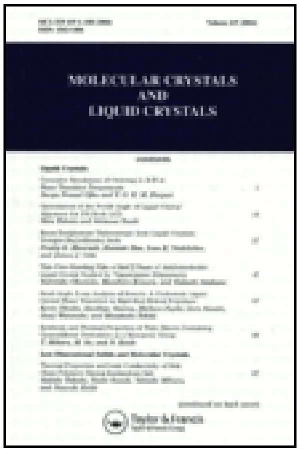

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Liquid Crystal Solvents as Reaction Media for the Claisen Rearrangement‡

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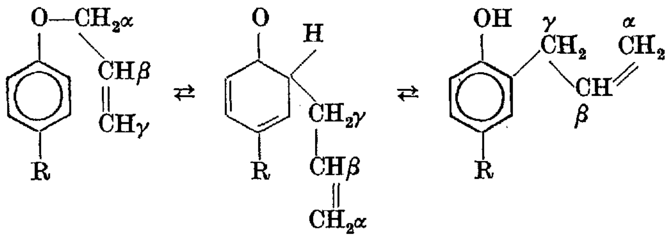
In the course of our investigations of liquid crystals as solvents, we wish to report some kinetic data for the Claisen rearrangement. The thermal rearrangement of allyl phenyl ethers (1) proceeds by an intramolecular path to give an ortho-dienone (II) which rapidly enolizes to 2-allylphenols (III).



(I) (II) (III)

The net result is that the γ-carbon atom of an allyl phenyl ether becomes attached to the phenyl ring in the formation of 2-allylphenol.[1] Kinetic results reported for the *ortho* rearrangement are first order and the negative entropies of activation indicate a highly ordered cyclic transition state.[2] A *para* rearrangement can also take place if that position is not blocked. It has been

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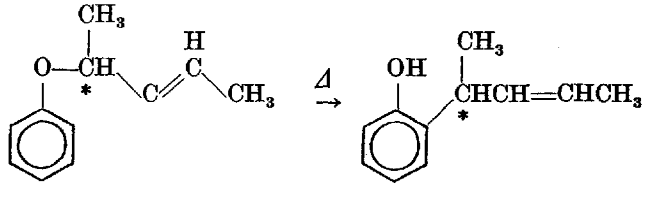
reported that the *para* rearrangement is also first order.[2] A considerable degree of stereospecificity attends the Claisen rearrangement. For example, the finding[3] that optical activity is present in the 2-(α, γ-dimethylallyl)-phenol (V) formed by rearrangement of (-)-*trans*-α,γ-dimethylallyl phenyl ether (IV) indicates



(IV) (V)

a stereoselective reaction.

One would expect this sterospecificity may be promoted by solvents in which the molecules are oriented in one direction along their long axes. Nematic liquids by their structure provide this directional alignment of the reaction intermediate and thereby maintain a fixed sterochemistry for the reaction.

Specifically, we used di (*p*-methoxyphenyl) *trans*-cyclohexane-1, 4-dicarboxylate, with a nematic range of 143–242°, as the nematic solvent and as the solute, allyl *p*-tolyl ether which undergoes the Claisen rearrangement to 2-allyl *p*-cresol.

We found that the nematic liquid catalyzes the rearrangement of allyl *p*-tolyl ether to such a degree that the rate of the rearrangement is comparable to that found in a proton-donating solvent such as carbitol.

Experimental

To prepare the solvent a commercial grade of cyclohexane-1, 4-dicarboxylic acid was extracted with toluene to dissolve the *trans* isomer. The *trans*-acid was recovered by crystallization and was then recrystallized from water.[4] The *trans*-acid was esterified by reaction with thionyl chloride and *p*-methoxyphenol.

The samples were prepared by filling a series of ampoules with about 2.0 g of nematic solvent under vacuum at 145° in a nitrogen atmosphere. A weighed sample of allyl *p*-tolyl ether was added and the ampoule sealed. The samples contained 9% ether by weight. The ampoules were placed in a constant temperature bath at 185° ± 0.04°, and removed for analysis at intermittent periods up to fifteen hours (88% completion). The entire sample from the ampoule was analyzed by extracting the unreacted ether and the phenol with diethyl ether and separating the insoluble nematic solvent by filtration. The ether extract was evaporated on the steam bath and the residue dissolved in chloroform. The composition of the chloroform solutions was determined from PMR spectra.‡ The area due to the absorption of the methylene protons adjacent to the oxygen at $\tau 5.50$ ppm is a measure of the concentration of the original ether, and the area of the doublet at $\tau 6.65$ ppm, due to the methylene protons adjacent to the phenyl ring, is a measure of the phenol.

Discussion

The data collected from the measurements described above were fitted to the first-order rate equation using the least squares method. Six points were used to draw the curve. Figure 1 represents the logarithm of the concentration of allyl *p*-tolyl ether plotted as a function of time. The rate constant calculated from the first-order rate equation is 3.35×10^{-5} sec^{-1}.

The rate constant for the rearrangement of allyl *p*-tolyl ether in the nematic solvent is twice that reported for decalin as the solvent at the same temperature and is of the same order of magnitude as found for carbitol, a proton-donating solvent.[5] The rate of rearrangment places this nematic solvent in a class with hydroxylic solvents.

With the preliminary results presented in this paper, it is obvious that we cannot draw major conclusions. A couple of

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‡ The PMR spectra were determined on a Varian A.60 spectrometer with an NMR specialties HD6058A heteronuclear decoupler.

observations, however, seem to be reasonable. The rate of the Claisen rearrangement of allyl *p*-tolyl ether in a nematic liquid is comparable to that found in some proton-donating solvents, conditions being comparable.

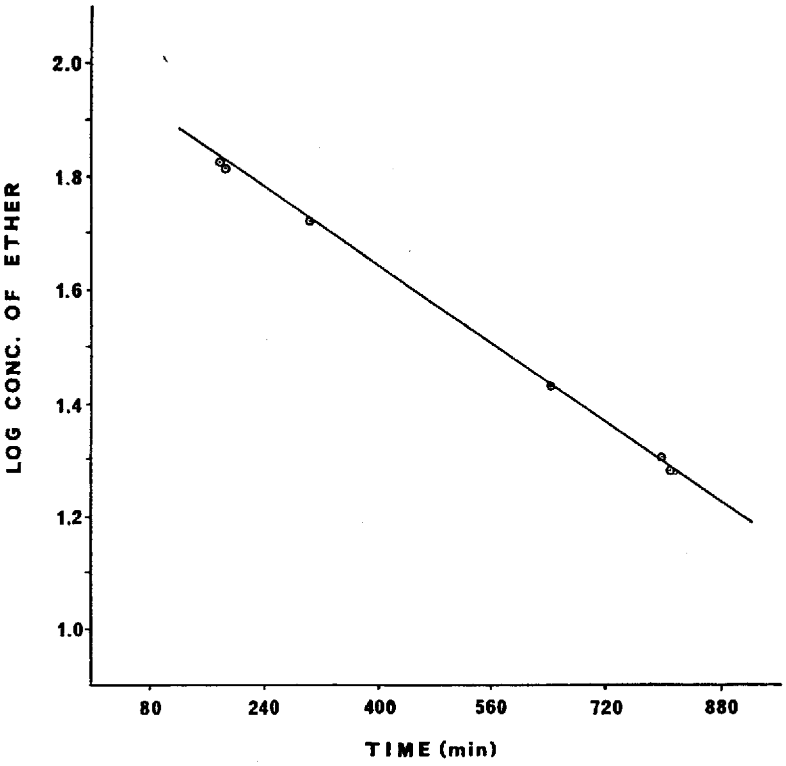

Figure 1. Plot of concentration of allyl *p*-tolyl ether *versus* time at 185°.

The nematic solvent used in this study does not donate protons to enhance the rate of the reaction. Therefore, the increased reaction rate in contrast to non-hydroxylic solvents, is attributed to the stereoselective character of the nematic solvent.

Studies are continuing on the rearrangement reported in this note. These studies include thermodynamic data collected at different temperatures and dielectric effects. The use of liquid crystals as solvents for several types of reactions are in progress.

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