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INTRAMOLECULAR ORIENTATION AT THE MICELLAR INTERFACE: CONTROL OF NORRISH TYPE I AND TYPE II REACTIVITY OF BENZOINALKYLETHERS VIA CONFORMATIONAL EFFECTS

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ABSTRACT

The photolysis of benzoinalkylethers **1–5** solubilized in detergents show a significant deviation from the course of reaction in isotropic organic solvents. Remarkable difference in photobehaviour is noticed between the short chain (**1–3**) and the long chain (**4** and **5**) benzoinalkylethers in the micellar media. However, the influence of the micellar media on the photobehaviour of alkyldeoxybenzoins **6** and **7** was small. The importance of 'cage effect' in controlling the product distribution was evident from its dependence on the micellar size and on the occupancy number. More importantly, a comparative analysis of the photobehaviour of the ketone **1–7** reveals that the micellar interface can be used to control the conformations of organic molecules.

Organized assemblies continue to attract the attention of photochemists.[1] Recent reports have demonstrated that a considerable degree of product control can be achieved by working in organized systems. Proximity, favourable orientation and microscopic environment are some of the factors which contribute to the required optimization of a particular chemical event in organized media. We illustrate below through the photobehaviour of benzoinalkylethers **1–5** (Scheme 1) that micelles can be used to control the conformations of the reactant guest species. Benzoinalkylethers are known to undergo Norrish type I reaction as the only photoreaction in organic solvents (Scheme 1).[2] The type II reaction, even if feasible in these substrates, is not observed, probably owing to the overwhelmingly faster type I process. The incorporation of such a system into the 'super cage' provided by the micelle[3] is expected to suppress the type I process, the initially formed α-cleavage radical being facilitated to recombine to regenerate the starting benzoin ether. Under such circumstances, the normally slow type II process would become detectable, provided the conformation of the molecule is suitable for H-abstraction process. We envisioned that the tendency of the polar oxygens of the carbonyl and the alkoxy groups in **1–3** to point towards the aqueous exterior would lead to conformation **B** (Figure 1) and thus to the type II products. To further probe such a conformational control in micelles compounds **4–7** were investigated. In one set of compounds, longer alkyl chains were introduced on the alkoxy moiety (**4** and **5**) that would

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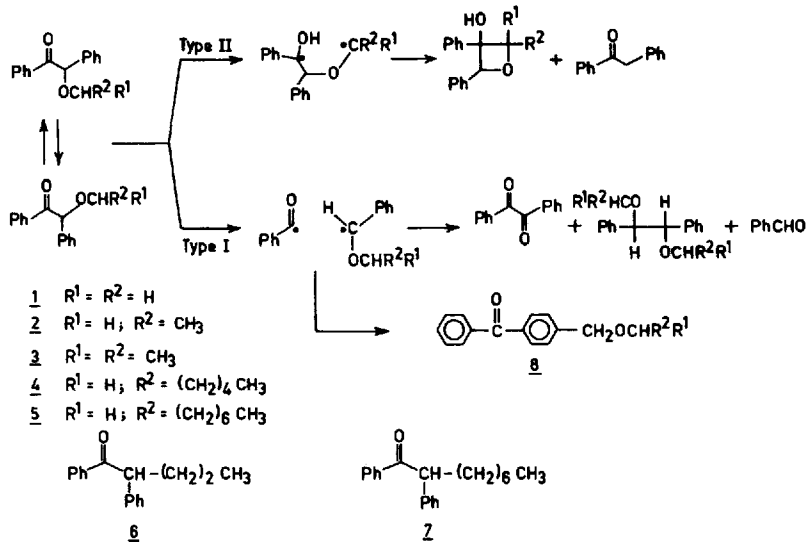
prefer to reside in the interior of the micellar core, thus attempting to populate conformer **A** (Figure 1) to increasing extents. In such an event, even in the presence of 'cage control' there is no possibility of obtaining the type II reaction. In the other set of compounds, alkoxy group was replaced by the alkyl substituent. α-Propyl and α-octyl deoxybenzoins (**6** and **7**) were investigated with the hope that in such molecules, in the absence of the second oxygen, the conformational control exerted by the micellar interface would be small.



Scheme 1

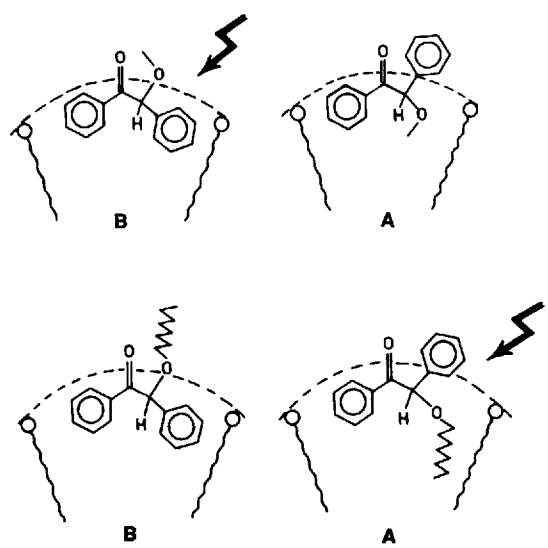


Figure 1. Probable conformations of short chain and long chain benzoinalkylethers at micellar-aqueous interface

RESULTS

Photolysis of benzoinalkylethers **1–3** in N_2 saturated benzene and methanol resulted in benzaldehyde, benzil and pinacol ethers (Tables 1 and 2). Under aerated conditions small amounts of benzoic acid and alkyl benzoates were also obtained. Irradiation of **4** and **5** in N_2 saturated benzene solution gave benzaldehyde, pinacol ethers, benzil and deoxybenzoin (Tables 2 and 3). While the first three products result from the Norrish type I α-cleavage process, deoxybenzoin arises from the intramolecular γ-hydrogen abstraction. The above solution results are unexceptional and are analogous to the literature reports.[2,4] On the basis of the earlier studies on similar systems, it is assumed that **1–5** have unit intersystem crossing efficiency and undergo α-cleavage and γ-hydrogen abstraction from the triplet excited nπ* state.

Table 1. Product distribution upon photolysis of benzoin methyl ether in various micelles[a,b]

Medium[d]	Benzaldehyde[c]	Methyl benzoate	Pinacol ether	Benzil	Deoxybenzoin	Oxetanol
Benzene	27	—	39	23	—	—
Methanol	17	—	62	11	—	—
Sodium octyl sulphate	45	9	27	4	5	2
Sodium decyl sulphate	32	8	45	—	4	1
Sodium dodecyl sulphate	32	17	24	1	12	6
Potassium decanoate	38	7	34	—	10	1
Potassium dodecanoate	28	10	38	—	10	5
Dodecyl trimethyl ammonium bromide	34	6	37	—	6	6
Dodecyl trimethyl ammonium chloride	40	10	30	—	5	5
Cetyl trimethyl ammonium bromide	17	15	13	—	3	44
Cetyl trimethyl ammonium chloride	14	14	8	7	4	52

[a]Products were analysed by gc using an internal standard; error limit ± 5%; Conversion < 20%.
[b]All irradiations were conducted under N_2 atmosphere.
[c]Benzaldehyde could not be estimated accurately due to its solubility in water during extraction. The extent of the type I reaction could be gauged from the yield of the pinacol ether.
[d]All micellar irradiations were conducted at an occupancy number of one.

Table 2. Photolysis of benzoin alkyl ethers in various micelles—dependence on micellar size

Medium[a]	Benzaldehyde	Alkyl benzoate	Pinacol ether	Benzil	*P*-Benzoyl benzyl alkyl ether (**8**)	Deoxybenzoin	Oxetanol
(i) **Benzoin ethyl ether**							
Benzene	34	—	50	8	—	—	—
Methanol	26	—	59	9	—	—	—
Sodium dodecyl sulphate	39	7	27	6	—	6	6
Dodecyl trimethyl ammonium bromide	41	10	29	—	—	10	2
Dodecyl trimethyl ammonium chloride	37	7	33	—	—	6	2
Cetyl trimethyl ammonium bromide	25	5	21	—	11	5	21
Cetyl trimethyl ammonium chloride	31	4	18	4	4	4	25
(ii) **Benzoin isopropyl ether**							
Benzene	28	—	39	23	—	—	—
Methanol	21	—	61	11	—	—	—
Sodium dodecyl sulphate	31	17	25	1	—	8	8
Dodecyl trimethyl ammonium chloride	14	21	43	4	—	2	4
Dodecyl trimethyl ammonium bromide	10	13	444	5	—	2	11
Cetyl trimethyl ammonium chloride	9	26	9	9	4	4	26
Cetyl trimethyl ammonium bromide	9	24	13	—	6	6	25
(iii) **Benzoin hexyl ether**							
Benzene	16	—	40	18	—	15	—
Sodium dodecyl sulphate	28	—	41	—	—	13	—
Dodecyl trimethyl ammonium chloride	25	—	40	9	—	13	—
Dodecyl trimethyl ammonium bromide	17	—	46	3	—	13	—
Cetyl trimethyl ammonium chloride	11	—	22	—	60	—	—
Cetyl trimethyl ammonium bromide	14	—	27	—	50	—	—

[a]All micellar irradiations were conducted at an occupancy number of one.

Table 3. Dependence of product distribution on the micellar size[a]—photolysis of benzoin octyl ether

Medium	Benzaldehye	Octyl benzoate	Pinacol ether	Deoxy benzoin	*p*-Benzoyl benzyl alkyl ether (**8**)
Benzene	12	—	49	3	—
Sodium dodecyl sulphate	4	18	73	—	—
Potassium decanoate	6	18	73	—	—
Potassium dodecanoate	5	18	71	2	—
Dodecyl trimethyl ammonium chloride	7	24	63	2	—
Dodecyl trimethyl ammonium bromide	6	21	68	2	—
Cetyl trimethyl ammonium bromide	4	18	30	2	42
Cetyl trimethyl ammonium chloride	3	15	36	2	45

[a]All micellar irradiations were conducted at an occupancy number of one.

Photolyses of the micellar solubilized **1–3** yielded Norrish type II products along with those from the type I process. The yield of the γ-hydrogen abstraction products was dependent on the micellar size (Table 1) and on the occupancy number (Table 4) of the guest ketone in the micelle. Larger size of the micelle and lower occupancy of the guest in the micelle favoured Norrish type II products. However, the product distribution was only marginally dependent on the head group and on the counter-ion of the surfactants used. As evident from Tables 1 and 4 Norrish type II products constitute > 60% of the product mixture when irradiation of benzoinmethlylether was carried out in cetyltrimethyl ammonium bromide (CTAB) and cetyltrimethyl ammonium chloride (CTAC) micelles.

In micellar media, benzoinhexylether and benxzoinoctylether behaved differently from that of **1–3**. Irradiation of **4** and **5** in CTAB and CTAC micelles gave, in major amounts, a rearranged product (Scheme 1) derived via the rearrangement of the α-cleavage radicals (Tables 2, 3 and 5). In contrast to the photobehaviour of **1–3**, γ-hydrogen abstraction products are formed only in minor amounts. However, the yield of the rearranged product **8** was dependent on the micellar size (Table 3) and on the occupancy number (Table 5).

α-Propyldeoxybenzoin and α-octyldeoxybenzoin undergo Norrish type I and type II reactions upon irradiation either in benzene or in methanol. Cyclobutanols and deoxybenzoin were obtained as the products of the type II process. The products resulting via the α-cleavage included benzaldehyde, benzil and diphenylethane. Similar to **1–5**, photolysis of **6** and **7** were conducted in micelles under varying occupancy number. Micellar influence on the photobehaviour of **6** and **7** was only marginal in comparison to isotropic solvents (Table 6).

All irradiations were limited to < 20% consumption of the starting benzoinalkylethers and alkyldeoxybenzoins. Products were recovered by diluting the micellar solution below the critical micelle concentration (CMC) and extracting repeatedly with either ether or

Table 4. Dependence of product distribution upon the occupancy number—photolysis of benzoin methyl ether in micelles

Occupancy Number (S)	Benzaldehyde	Methyl benzoate	Pinacol ether	*p*-Benzoyl benzyl alkyl ether (**8**)	Deoxy-benzoin	Oxetanol
(i) Sodium dodecyl sulphate						
0·5	28	6	33	—	6	7
1·0	31	17	24	—	12	6
2·0	26	7	36	—	14	7
4·0	34	14	28	—	8	6
(ii) Cetyl trimethyl ammonium bromide						
0·5	21	6	6	6	3	47
1·0	13	15	13	5	3	42
2·0	14	5	24	9	9	38
4·0	9	11	37	7	14	18
(iii) Cetyl trimethyl ammonium chloride						
0·5	19	—	7	7	1	61
1·0	9	14	8	4	4	52
2·0	8	7	17	4	4	48
4·0	13	14	27	2	5	27

Table 5. Photolysis of benzoin octyl ether in micelles—dependence of product distribution on occupancy number

Occupancy Number	Benzaldehyde	Octyl benzoate	Pinacol ether	Deoxy-benzoin	*p*-Benzoyl benzyl alkyl ether (**8**)
(i) Dodecyl trimethyl ammonium bromide					
0·5	14	14	71	2	—
1·0	13	23	63	2	—
2·0	12	30	58	2	—
4·0	8	28	64	2	—
(ii) Cetyl trimethyl ammonium bromide					
0·5	6	—	42	2	53
1·0	10	18	30	2	42
2·0	4	25	42	2	28
4·0	6	24	48	2	22

Table 6. Photolysis of α-propyldeoxybenzoin and α-octyldeoxybenzoin in micelles

Media	Benzaldehyde	Diphenyl alkane	Deoxybenzoin	Cyclobutanol
α-Propyldeoxybenzoin				
Benzene	11	16	37	27
DTAB	17	5	47	29
CTAB	21	7	42	28
DTAC	23	7	46	23
CTAC	18	9	45	27
α-Octyldeoxybenzoin				
Benzene	33	14	41	8
DTAB	20	10	50	20
CTAB	12	12	50	25
DTAC	11	11	55	22
CTAC	25	12	50	12

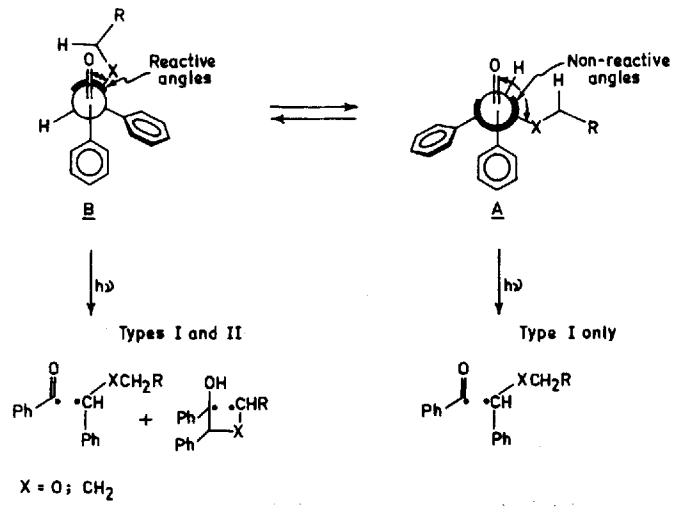
Irradiations in micelles were conducted at an occupancy number one.

chloroform. Excess sodium chloride was added in several cases to avoid foaming. Although the recovery of products from the irradiated micellar solutions was tedious, extraction efficiency was reasonably good. However, benzaldehyde, due to its solubility in water could not be estimated accurately. Each micellar irradiation was repeated five times and the product distribution between runs differed only within ± 10%. Therefore, we assume extractability of products from the various surfactant solutions is reasonable and the relative product distributions shown in Tables 1–6 can be used to draw mechanistic conclusions.

All the photoproducts were characterized based on their spectral properties and in the majority of cases by comparison with authentic samples. The spectral data for oxetanols, cyclobutanols, deoxybenzoin, pinacol ethers and diphenyl ethanes are already reported[5] and those for *p*-benzoylbenzylalkylether (**8**) are provided in the experimental section.

DISCUSSION

Lewis and co-workers have analysed various aspects of the conformational effect on the photochemical behaviour of a large number of arylalkylketones.[6] Detailed presentation pertaining to alkoxybenzoinethers has recently been made by us[5] and by de Mayo and co-workers.[7] Points of interest are the following: in principle, benzoinalkylethers can exist in two general conformations limited by the geometry of the γ-hydrogen (Schème 2). Owing to non-bonded interactions of the electron pairs on the oxygen atoms, form **A** is preferred over **B** in isotropic organic solvents. Such is the case even in the crystalline state, where the minimum energy conformation is generally preferred.[8] Of these two forms, form **A** can give only the type I, whereas **B** is expected to undergo both the type I and the type II reactions. On the basis of this model, the predominance of type I cleavage in solution is attributable to the preponderance of the conformer **A** in the medium and to the high rate of α-cleavage. Therefore, the type II process in benzoinalkylethers, which is generally absent in isotropic solvents, can be brought about by encouraging the molecules to adopt the conformation **B** and



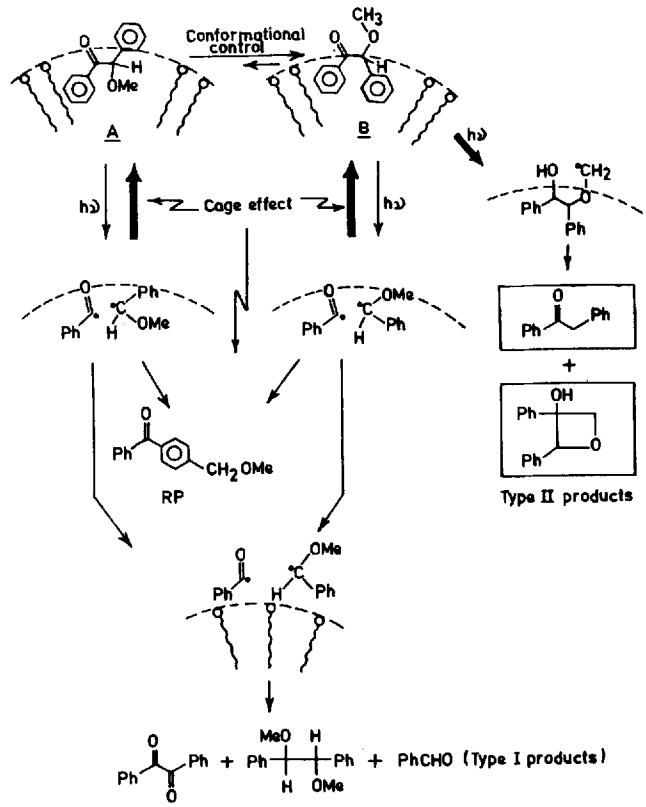
Scheme 2

by having a condition under which the rates of photoprocesses are higher than the rates of conformational isomerism.

We infer below that both 'cage effect' and 'conformational control' are responsible for the variation in product distribution in micellar media as compared to that in isotropic organic solvents. The benzoyl–benzyl radical pair generated by the α-cleavage process would be restricted in their movement by the hydrophobicity of the micellar interior. This would facilitate recombination of the radical pair with and without rearrangement. This increase in cage recombination is indeed reflected in the increased formation of the rearranged product *p*-benzoylbenzylalkylether in various micelles. Such an effect has earlier been reported for dibenzyl ketone systems.[9]

While the 'cage effect' may undoubtedly be responsible for the formation of the type II products in micellar medium, it cannot be the only reason. While the cage effect can reduce the efficiency of the type I product formation there must be other features which facilitate the occurrence of γ-hydrogen abstraction. This, we propose, is the 'conformational control' or the control of *intramolecular orientation* at the micellar interface. On the basis of the hydrophobic parameters[10] and the tendency of the polar oxygens of the carbonyl and the alkoxy group to point towards the aqueous exterior one would anticipate that the conformer **B** would dominate at the interface. The proposed model for the reaction is illustrated in Scheme 3. According to this scheme, the formation of the type II products in micellar media is the result of two features—'conformational effect and cage effect'—the former facilitates the occurrence of the type II reaction and the latter suppresses the formation of the type I products.

Results presented in Tables 2, 3 and 5 further support the phenomenon of conformational control. Photolysis of **4** and **5** in a variety of micelles under different conditions did not give type II products, a behaviour different from that of **1–3**, and yielded products derived only from the α-cleavage process. Surprisingly, a para rearranged isomer, *p*-benzoylbenzylalkylether (**8**) was obtained in substantial yield in CTAB and CTAC micelles. The yield of **8** was dependent on the occupancy number. The negligible enhancement of the type II products with respect to benzene is indeed consistent with the expectation that **4** and **5** would prefer to be present in the conformation **A** at the micellar interface. The visualized mechanistic picture is illustrated in Scheme 4. Smaller volume of the micelle and the higher

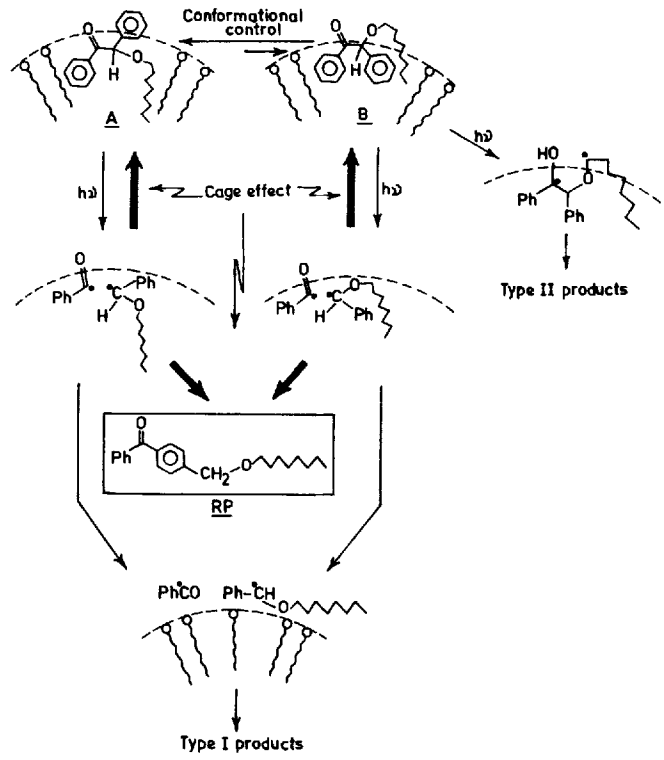


Scheme 3

occupancy facilitate cage escape and combination between different benzoyl–benzyl radical pairs, resulting in poor or negligible yields of the rearranged product **8** (Tables 3 and 5). The results on short chain and the long chain alkoxybenzoinethers (**1–3** and **4**, **5**) when viewed together, reveal that an excellent conformational control can be achieved at the micellar interface by a suitable tailoring of the substrates. The basic strategy of such an approach involves the utilization of the difference in hydrophobicity of individual substituents in a molecule.

One of the important factors that contributed to our success in altering the photobehaviour of benzoinalkylethers is their rapid rates of α-cleavage (10^{10} s^{-1}) and γ-hydrogen abstraction (10^{9} s^{-1}).[11] This inherent property of the reacting system was further favoured by the micellar restriction of the rotational motions interconverting **A*** and **B***. Presence of hydrogen bonds between the oxygen atoms (alkoxy and carbonyl) in **1–3** and the aqueous exterior (of the micellar interface) is expected to enhance the barrier for conversion of **B*** to **A*** (Scheme 3). Similarly, the hydrophobic effect and the inherent anomeric effect would reduce the rate of conversion of **A*** to **B*** in **4** and **5** (Scheme 4).

The results obtained with alkyldeoxybenzoins **6** and **7** discussed below further amplify this aspect of the micellar control of photoreactions. As illustrated in Table 6, micellar effect on the product distribution of short chain (**6**) and long chain (**7**) alkyldeoxybenzoins is negligible. This observation leads us to conclude that in order to achieve selectivity in photoreactions it is



Scheme 4

essential to control the rotational motion of the single bond that interconverts **A** and **B**. In the case of alkyldeoxybenzoins, the absence of an oxygen in the side chain probably leads to poor conformational control at the micellar interface. Although, on the basis of the difference in the hydrophobicities of the alkyl and the phenyl substituents, one would expect some preferential orientation, apparently the forces are not sufficiently strong to arrest the rotational motion.

Results presented here establish that conformational control can be achieved at the micellar interface and that it can be used to bring about selective organic phototransformations.[11] Although, micelles are probably one among the least organized of microheterogeneous assemblies, it has become evident that inter-[11] and intra-molecular orientation of organic molecules can be achieved using this medium. This would be of considerable synthetic interest. Furthermore, the fact that benzoinalkylethers and alkyldeoxybenzoins, investigated here, have lent themselves to a certain amount of predictability encourages further exploration of micelles as a reaction medium.

EXPERIMENTAL

Materials

The detergents sodium octyl sulphate, sodium decylsulphate, sodium dodecylsulphate, dodecyl trimethyl ammonium bromide, cetyl trimethyl ammonium bromide (all from Sigma), dodecyl tri-methyl ammonium chloride and cetyl trimethyl ammonium chloride (Eastman–

Kodak) were recrystallized twice from 95% ethanol and methanol–ether mixture and dried at room temperature. Potassium decanoate and potassium dodecanoate were prepared[13] from the corresponding acids by the neutralization of a hot methanolic solution of the acid with a hot methanolic solution of potassium hydroxide. The solution was filtered hot and allowed to crystallize at room temperature. The colourless crystals were filtered and recrystallized twice from methanol.

Doubly distilled water was used for micellization. Benzene, hexane and chloroform were distilled prior to use. Benzoinalkylethers **1–5** and alkyldeoxybenzoins **6** and **7** were prepared by reported procedures.[14] Details of preparation and spectral properties of **1–7** have been reported earlier. Solid samples were recrystallized several times from petroleum ether and liquid samples were distilled before use. The para substituted benzophenone **8a–e**, the rearranged product from **1–5** were prepared from *p*-methylbenzophone as follows.[15] These were required as authentic samples for identification of products of photolysis.

A mixture of *p*-methylbenzophenone (5 g), N-bromosuccinimide (5 g) and azobisisobutyronitrile (5 mg) in carbon tetrachloride (100 ml) was refluxed for 12 h. After cooling, the precipitated succinimide was filtered from the solution and the filtrate concentrated in vacuo to give *p*-benzoylbenzylbromide (5 g).

From *p*-benzoylbenzylbromide, **8a–e**, were prepared by using the corresponding alcohols and sodium hydroxide. A mixture of sodium hydroxide (22 mg) and the corresponding alcohol (2 ml) were added to the above *p*-benzoylbenzylbromide at reflux temperature and further refluxed for 9 h. The crude mixture was extracted with ether, dried and evaporated. The products were purified by repeated column chromatography (silica gel-hexane/chloroform). IR and NMR spectral data of **8a–e** are provided below.

8a: IR (Neat) cm^{-1} - 1660.
^{1}H-NMR($CDCl_3$) - δ 3·4(s, 3H); 4·5(s, 2H); 7·28–7·92(m. 9H)

8b: IR (Neat) cm^{-1} - 3040, 3020, 1660.
^{1}H-NMR($CDCl_3$) - δ 1·1(t, 3H); 3·51(q, 2H); 4·6(s, 2H); 7·28–7·92(m, 9H).

8c: IR (Neat) cm^{-1} - 1660, 1380–1370.
^{1}H-NMR($CDCl_3$) - δ 1·1(d, 6H); 3·8(h, 1H); 4·6(s, 2H); 7·28–7·92(m, 9H).

8d: IR (Neat) cm^{-1} - 3040, 3020 and 1660.
^{1}H-NMR($CDCl_3$) - δ 0·99(t, 3H); 1·0–1·6(m, 8H); 3·51(t, 2H); 4·59(s, 2H); 7·3–7·8(m, 9H).

8e: IR (Neat) cm^{-1} - 3020, 3010, 1660.
^{1}H-NMR($CDCl_3$) - δ 0·99(t, 3H); 1·0–1·6(m, 12H); 3·46(t, 2H); 7·23–7·95(m, 9H).

Solubilization and Irradiation of Benxoinalkylethers and Alkyldeoxybenzoins in Micelles

Weighed amounts of **1–7** were stirred for 12 h with 100 ml of the surfactant solutions of concentrations well above the critical micelle concentration. The micellar solutions were filtered through Whatman No. 1 filter paper to remove suspended particles, if any. By a similar procedure, micellar solutions containing various occupancy numbers of **1** and **5** were prepared.

Transparent micellar solutions were taken in Pyrex tubes, deaerated by bubbling N_2 through the solution for about 30 mins and tightly stoppered. These solutions were photolysed in a Rayonet reactor fitted with RPR-3000 lamps for 2 h. Conversions were kept below 15% for analytical irradiations and were taken to $< 60\%$ for product identification.

At the end of the photolysis, a known amount of the internal standard (biphenyl) was added, the micellar solution was diluted below CMC and extracted with ether and chloroform. To improve the efficiency of the extraction of photoproducts excess of sodium chloride was added to the aqueous solution to salt out the organic material. The products were analysed by gas chromatography (Chemito Model 3800, 10% SE-30; 5″ × 1/8″; temperature 120–250 °C programmed). All products except **8** have already been identified on the gc trace. Products **8a–e** were characterized on the basis of their spectral properties and by comparison with authentic samples prepared as described above. Distribution of products were estimated with reference to the internal standard. Results are summarized in Tables 1–6.

Irradiation of **1–7** were also conducted in benzene and methanol. The procedure for irradiation and analyses were similar to the one described above.

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