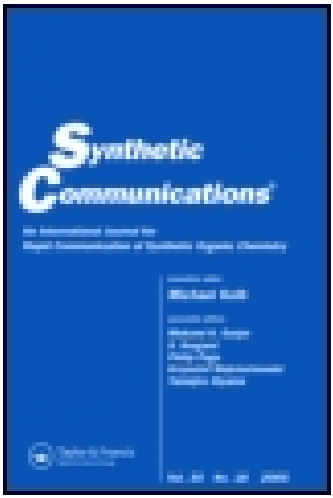

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The Asymmetric Solvomercuration-Demercuation of Olefins in Chiral Micellar Systems

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THE ASYMMETRIC SOLVOMERCURATION-DEMERCURATION OF OLEFINS IN CHIRAL MICELLAR SYSTEMS

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ABSTRACT: The solvomercuration-demercuration of olefins in chiral micelles were investigated. The chiral carbinols can be obtained by asymmetric oxymercuration of prochiral olefins with $NaBH_4$. A satisfactory result was achieved. The highest e.e.% was up to 96%.

Chiral micelles are very important in enantioselectively catalyzed reactions, for instance the hydrolysis of enantiomeric p-nitrophenyl esters[1-2]. However asymmetric synthesis by using chiral micelles as an

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asymmetric enviroment to induce the formation of a new chiral center is a relative new area.

Goldberg[3] first reported the reduction of prochiral ketones in an aqueous micellar solution of (+)-(R)-N-dodecyl-N,N'-dimethyl-a-phenylethylammonium bromide gave chiral alcohols but the optical yield was only 1.7%.

Recently we have utilized chiral micelles as an asymmetric enviroment in the reaction of many types of prochiral substrates such as reduction of ketones[4], oxidation of sulfides[5], epoxidation of chalcones[6] and the addition of carbene to aromatic aldehydes[7]. Our results demonstrate that enantioselectivity was achieved in every case, although optical yields are generally less than 20% with one exception in which enantiomer excess(e.e.) was up to 28%[7].

Here we wish to report the solvomercuration- emercuration of olefins in chiral micellar systems.

Chiral surfactants I and II were synthesized from natural ephedrine. In chiral micellar systems composed of these surfactants, the chiral carbinol can be obtained by asymmetric solvomercuration-demercuration of prochiral olefins with $NaBH_4$. The highest e.e.% being 96%.

The synthesis involves oxymercuration of the olefinic compound with mercuric acetate in the presence

of a THF-H_2O medium of chiral micelles, followed by in situ reduction of the oxymercurial with sodium borohydride.

$$RCH{=}CH_2 \xrightarrow[2,\ NaBH_4]{1,\ Hg(OAc)_2/H_2O/I \text{ or } II} RCHOHCH_3$$

R=Ph-, $CH_3(CH_2)_3$, $CH_3(CH_2)_4$, $CH_3(CH_2)_5$, $CH_3(CH_2)_7$

I: $Ph\text{-}\underset{OH}{CH}\text{-}\underset{CH_3}{CH}\text{-}\overset{CH_3}{\overset{|}{\overset{+}{N}}}\text{-}C_{12}H_{25}\ \underset{CH_3}{|}\ Br^-$

II: $Ph\text{-}\underset{OH}{CH}\text{-}\underset{CH_3}{CH}\text{-}\overset{CH_3}{\overset{|}{\overset{+}{N}}}\text{-}C_{16}H_{33}\ \underset{CH_3}{|}\ Br^-$

The results shown in Table 1 clearly demonstrate that the stereochemical selectivity was achieved in all chiral micelles employed. The enantioselectivity was strongly indicated by the fact that with same surfactant, all the enriched enantiomer of the carbinols have the same absolute configuration. The most significant fact provided from the obtained results is, perhaps, the chain length effect. The variation in enantioselectivity among the olefins is remarkable: with the same chiral micellar systems, higher enantiomeric excess was generally achieved by increasing the alkyl chain length of the substrates.

On the other hand, it is shown in table 1 that the micelles formed from surfactants with longer alkyl

Table 1. Asymmetric oxymercuration of olefins in chiral micelles formed by surfactant I or II

Surfactant	Product	$[\alpha]_D^{25}$	Conc. (g/l)	Config.	e.e.%
	$PhCH(OH)CH_3$	+13.78	4[c]	R	27.3[a]
	$CH_3(CH_2)_3CH(OH)CH_3$	+1.69	11.9[d]	R	12.1[a]
I	$CH_3(CH_2)_4CH(OH)CH_3$	+2.90	17.3[d]	R	21.1[a]
	$CH_3(CH_2)_5CH(OH)CH_3$	+3.14	6.36[d]	-	-[b]
	$CH_3(CH_2)_7CH(OH)CH_3$	+6.6	4.55[d]	R	57.59[a]
	$PhCHOHCH_3$	+20.0	1.1[c]	R	39.5[a]
	$CH_3(CH_2)_3CH(OH)CH_3$	+2.76	18.1[d]	R	19.8[a]
II	$CH_3(CH_2)_4CH(OH)CH_3$	+3.79	26.4[d]	R	27.7[a]
	$CH_3(CH_2)_5CH(OH)CH_3$	+4.12	7.27[d]	-	-[b]
	$CH_3(CH_2)_7CH(OH)CH_3$	+12.1	9.09[d]	R	96.0[a]

e.e%=$([\alpha]_{D,\ max})$x100%; a. $[\alpha]_{max}$ was cited from the literature[9]; b. No literature was reported on $[\alpha]_{max}$; c. Toluene was used as solvent; d. Benzene was used as solvent.

chain(II) provided better enantioselectivity than the shorter chain analogues(I). Evidently, these results can be naturally attributable to hydrophobic-lipophilic interactions between the substrate and the micelle.

The binding of the prochiral olefins by the chiral micelle is a dynamic process, micelles and their monomeric surfactants are also in a dynamic equilibrium. Therefore increasing alkyl chain length either in surfactants or in sulfides could improve the complexation of olefins by chiral micelles and then gave better enantioselectivity.

EXPERIMENTAL

The optical rotations were obtained from a WZZ-1 automatic rotation detector(Shanghai). The ^1H NMR spectra in $CDCl_3$ were recorded on a JEOL JUM-PMX 60 SI (60MHz) spectrometer using TMS as the internal standard. The IR spectra were recorded on Perkin Elmer 683 spectrometer. The surfactants I and II were prepared as previously described[8].

General procedure: To a 0.03M(335ml) micellar solution (H_2O:THF=1:1) added 15mmol olefin and stirred 20mins. 50ml of 15mmol $Hg(OAc)_2$ in H_2O-THF solution was added to the olefin micellar solution and stirred until the solution became clear. 3M(15ml) NaOH solution was added , then a solution of 15ml(0.5M) $NaBH_4$ in 3M NaOH

was added, stirring for 2-3h. Sodium chloride was added for saturation. Seperate the THF layer. The aqueous layer was extracted with ether and the organic phase was dried over $MgSO_4$. Removal of the solvent gave the crude product which was then purified by vaccum distillation first, then by column chromatography on silica gel eluted with petroleum ether:benzene =1:3. The boiling point and ^1H NMR data of products are as follows.

$PhCHOHCH_3$: bp. 98-99°C/20mmHg. ^1H NMR: δ 7.2(5H, s, ArH), 4.7(1H, q, CH), 1.4(3H, d, CH_3), 2.7(1H, s, OH).
$CH_3(CH_2)_3CHOHCH_3$: bp. 137-138°C. ^1H NMR: δ 3.7(1H, m, CH), 3.0(1H, s, OH), 1.13(3H, d, CH_3).
$CH_3(CH_2)_4CHOHCH_3$: bp. 158-160°C. ^1H NMR: δ 3.7(1H, m, CH), 2.0(1H, s, OH), 1.13(3H, d, CH_3).
$CH_3(CH_2)_5CHOHCH_3$: bp. 86-87°C/20mmHg. ^1H NMR: δ 3.5-4.0 (1H, m, CH), 1.52(1H, s, OH), 1.15(3H, d, CH_3).
$CH_3(CH_2)_7CHOHCH_3$: bp. 111°C/11mmHg. ^1H NMR: δ 3.5-4.0 (1H, m, CH), 1.66(1H, s, OH), 1.15(3H, d, CH_3).

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