terized by high iodide concentration and a condition of radical reactions characterized by low iodide concentration. Such a mechanism resembles that of the oscillatory Belousov-Zhabotinskii reaction.[9,10] Illumination can promote oscillations in a system that would otherwise remain mostly in the nonradical condition, and it can eliminate oscillations by forcing a susceptible system entirely into the radical condition.

Although elementary oxygen is a thermodynamically stable product of hydrogen peroxide decomposition in this system, our observations indicate it is not inert to interactions with some of the reaction intermediates. Depending upon the conditions, oxygen can apparently function either to promote radical formation or to reduce the reactivity of radicals already present.

We are now developing and testing a detailed chemical mechanism for the processes in this remarkable system.

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Asymmetric Synthesis in a Cholesteric Liquid Crystal Solvent

Sir:

The simple introduction of a center of chirality into achiral compounds is extremely relevant to the prebiological origin of optical activity.[1-3] Asymmetric syntheses of this type have been the subject of considerable research[4] and recently were observed to occur in a lattice-controlled reaction within a single crystal.[5,6] In this communication we describe a "lattice-controlled" reaction utilizing the *anisotropic* ordering of solutes in liquid crystalline mesophases to direct the course of a chemical reaction in a manner not normally achieved in *isotropic* media. Several authors have reported their attempts to utilize the anisotropic ordering of reactants to produce unusual reaction products or rate variations.[7-15] However, to date there is a lack of sufficient evidence to demonstrate clearly the effect of anisotropic ordering on chemical reaction sequences.[15]

In the cholesteric mesophase there exists a macroscopic helical structure formed by the chiral organization of "nematic-like" layers with uniaxial molecular arrangement within the layers. This mesophase can be considered to be a super chiral environment where rod-shaped solute molecules are readily organized within the nematic layers. It is expected that this special type of ordering within the cholesteric mesophase will effect chemical reactivity unlike that of asymmetric solvation in an isotropic media.

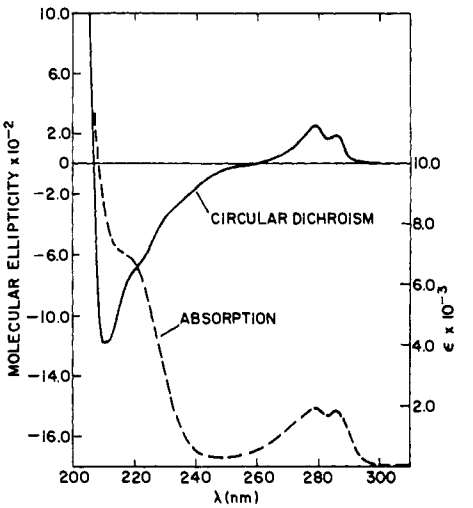
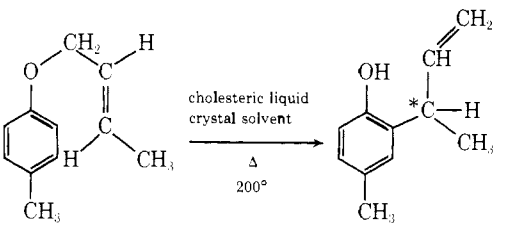


Figure 1. Circular dichroism and absorption spectra of 2-(α-methylallyl)-4-methylphenol (**2**) in methylcyclohexane.

We report a novel asymmetric synthesis using a cholesteric liquid crystalline solvent as an asymmetric catalyst. γ-Methylallyl-*p*-tolyl ether (**1**) undergoes an ortho Claisen rearrangement in a stereospecific manner to produce chiral 2-(α-methylallyl)-4-methylphenol (**2**) in a cholesteric liquid crystalline solvent as shown below.



1 2

The rearrangement of **1** was carried out in the cholesteric mesophase formed by cholesteryl-*p*-nitrobenzoate (**3**) at 200°, using 5 wt % of **1** in **3**. The reaction was run for 6 hr and the product (~60% yield) of the rearrangement isolated from the acidic phenolic fraction by means of glc on a ½ in. × 6 ft Carbowax 20M column.

The optical activity of compound **2** was demonstrated by the presence of circular dichroism (CD) within its electronic transitions between 205 and 290 nm (see Figure 1). Compound **2** shows positive CD throughout the 280-nm $^1L_b \leftarrow {}^1A$ ($\Delta\epsilon/\epsilon = 3.7 \times 10^{-5}$) transition and negative CD within the $^1L_a \leftarrow {}^1A$ transition. CD measurements were made on a Cary 61 spectropolarimeter at 22° in methylcyclohexane solvent, and compounds **1** and **2** were characterized by nmr, uv, as well as by their physical constants.

Rearrangement of **1** (200°) in an anisotropic cholesteric composition containing 30% of **1** and in an isotropic solution containing 50% of the Claisen ether in **3** yielded **2** which exhibited no observable CD between 205 and 290 nm. The existence of the mesophase in the 5 and 30% mixtures was determined by optical microscopy and was readily apparent by visual inspection. From the above experimental observations it is concluded that the diastereomeric interaction that exists in the isotropic chiral cholesteryl-*p*-nitrobenzoate is not sufficient to produce an observably chiral **2**. The same is true for high concentration of **1**, *i.e.*, 30 wt % **1** in **3**, where the ability of the liquid crystal matrix to order solute molecules falls off with increasing solute concentration.[16]

Optical polarization studies indicate that the molecules of **1** align within the "nematic-like" layers of the cholesteric mesophase with their long axis parallel with the long axis of the liquid crystal molecules. We anticipate that the twisting of the allyl group required for the Claisen rearrangement would be more preferred in one direction than the other depending on the chirality, *i.e.*, helicity of nematic layers, of the cholesteric mesophase.

In the absence of an "asymmetric catalyst" there is no difference in the transition state energies leading to the production of the enantiomeric phenols, *i.e.*, $\Delta E_a^R = \Delta E_a^S$, and a racemic product is formed. However, in the cholesteric liquid crystal solvent which behaves as an "asymmetric catalyst," there exists a diasteromeric relationship between these transition states which leads to the formation of an optically active product, *i.e.* $\Delta E_a^R \neq \Delta E_a^S$.

While the optical purity and chirality of **2** is not known and estimates made based on related systems are often misleading, we feel that a clear demonstration of the effect of anisotropic ordering on a chemical reaction stereospecificity has been achieved and an exciting novel application of liquid crystalline phenomena has been identified. The possibility then exists that a preponderance of either the *R* or *S* enantiomer could be achieved by the proper choice of the cholesteric mesophase chirality, while the pitch of the cholesteric helix may effect the optical purity.

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Rate Constants for the Addition of Phenyl Radicals to *N*-(*tert*-Butyl)-α-phenylnitrone (Spin Trapping) and Benzene (Phenylation) as Studied by Electron Spin Resonance

Sir:

In previous reports we have shown that spin trapping[1] can be used to monitor the number and kinds of radicals produced from certain initiators as a function of time.[2,3] Thus in benzene at ambient temperatures essentially all benzoyloxy or *tert*-butoxy radicals can be trapped in the thermal decomposition of benzoyl peroxide[2] or di-*tert*-butyl peroxalate,[3] respectively, at sufficiently high concentrations of spin trap (*e.g.*, 0.1 *M*). Trapping rate constants have been estimated for both *tert*-butoxy[3] and benzoyloxy radicals.[2] The purpose of this paper is to report on a determination of the absolute rate constant for trapping phenyl radicals by PBN and by benzene. The value for the latter suggests a rate of decarboxylation for the benzoyloxy radical which is considerably faster than presently assumed in the literature.

As originally reported[4] phenyl radicals are readily trapped by *N*-(*tert*-butyl)-α-phenylnitrone (PBN) to give diphenylmethyl *tert*-butyl nitroxide, $a^N = 14.41$, $a_\beta^H = 2.21$ G in benzene. However, a quantitative study in benzene shows that at room temperature only a fraction of the phenyl radicals produced from phenylazotriphenylmethane (PAT) are trapped by PBN at concentrations which trap benzoyloxy and *tert*-butoxy radicals quantitatively. Since estimates for the rate constant of addition of phenyl radical to benzene are only about 1000 times slower than typical rate constants for spin trapping ($\sim 10^3$ *vs.* 10^6-10^7), it seems likely that a substantial portion of the untrapped phenyl radicals add to benzene to produce untrapped phenylcyclohexadienyl radicals. This possibility was tested by obtaining the initial rate of formation of the phenyl adduct as a function of PBN concentration in benzene. Thus, if the following mechanism is assumed

$$\underset{\text{PAT}}{\text{PhN=NCPh}_3} \longrightarrow \text{Ph}\cdot + \text{N}_2 + \underset{\text{(not trapped)}}{\text{Ph}_3\text{C}\cdot} \quad (1)$$

$$\text{Ph}\cdot + \underset{\text{PBN}}{\text{PhCH=N(O)CMe}_3} \longrightarrow \underset{\text{Ph-SA}}{\text{Ph}_2\text{CHN(O}\cdot\text{)CMe}_3} \quad (2)$$

$$\text{Ph}\cdot + \text{PhH} \longrightarrow \underset{\text{(not trapped)}}{\text{Ph-C}_6\text{H}_5} \quad (3)$$

then

$$\frac{d[\text{Ph-SA}]}{dt} = \frac{k_1[\text{PAT}]}{(1 + k_3[\text{PhH}])/k_2[\text{PBN}]}$$

and

$$\frac{[\text{PAT}]}{d[\text{Ph-SA}]/dt} = \frac{k_3[\text{PhH}]}{k_1k_2[\text{PBN}]} + \frac{1}{k_1}$$

A plot of the reciprocal of the initial slopes at 30° as a function of 1/[PBN] gives a good straight line over the concentration range 0.01-0.4 *M* PBN. From the intercept, $k_1 = (1.5 \pm 0.2) \times 10^{-5}$ sec^{-1}. Alder and Leffler[5] report 1×10^{-5} sec^{-1} obtained by following the disappearance of PAT in benzene. The good agreement lends support to the above mechanism. The slope of the above plot gives $k_3/k_2 = 0.0065$. If k_2 were known the phenyl spin trapping data could be used to estimate the rate of phenyl radical addition to benzene.

The rate constant for hydrogen atom abstraction from methanol of *p*-methylphenyl radical has been determined by a pulse radiolysis study of toluene-*p*-diazonium tetrafluoroborate in methanol.[6] Thus PAT was allowed to decompose in methanol containing PBN at concentrations where both the phenyl and hydroxymethyl radical spin adducts could be detected simultaneously.[7] If the following mechanism is assumed