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Asymmetric Synthesis in Liquid Crystals: Independence of Stereochemistry on the Handedness of the Cholesteric Liquid Crystal

Sir:

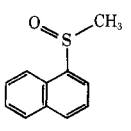
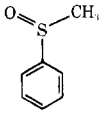
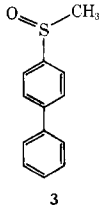
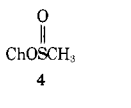
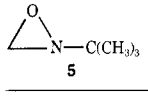
Two groups have recently reported asymmetric transformations induced solely by the use of cholesteric liquid crystals as chiral reaction media.[1,2] Saeva found that the Claisen rearrangement of methylallyl *p*-tolyl ether affords optically active 2-(α-methylallyl)-4-methylphenol when conducted in cholesteryl *p*-nitrobenzoate (ChNB);[1] Verbit found that decarboxylation of ethylphenylmalonic acid in cholesteryl benzoate (ChB) gives (*R*)-(−)-2-phenylbutyric acid of 18% enantiomeric excess.[2] Verbit has suggested[2] that the helical macrostructure of the cholesteric mesophase rather than the "local" asymmetry of the steroid system controls the stereochemical sense of the asymmetric transformation. He further postulated that had the decarboxylation of ethylphenylmalonic acid been conducted in a cholesteric liquid crystal of the opposite macrostructural handedness, the opposite enantiomer of the α-phenylbutyric acid would have been obtained in excess.

We now report the use of cholesteric liquid crystalline reaction media to cause interconvertible enantiomers to assume a nonracemic composition. We also offer evidence that factors other than the macrostructural handedness of the mesophase controls the stereochemical outcome of such equilibrations.

Sulfoxides have appreciable barriers to inversion at sulfur and generally racemize only at temperatures above 150 °C.[3] When low concentrations (<5%) of racemic sulfoxides are dissolved in cholesteryl esters and heated in sealed degassed ampules at temperatures such as to maintain the liquid crystal in the cholesteric mesophase, the enantiomeric composition of the sulfoxides can be changed. After heating, the sulfoxides were recovered (>80%) by chromatographing the entire contents of the ampule upon silica gel. The enantiomeric compositions and absolute configurations of the thus purified sulfoxides were determined by polarimetry or by NMR[4,5] using a chiral solvating agent such as 2,2,2-trifluoro-1-(1-naphthyl)ethanol.[6]

In general, the sulfoxides show small but reproducible amounts of asymmetric induction (0–9% e.e.) comparable in magnitude to those observed for oxidation of sulfides by chiral peracids. Table I shows the results of several such equilibra-

Table I. Equilibration[7] of Enantiomers in Cholesteric Liquid Crystals

Solute	Solvent	*T*, °C	Time, hr	E.e.[a]	Configuration[b]	Solute/solvent[c]	Transition temp[d] Solid–Chol	Chol–Isotropic
 1	ChB	145	6	2.4	*R*	100/2.5	145	162
	ChNB	190	3	9.2	*R*	100[e]/2.0	182	230–260 dec
	ChDCB	150	6	0		100/2.5	129	196
	ChN	170	3	1.0	*S*	150/3.0	165	222
	ChC	175	3	1.4	*S*	100[e]/2.5	158	195
	ChS	200	2	1.4	*S*	40/0.9		
	ChPB	175	3	2.4	*S*	100/2.5	156	220
 2	ChNB	190	3	2.4	*R*	100[e]/2.5	182	220–260 dec
	ChT	110	4	0		100/2.0	110	123
 3	ChNB	190	3	6	*S*	100[e]/2.5	182	254 dec
	ChPB	190	3	<3	*R*	100/2.5	161	226
 4	ChDCB	100–140[f]	8	6.8	*S*	1000/1.0	108	185
	ChB	145	0.5	16.9	*R*	250/3.0	131	153
	ChL	85	2	12.3	*R*	100/1.5	76	86
	Toluene	110	3	20	*S*			
	ChL (isotropic)	110	3	5	*S*	100/1.5		
 5	ChB	148	0.08	20		100/2.0	147	183

[a] Enantiomeric excess. [b] Absolute configuration of major enantiomer. [c] Milligrams of solute/gram of solvent, solute and solvent were sealed in an ampule under vacuum, and the ampule was slowly rotated in an oil bath or oven for the specified time. [d] Determined by differential thermal analysis. [e] It was verified by CD[9] that this mixture has the same pitch handedness under the reaction condition as that of the pure ester. [f] Exhibits the frozen cholesteric mesophase. Mixture was heated to 140 °C, mixed, then cooled and kept at 100 °C.

tions[7] in cholesteryl esters, including those of lauric acid (ChL), β-naphthoic acid (ChNaph), *o*-toluic acid (ChT), 2,4-dichlorobenzoic acid (ChDCB), *p*-phenylbenzoic acid (ChPB), *trans*-cinnamic acid (ChC), and *trans*-4-carboxystilbene (ChS). No asymmetric induction was observed in control experiments in which the samples were heated slightly above the cholesteric to isotropic liquid transition temperature.

All of the cholesteryl esters used are either known[8] to form a right-handed helix in the cholesteric mesophase, or were shown to do so by the CD signs of their pitch bands.[9] Therefore, the observation that equilibration of methyl α-naphthyl sulfoxide (**1**) affords enrichment in the *R* enantiomer in ChB and ChNB, but in the *S* enantiomer in ChN, ChC, ChS, and ChPB, demonstrates that the sense of helical macrostructure alone does not control the stereochemical sense of enrichment. Note also that whereas ChNB equilibration enriches naphthyl **1** and its phenyl analogue **2** in the same sense, this sense is inverted for biphenyl sulfoxide (**3**). Enrichment senses of **1** and **3** also differ in ChPB.

While it is premature to speculate upon the details of how a chiral mesophase actually effects asymmetric transformation, we consider it probable that rather specific solute-solvent interactions play a role in "locating" the solute molecules in the chiral mesophase, the helical order of which is essential to the success of the asymmetric transformation.

On the supposition that solutes capable of structurally "mimicking" the mesophase should show still greater extents of asymmetric transformation, the diastereomeric cholesteryl methane sulfinates, **4** were prepared. Like sulfoxides, sulfinates can undergo inversion at sulfur upon heating. Although these diastereomers were not readily obtained free from one another, their absolute rotations were calculated from rotational data obtained from mixtures of different, but known ratios of the two diastereomers.[10] Equilibration of the epimers in toluene at 110 °C affords a 20% diastereomeric excess of the epimer with the *S* configuration at sulfur. When heated in ChL at a temperature slightly above the cholesteric–isotropic transition point, the sulfinates show a 1.4% enrichment in the *S* isomer. When conducted in cholesteric ChL, the sulfinate epimerization affords a 12.3% enrichment in the *R* epimer, a shift of approximately 32% from the equilibrium position in the achiral solvent and 13.7% from isotropic ChL. Use of cholesteric ChB biases the equilibrium even more strongly (16.9%) in the same direction.

Oxaziridines constitute yet another class of compounds configurationally stable at 25 °C, yet racemizable at elevated temperatures. Upon brief heating (5 min) at 148 °C in ChB, oxaziridine **5** underwent substantial decomposition. Recovery of residual **5** by molecular distillation afforded (−)-enriched **5** of 20% e.e.[11] The only prior synthesis[13] of chiral **5** (from oxidation of the imine with percamphoric acid) proceeds in low (*ca.* 3%) optical yield.[11] However, the thermal instability of **5** under the conditions needed for asymmetric induction led to highly variable results; often, no oxaziridine was recovered. In this instance, the asymmetric induction may involve selective destruction of one enantiomer rather than thermal equilibration. Recovery of **5** from mixtures of the racemate and the cholesteryl ester *without prior heating* afforded no enantiomeric enrichment.

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(11) The absolute configuration and enantiomeric composition of a number of oxaziridines can be determined by NMR methods using chiral solvating agents such as 2,2,2-trifluoro-1-(9-anthryl)ethanol.[12] This work is being described elsewhere.
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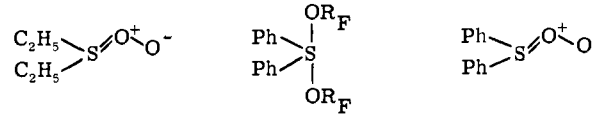
Evidence for the Formation of Sulfinyl Oxides in the Reactions of Alkoxysulfuranes with Hydrogen Peroxide. The Oxidation of Sulfides to Sulfoxides, and Olefins to Epoxides[1]

Sir:

The reactions of sulfur compounds with singlet oxygen have received much recent attention.[2] Foote[2a,c] has reported the trapping of a transient intermediate in the singlet oxygen oxidation of diethyl sulfide to which he assigns the sulfinyl oxide (or persulfoxide)[2a] structure **1**. We here report evidence for similar intermediates in reactions of di- and trialkoxysulfuranes with hydrogen peroxide.



1 **2** [R_F = $PhC(CF_3)_2$] **3**

The reaction of **2**[3] with H_2O_2 to give **3**, or its functional equivalent, is evidenced by the change in products as a function of added dimethyl sulfide. Treatment, at −78 °C, of a CH_2Cl_2 solution 1.3 M in dimethyl sulfide and 1.5 M in sulfurane **2** with an amount of H_2O_2 (in ether)[4] equivalent to the sulfurane rapidly gave 52% of dimethyl sulfoxide (Me_2SO).[5] The reaction of dimethyl sulfide with H_2O_2 is slow under these conditions in the absence of **2**. In the absence of dimethyl sulfide, the reaction of **2** with H_2O_2 at −78 °C gives diphenyl sulfone (80%), diphenyl sulfoxide (15%), and a trace of diphenyl sulfide.[6]

The ligand exchange reactions of Scheme I might be expected to be fast on the basis of earlier work on sulfuranes.[3,7] The rearrangement of **3** to sulfone is shown by the above product data to be competitive with the loss of oxygen to give sulfide or, in the presence of dimethyl sulfide, with the pictured reductive scavenging reaction. Diphenyl sulfoxide could result either from hydrolysis of **2** by reaction with adventitious water, or from the reduction of **3** by added sulfide, or from the oxidation by **3** of the diphenyl sulfide generated in the reaction.[8]