti head–tail (anti HT) dimer of 9: mp 158–160 °C; UV ($CHCl_3$) λ_{max} 280 (ϵ 2100), 243 (3600); IR (Nujol) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, 6 H, 6 Hz), 1.2–1.4 (m, 64 H), 3.54 (m, 2 H, 8 Hz, 4 Hz), 3.95 (t, 4 H, 8 Hz), 4.10 (m, 2 H, 4 Hz, 8 Hz), 6.6 (d, 2 H, 2 Hz), 6.73 (d × d, 2 H, 2 Hz, 10 Hz), 7.18 (d, 2 H, 10 Hz); mass spectrum (70 eV), *m/e* 828, 414, 386, 162.

Benzophenone-Sensitized Irradiations. A solution of alkoxycoumarins **6–9** (0.18 g) and benzophenone (0.7 g) in 25 mL of benzene was irradiated in a Pyrex tube for 72 h by using a 450-W medium-pressure mercury arc lamp. After the irradiation, solvent was distilled off and the remaining material separated by column chromatography (silica gel/hexane–benzene). Only alkoxycoumarins and benzophenone were isolated. No dimer was present.

A solution of **9** (0.007 M) and benzophenone (0.01 M) solubilized in 80 mL of 0.1 M SDS was irradiated for 100 h. Workup of the irradiated solution by dilution and extraction technique gave only **9**. No anti head–tail dimer of **9** was formed.

Under the above conditions, benzophenone is expected to absorb at least 50% of the incident light. Furthermore, phosphorescence quenching experiments revealed that alkoxycoumarins quenched the triplet state of benzophenone. Therefore, absence of reactivity under the above conditions we believe is not due to the nonformation of the triplets of alkoxycoumarins.

Registry No. **1**, 531-59-9; **1** (syn HT dimer), 37786-10-0; **2**, 71783-00-1; **2** (syn HT dimer), 90741-67-6; **3**, 71783-02-3; **3** (syn HT dimer), 85389-91-9; **4**, 85389-84-0; **4** (syn HT dimer), 90741-68-7; **5**, 85405-69-2; **5** (syn HT dimer), 90741-69-8; **6**, 85389-85-1; **6** (syn HT dimer), 85389-92-0; **7**, 77140-51-3; **8**, 90741-63-2; **9**, 90741-64-3; **9** (syn HT dimer), 90821-10-6; **9** (anti HT dimer), 90741-65-4; **10**, 2555-28-4; **10** (syn HT dimer), 89105-46-4; **11**, 85389-86-2; **11** (syn HT dimer), 85389-93-1; **12**, 85389-87-3; **12** (syn HT dimer), 90741-70-1; **13**, 85389-88-4; **14**, 85389-89-5; **14** (syn HT dimer), 85389-94-2; **15**, 85389-90-8; **15** (syn HT dimer), 90741-71-2; **16**, 85297-30-9; **16** (syn HT dimer), 90741-66-5; CTAB, 57-09-0; CTAC, 112-02-7; SDS, 151-21-3.

(13) Hautala, R. R.; Turro, N. J. *Mol. Photochem.* **1972**, *4*, 545. Hautala, R. R.; Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 5508.
(14) Wolff, T. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 1132.
(15) Wolff, T.; Muller, N.; Von Bunau, G. *J. Photochem.* **1983**, *22*, 61.
(16) Ramesh, V.; Ramamurthy, V. *J. Photochem.* **1984**, *24*, 395. Mayer, H.; Sauer, J. *Tetrahedron Lett.* **1983**, *24*, 4091.