

Photochemical reaction of cyclohexyl phenyl ketone within lyotropic liquid crystals

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Abstract

Lyotropic liquid crystals (LCs) formed by sodium dodecyl sulfate (SDS), *n*-pentanol, and H₂O at room temperature in their tertiary phase diagram have been explored as a confined medium for the typical photochemical reaction of cyclohexyl phenyl ketone (**1**), which can lead to either *intramolecular* hydrogen abstraction product **2** or *intermolecular* reduction product **3** in isotropic solutions upon irradiation. Studies on the product distributions of ketone **1** in the absence and presence of electron donors in this work demonstrate that LC not only restricts the movement of the substrates and intermediates but also encapsulates the substrates and electron donors together during photoirradiation, thereby giving rise to the formation of *intermolecular* hydrogen abstraction product **3** with high efficiency. A comparison of the same reaction in SDS micelle reveals that LC provides much better constraint than the micelles. The solution-like LC can be used as a microreactor to direct the reaction pathway of ketone **1** by controlling the viscosity and close contact between substrates and electron donors.

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1. Introduction

Optimizing selectivity of photochemical reactions is one of the most important topics of current research since photochemical reactions generally tend to give more than one product.¹ During the past decades, many elegant and efficient strategies have been designed toward this goal. The use of supramolecular systems for selective photochemical reactions turns out to be one of the successful approaches because the interactions of substrates with supramolecular systems may alter the photochemical behaviors of the confined substrates, and thus may direct the photochemical reaction to the desired product(s).² It has been known that photochemical reactions in isotropic solutions and supramolecular systems often lead to different product distributions or in some cases, totally different products.^{1,2}

Lyotropic liquid crystals (LCs) that are formed by surfactants in either water or oil, or both of them usually consist of an amphiphile and a typically aqueous solvent, and possess highly ordered nanostructures. Lamellar liquid crystals (LLCs) and hexagonal liquid crystals (HLCs) are the two representatives of LC family.^{3,4} As shown in Figure 1, the hydrocarbon chains and the head group of the surfactants compose the hydrophobic and hydrophilic domains of thermodynamically stable LC systems, respectively. In LLC, the surfactant

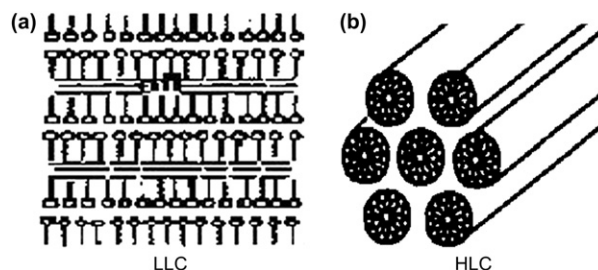


Figure 1. Schematic representative structures of the liquid crystals.

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molecules aligned orderly (on average) with their long axes parallel to one another affording a compact structure. Alternatively, the oriented rod-like surfactant molecules in HLC lead to a helical column. The viscosity and compaction of HLC have been known to be much higher than that of LLC.³ These unique features of LC have recently been of great interest for the templates of various ordered inorganic and organic nanostructures.^{5,6} In this report, we are particularly interested in the photochemical reactions within LC because the large interfaces and hydrophobic and hydrophilic domains present in the LC are expected to increase the local concentration of substrates, and even to mediate their orientations. More importantly, the high viscosity and compact structures are believed to restrict the movements of both substrates and intermediates greatly. As a result, the optically transparent supramolecular assemblies may be amenable to selective photochemical investigations.

Previous work in this area was mainly focused on the thermotropic liquid crystals that are formed by certain organic molecules through heating.^{7,8} Weiss and Nerbonne took the lead in developing the photochemical reactions in liquid crystals.^{7a} They found that the cholesteric liquid crystals could influence the efficiency of photodimerization of acenaphthylene largely. Later on, Turro et al. investigated the photolyses of dibenzyl ketones in thermotropic liquid crystals.^{7b} They rationalized the relatively low cage effects observed by the fact that the probability of recombination of benzyl radical pairs from decarbonylation of 1-(4-methylphenyl)-3-phenylpropan-2-one is very sensitive to the nature of the local solvent organization even though the thermotropic liquid crystals are very viscous. Photochemical asymmetric induction in chiral liquid crystals has also been explored, but the obtained optical yields are generally low.⁸

Compared with thermotropic liquid crystals, lyotropic liquid crystals (LCs) can be prepared at ambient temperature and are easier to manipulate photochemical studies. To examine whether LC could be used as a confined medium for selective photochemical reactions, the typical reaction of cyclohexyl phenyl ketone (**1**),^{9,10} which can lead to either *intramolecular* hydrogen abstraction product (**2**) or *intermolecular* reduction product (**3**), in isotropic solutions upon irradiation, was investigated in this work (Scheme 1). It was noted that product **3** is formed as the major product in the presence of electron donors within LC, while product **2** is mainly produced in most micellar cases under the same conditions. These results demonstrate that LC including both LLC and HLC not only restricts the movement but also encapsulates the substrates and electron donors together during photolysis, and thus leading to the formation of *intermolecular* hydrogen abstraction product **3** with high efficiency. A comparison of the same reaction in sodium dodecyl sulfate (SDS) micelle reveals that LC provides much better constraint than the micelle. By controlling the viscosity and

close contact between substrates and electron donors, a new type of microreactor has been established.

2. Results and discussions

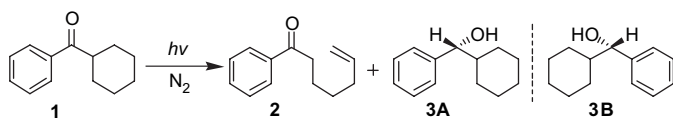
2.1. Preparation of LC samples for irradiation

Lamellar liquid crystals (LLCs) and hexagonal liquid crystals (HLCs) used in this work were prepared by sodium dodecyl sulfate (SDS), *n*-pentanol (C₅H₁₁OH), and H₂O at room temperature in their tertiary phase diagram,⁴ in which SDS 1.875 g, C₅H₁₁OH 1.250 g, and H₂O 1.875 g were used for LLC and SDS 1.875 g, C₅H₁₁OH 0.313 g, and H₂O 2.813 g for HLC. Appropriate amounts of components, including LC, substrates, and/or electron donors, were added into a Pyrex tube, and stirred for 10–20 h till the mixture became a uniform transparent system to make the samples for photoirradiation. Because the product distributions are always the same as the ratio of electron donors to **1** beyond 7:1, we set the ratio as 7:1 to guarantee many electron donors around one substrate. Namely, the substrate loading level was kept at 1 mg of ketone **1** in 1 g of LC. The texture patterns of the prepared samples were examined by a polarizing microscope. Similar to that pure LC,³ the LLC was formed as maltese cross textures, while HLC was formed as focal conic textures (Fig. 2). These observations suggest that the LC phases remain unchanged when the substrates and electron donors were added under the conditions investigated.

2.2. Photochemical reaction of **1** within LC in the absence of electron donors

The photoreaction of cyclohexyl phenyl ketones (**1**) is a well-known reaction (Scheme 1),^{9,10} which gives 1-phenylhept-6-en-1-one (**2**) and α -cyclohexyl benzyl alcohol (**3**) upon irradiation of **1** in organic solvents. Product **2** comes from the *intramolecular* hydrogen abstraction (Scheme 2), in which hydrogen abstraction occurs via a six-membered ring transition state. Alcohol **3** arises from the electron-transfer-initiated *intermolecular* photoreduction (Scheme 3). Evidently, the *intermolecular* photoreduction may be facilitated when electron donors are introduced. Furthermore, the ratio of **2** to **3** is very sensitive to the solvents used. It was reported⁹ that in degassed benzene **2** and **3** were present in a 3:1 ratio, while in 1-propanol irradiation of **1** resulted in much rapid formation of **2**, but quickly changed the ratio to 30:1 at low reaction conversion.

The photochemical reaction of ketone **1** within LC was performed at room temperature in this work. Typically, the blank Pyrex tube was connected to a vacuum system through a stopcock adapter to remove air by three freeze–thaw cycles before irradiation. The mixture was extracted with ether for further gas chromatograph (GC) detection after irradiation with a 500 W high-pressure Hanovia mercury lamp. The photochemical behavior of **1** within LC is summarized in Table 1. It was found that the efficiency of the typical photoreaction is extremely higher as compared with that in hexane solutions.



Scheme 1.

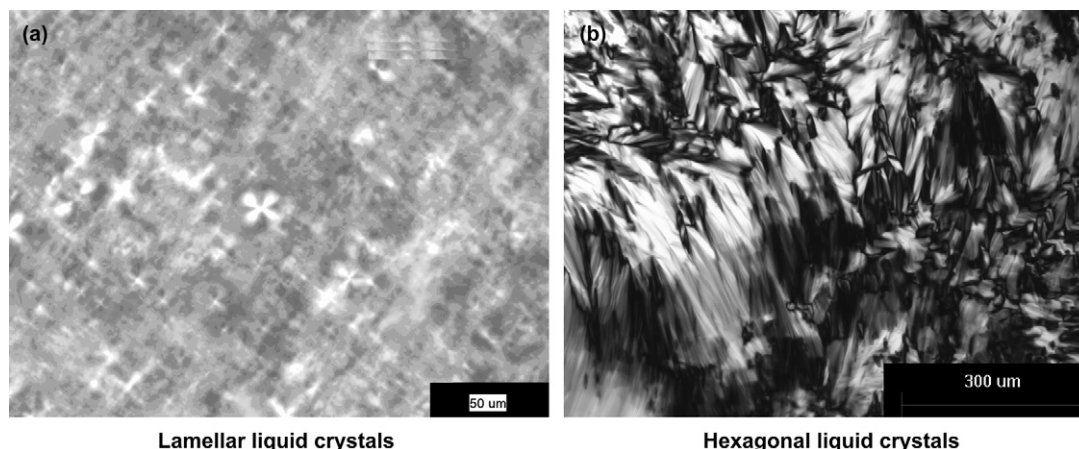
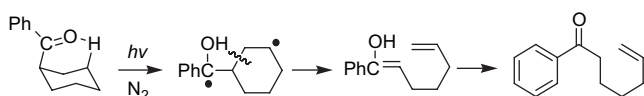
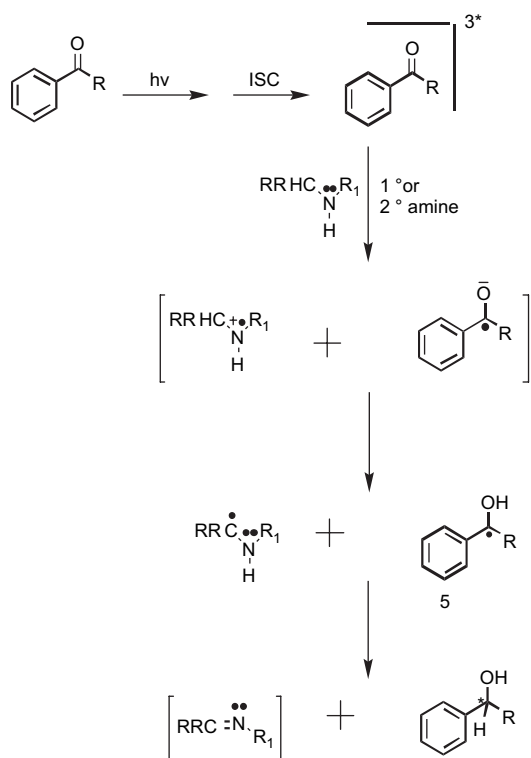


Figure 2. Polarized light micrographs of liquid crystals made of SDS/C₅H₁₁OH/H₂O.



Scheme 2.



Scheme 3.

To avoid secondary reactions, the irradiation time was kept less than 5 min for all the samples studied in LC (conversion 30%). Some important features are worthy of noting based on the correlated calculation of the product ratio. In contrast to that obtained in micelle (30:1), the ratio of *intra*- and *intermolecular* products (**2/3**) was found to be 3:1 in both LLC and HLC. Clearly, the *intramolecular* reaction is hampered within LC as compared with that in micelle.

We employed pyrene as the probe to determine the micro-polarity of the LC interior. It is well established that the ratio of intensities of the vibrational peaks of **1** and **3**, namely I_1 and I_3 , in the fluorescence spectrum of pyrene is an excellent measure of polarity of its immediate environment.¹¹ Table 2 presented the I_1/I_3 values of pyrene in aqueous LC media. A comparison of the I_1/I_3 of LC with that of common solvents indicates that the polarity experienced by pyrene in LLC and HLC is similar to that of ether, while that in micellar solution is very close to that of 1-propanol. Evidently, the polarity of the microdomains within HLC and LLC is similar but more hydrophobic than that of the micelles. Additionally, excimer emission from pyrene could not be observed both in LC and

Table 1

Product distributions of **1** in the absence and presence of electron donors within LC

Entry	Electron donor	Reaction media	Molar ratio of 2/3 ^a	% ee in 3
1	No	1-Propanol	30:1 ⁹	0
2	No	Ether	3:1	0
3	(-)-Prolinol	Ether	1:2	0
4	No	HLC	3:1	0
		LLC	3:1	0
		Micelle ^b	30:1	0
5	(-)-Prolinol	HLC	1:12	4B ^c
		LLC	1:3	4B
		Micelle	1:2	0
6	(-)-Ephedrine	HLC	1:6	4B
		LLC	1:3	4B
		Micelle	1:2	0
7	(-)-N-Methylephedrine	HLC	1:2	4B
		LLC	1:2	4B
		Micelle	1:1	0
8	(+)-Norephedrine	HLC	2:1	5A
		LLC	2:1	5A
		Micelle	3:1	0
9	(-)-Menthol	HLC	2:1	—
10	(-)-Proline	HLC	3:1	—

^a Conversion was estimated by GC using hexadecane as the internal standard and was controlled at less than 30%.

^b The concentration of ketone **1** and electron donors was set to 1:7 in micelle, LLC, and HLC.

^c A represents the first peak of the two enantiomers observed in GC and B refers to the second one.

Table 2
 I_1/I_3 Ratio of pyrene within LC and common solvents

Medium	I_1/I_3
HLC	0.97
LLC	0.99
Micelles	1.11
Ether	0.98
1-Propanol	1.09
1-Pentanol	0.93
Water	1.87

micelle at the concentration studied, suggesting that pyrene molecules are isolated from each other in LC, namely, one molecule of pyrene in the excited singlet state is unable to meet the other one in the ground state within the excited-state lifetime (Fig. 3). A comparison of the reaction occurred in ether and 1-propanol, we found the product distribution of photoirradiated **1** in LC and micelle should not be only related to the polarity of the domains (Table 2). Since the *intramolecular* hydrogen abstraction occurs via a six-membered ring transition state (Scheme 2),⁹ the viscous media of LLC and HLC may restrict the movement of substrate **1**, and suppress the formation of the rigid transition state to some extent. On the contrary, the relatively flexible micelles allow substrate **1** to adopt the conformation suitable for hydrogen abstraction, leading to the formation of *intramolecular* product **2** predominantly.

2.3. Photochemical reaction of **1** within LC in the presence of electron donors

It is of significance that in the presence of electron donors the ratio of **2/3** is altered dramatically in LC as compared with that in micelle (Table 1). The photoreduction *intermolecular* product **3** could be formed as the major product in LC, while the *intramolecular* product **2** still dominates in micelle in most cases. In particular, a significant selectivity (**3/2**=12:1) in HLC, even higher than that observed by Ramamurthy et al. in zeolite (**3/2**=5:1),^{10b} could be achieved when electron donor of (–)-prolinol was present (Fig. 4). As we know, the photoreduction of ketone **1** by electron donor is an electron-transfer-initiated process (Scheme 3), which involves at least one electron transfer and two hydrogen abstraction processes.^{9,10} The multistep nature of the reaction requires that in addition to the redox potential allowance, the molecules of ketone **1** should be close to the electron donors for a relatively long time. Due to the hydrophobic characteristics and polar carbonyl group, ketone **1** would prefer to stay in the hydrophobic domains near the interface in HLC, as shown in Figure 5. In this situation, the electron donor of (–)-prolinol with similar polarity may be very close to substrate **1**. The remarkable selectivity (**3/2**=12:1) obtained in HLC indicates that such a close contact does not dissociate during the intermolecular reduction process. That is to say, the compact HLC is able to encapsulate the molecules of **1** and electron donors forming a ‘microreactor’ (Fig. 5a), where the substrate is next to the electron donors.

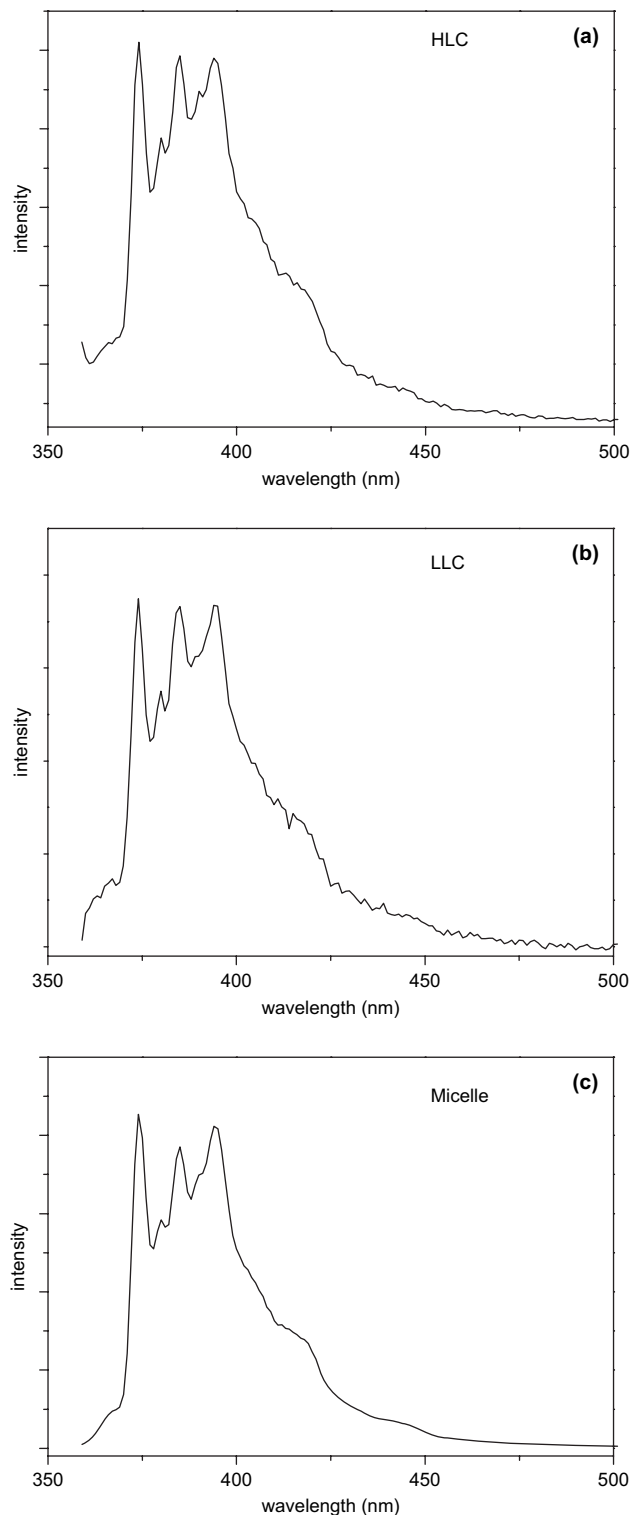


Figure 3. Fluorescence spectra of pyrene in LC and micelle: [pyrene]=10 μ M; excited at λ =339 nm.

To shed more light on the microreactor, a series of electron donors have been investigated (Scheme 4). It is anticipated that subtle change of structure and electron-donating ability may alter the product distributions subsequently. Indeed, not all the electron donors could dominate the formation of *intermolecular* product **3**. With (–)-prolinol and (–)-ephedrine as the

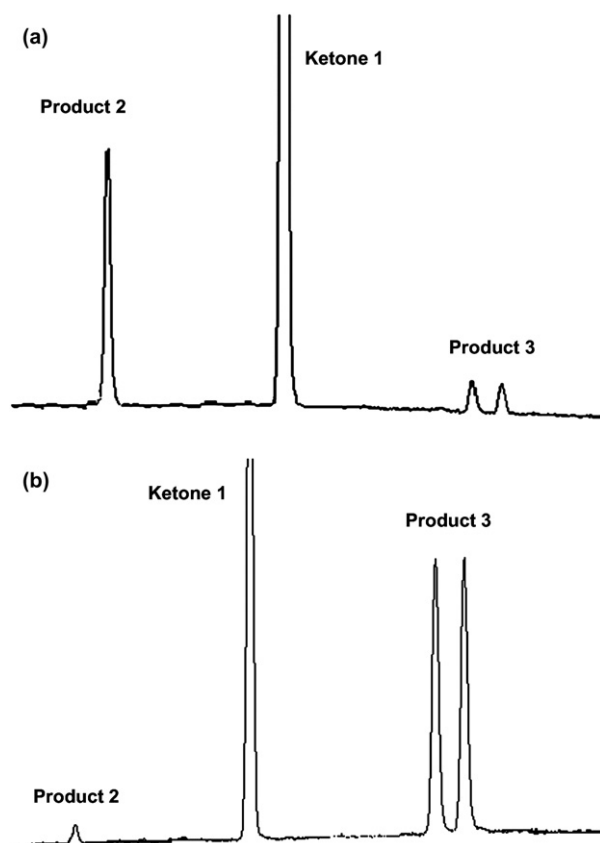


Figure 4. GC traces of the product mixtures (Supelco β -dex 325 column) of **1** in the presence of (–)-prolinol in (a) ether; (b) HLC.

electron donors, the ratio of **2/3** could be achieved to 1:12 and 1:6, respectively. However, this ratio drops to 1:2 when (–)-*N*-methylephedrine was incorporated. (+)-Norephedrine and (–)-menthol can even change the preference and *intramolecular* product **2** was present as a major product (**2/3**=2:1) in HLC. Such a reverse trend observed in the product distributions implies that small changes in the electron-donating ability and molecular structure of electron donors can influence the selectivity of the photochemical reaction remarkably. Since alcohol **3** is the product of electron-transfer-initiated *intermolecular* photoreduction, the rate of the *intermolecular* reaction should be related to the electron-donating ability of electron donors. With reference to the previous work on the photochemical reaction of ketones,^{9,10} the photoreduction efficiency should be in an order of tertiary amine $\geq$ secondary amine $\geq$ primary amine. However, in the case of HLC, the ratio of **3/2** increased as secondary amine $\geq$ tertiary amine $\geq$ primary amine when the ephedrine-like amine was incorporated, respectively (Table 1, entries 6–8). Considering the compact structure of HLC, this may be attributed to the relatively bulky tertiary amine that cannot align with the hydrophobic chains of surfactant very well, thus affording (–)-*N*-methylephedrine a little bit far from the substrate **1**. Similar behavior was also observed in photoreaction of **1** in (–)-menthol-incorporated HLC (Table 1, entry 9).

A comparison of (–)-prolinol and (–)-proline mediated photoreaction further evidenced that the closer the contact

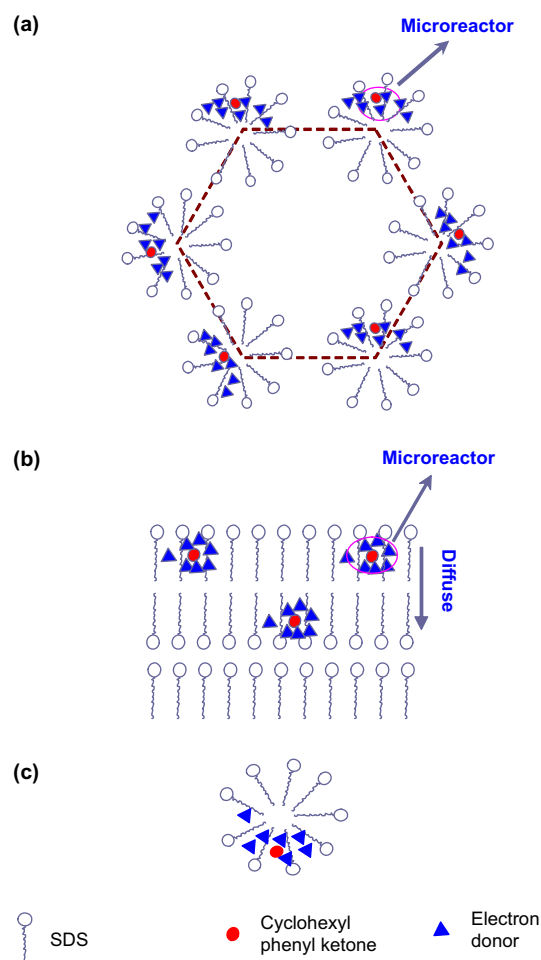
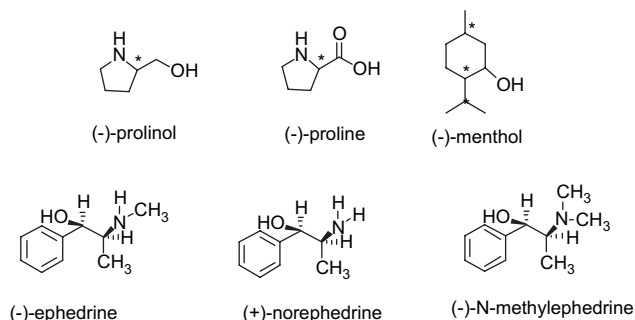


Figure 5. The interaction models of **1** and electron donors within (a) HLC; (b) LLC; (c) micelle.

between the incorporated electron donors and substrate **1** is, the higher the ratio of **3/2** will be. The product distribution in (–)-proline-incorporated HLC is the same as that observed in the absence of electron donors in HLC (Table 1, entries 4 and 10), suggesting that (–)-proline is actually out of the microreactors in HLC. When carboxyl group replaced hydroxyl group in (–)-prolinol, the carboxyl group would decrease the electron-donating ability of the amine group in (–)-proline. More importantly, the polar carboxyl group would



Scheme 4.

move (–)-proline toward the hydrophilic domains in HLC. In contrast, the similar hydrophobic property and polarity render (–)-prolinol and substrate **1** stay in the microreactors in proximity. As a result, the highly viscous HLC strictly prevents excess (–)-prolinol around **1** escaping from the microreactors (Table 1, entry 5), thereby guarantees the reaction occurrence with highest selectivity and large rate acceleration.

The changes in product distributions are also pronounced in LLC but less than that in HLC. In view of the surfactant molecules aligned orderly (on average) with their long axes parallel to one another, the substrate and the excess electron donors would also reside in the ‘microreactors’ (Fig. 5b). Nevertheless, the softer walls of LLC may allow the substrate and electron donors to diffuse along the long axes slowly, resulting in the ratio of **3/2** in LLC lower than that in HLC. Similarly, the more flexible micelles show much weaker restriction in the product distributions of all the cases under the same conditions. In addition, the *intramolecular* hydrogen abstraction may be favored to some extent in the looser microreactors present in micelles.

Evidently, the ordered viscous LC can encapsulate the substrate and electron donors together during photoirradiation. By controlling the viscosity and close contact between substrates and electron donors, the solution-like LC can be used as a microreactor to direct the reaction pathway of ketone **1**. Nevertheless, the ee values for the *intermolecular* hydrogen abstraction product **3** obtained in this study were less than 5% (Table 1). Such a low stereoselectivity should be related to the multistep nature of the *intermolecular* photoreduction,^{9,10} in which both ketone **1** and the intermediate radical **5** possess pro-chiral faces (Scheme 3). Although the LC is stiff enough to restrict the translational motions of ketone **1** and the chiral electron donors affording product **3** with high efficiency, it cannot control their rotation efficiently. Moreover, the pro-chiral faces of both ketone **1** and the intermediate radical **5** allow subtracting hydrogen from their surrounding environment, rather than from the chiral inductor, thereby resulting in low enantioselectivity observed. To this end, we are actively performing the photochemical reactions with simple intermediates in LC and will report examples in due course.

3. Conclusion

The photochemical reaction of cyclohexyl phenyl ketone **1** within LC has been investigated to probe whether LC could be used as a confined medium for selective photochemical reactions. Studies on the product distributions of ketone **1** in the absence and presence of electron donors reveal that LC not only restricts the movement of the substrates and intermediates but also encapsulates the substrates and electron donors together during photoirradiation. A comparison of the same reaction in SDS micelle further evidence that LC provides a much better constraint. By controlling the viscosity and close contact between substrates and electron donors, the solution-like LC can be used as a microreactor to direct the reaction pathway of photochemical reactions.

Acknowledgements

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