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

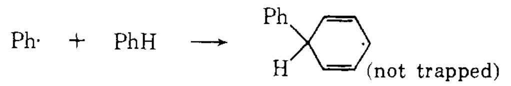
Sir:

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 (~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

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

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

 (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 $1/[\text{PBN}]$ gives a good straight line over the concentration range 0.01–0.4 M PBN. From the intercept, $k_1 = (1.5 \pm 0.2) \times 10^{-5}\ \text{sec}^{-1}$. Alder and Leffler[5] report $1 \times 10^{-5}\ \text{sec}^{-1}$ 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

$$\text{PAT} \longrightarrow \text{Ph}\cdot \qquad (1)$$

$$\text{Ph}\cdot + \text{PBN} \longrightarrow \text{Ph-SA} \qquad (2)$$

$$\text{Ph}\cdot + \text{CH}_3\text{OH} \longrightarrow \cdot\text{CH}_2\text{OH} \qquad (4)$$

$$\cdot\text{CH}_2\text{OH} + \text{PBN} \longrightarrow \text{HM-SA} \qquad (5)$$

then

$$\frac{d[\text{Ph-SA}]/dt}{d[\text{HM-SA}]/dt} = \frac{k_2[\text{PBN}]}{k_4[\text{CH}_3\text{OH}]}$$

From computer simulation matching of partially overlapped spectra, the relative concentrations of the two spin adducts could be obtained. This analysis gave $k_2/k_4 = 86$. Using the value of $1.4 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ for k_4 reported by Packer[6] for the *p*-methylphenyl radical, $k_2 = 1.2 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ for the rate constant of phenyl radical trapping by PBN in methanol at 25°. The rate constants for spin trapping other radicals with other traps[3] fall in the range 1×10^6 to $5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at room temperature.

The phenylation of benzene in benzene gave $k_3/k_2 = 0.0065$ as stated above. If the value $k_2 = 1.2 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ determined in methanol is used for benzene, $k_3 = 7.8 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. A recent study is in agreement with this estimate.[8] The ratio of the rate constants for phenylation of benzene and for the reaction of phenyl radicals with iodine in methylcyclohexane was found to be[8] $k_3/k_{\text{I}_2} = 5.0 \times 10^{-5}$. These authors assumed that the rate of reaction of phenyl radicals with I_2 is diffusion controlled. Thus as an upper limit $k_{\text{I}_2} \sim 10^{10}\ M^{-1}\ \text{sec}^{-1}$ and $k_3 \sim 5 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, only a factor of 6 larger than our value in benzene. For the phenylation of chlorobenzene in methylcyclohexane $k_3^{\text{PhCl}}/k_{\text{I}_2} = 7.7 \times 10^{-5}$ was obtained[8] and thus $k_3^{\text{PhCl}} \sim 8 \times 10^5\ M^{-1}\ \text{sec}^{-1}$. From trapping phenyl radicals in chlorobenzene, we[9] obtain $k_3^{\text{PhCl}} = 1.8 \times 10^5\ M^{-1}\ \text{sec}^{-1}$. The relatively good agreement obtained from these different sources lends support to the conclusion that the absolute rate constant for phenylation of benzene is $\sim 10^5\ M^{-1}\ \text{sec}^{-1}$.[11]

In an extensive analysis of the rate constants involved in the phenylation of benzene using benzoyl peroxide as a source of phenyl radicals DeTar[14] used $k_3 = 2 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ at 87° for his calculations. Although this value now appears to be too low, the ratio of the rate constants of decarboxylation of benzoyloxy radicals and phenylation of benzene reported by DeTar ($1 \times 10^4/2 \times 10^3 = 5$) may still be correct because this ratio was based on yields of products isolated for the experiments considered. Using the present estimate for phenylation of benzene ($\sim 10^5\ M^{-1}\ \text{sec}^{-1}$), one obtains $\sim 5 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ for the rate constant of decarboxylation of benzoyloxy radicals. Assuming an energy of activation of 13.6 kcal/mol for this reaction,[15] decarboxylation rate constants of 5×10^7 to $1 \times 10^8\ \text{sec}^{-1}$ are calculated at 100 and 130° in benzene. These numbers are of interest because they overlap with CIDNP estimates of the lifetime of benzoyloxy radicals produced by the thermal decomposition of propionyl benzoyl peroxide in *o*-dichlorobenzene at 100°[16] and 130°.[17]

Combining data previously obtained on trapping benzoyloxy radicals[2] with the rate constants reported here on the addition of phenyl radicals to PBN and benzene, an absolute rate constant of trapping benzoyloxy radicals by PBN in benzene at room temperature of $4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ is estimated.[18]

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Synthesis of an Organic Adduct of the P_4O_{10} Cage Structure

Sir:

In spite of considerable effort being devoted to the problem for more than a century, no one prior to this time has been able to adduce any reasonably acceptable evidence for the production of the P_4O_{10} birdcage structure in solution nor has there been any evidence to show that phosphorus pentoxide could be dissolved in any solvent without rupture of the P-O-P bridges. In previous studies, we have shown[1,2] that simple orthophosphoric acid as well as the various chain polphosphoric acids, the ring metaphosphoric acids, and/or mixtures of any of these can be condensed to 1,5-μ-oxo-tetrametaphosphoric acid, $\text{H}_2\text{P}_4\text{O}_{11}$, which is the product that would be formed by scission of a single P-O-P bridge in the P_4O_{10} molecule through interaction with a single molecule of water. When a carbodiimide condensing agent is employed at the usual concentration range (around 0.8 *M* of RNCNR per 0.2 *M* of phosphate phosphorus), it is found that the reaction stops (and indeed seems to come to equilibrium) at an overall $\text{H}_2\text{O}/\text{P}_2\text{O}_5$ mole ratio of 0.5, with the $\text{H}_2\text{P}_4\text{O}_{11}$ molecule accounting for essentially all of the phosphorus. Not surprisingly, the cleanest condensation reaction to make 1,5-μ-oxo-tetrametaphosphoric acid involves tetrametaphosphoric acid as the phosphatic reagent.

In thinking about this reaction, we reasoned that by a simple application of the law of mass action, it ought to be possible to push the reaction to an even higher degree of