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Nematic Solvents as Media for the Claisen Rearrangement†‡

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Abstract—The kinetics and mechanism of the Claisen rearrangement of a series of *para*-substituted allyl phenyl ethers are determined in nematic and isotropic solvents. The influences of the solvent systems are compared. The rearrangement reactions are first-order in both solvents, and the Arrhenius plots show the same energy of activation in the nematic and isotropic phases of the solvents. The reactions are unimolecular in both solvent systems.

The influence of a nematic solvent in the kinetics and mechanism of the Claisen rearrangement and the thermodynamic quantities by which this influence can be described is the subject of this investigation. The nematic liquid crystalline phase is a state of matter with properties intermediate between solids and isotropic liquids, possessing the mechanical behavior of liquids. The nematic phase differs from the isotropic in that the molecules in the nematic phase are oriented with their long axes parallel.

The addition of a solute to a liquid crystalline solvent lowers both the crystal-liquid crystal and the nematic-isotropic transition temperatures, and in many cases the mesophase becomes monotropic or is lost completely.(1) If the structure of the solute is similar to that of the solvent, it is possible to dissolve a large amount of solute and still maintain liquid crystallinity. The solutions of *para*-substituted allyl phenyl ethers in the nematic liquid crystalline solvent reported in this investigation are homogeneous anisotropic

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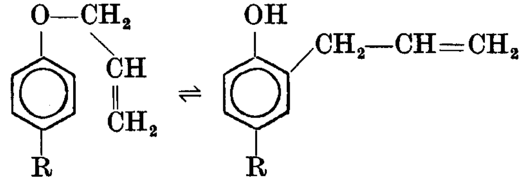
single phases. The properties of the nematic solvent, di(*p*-methoxyphenyl)-*trans*-cyclohexane-1,4-dicarboxylate, and the experimental conditions used throughout this work were reported in the initial rate studies of the Claisen rearrangement.(2) In our first report, we proposed that the nematic liquid influenced the rate of the rearrangement, but further investigation has not confirmed a catalytic effect of the nematic structure.

The Claisen rearrangement in the nematic solvent is evaluated by measuring the rates of rearrangement of a series of *para*-substituted allyl phenyl ethers in two different solvent systems, i.e., a nematic solvent and an isotropic solvent. The rates of rearrangement of selected *para*-substituted allyl phenyl ethers were measured in the nematic liquid crystalline and isotropic solvents at three temperatures. The rearrangement under consideration is



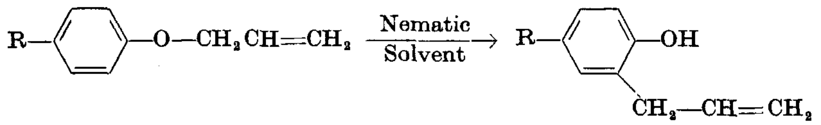
Where, R is —CH_3, —Cl, —CN and —NO_2

Results

The rate constants for the rearrangements at 160°, 185° and 200°, calculated from the first order rate equation, are recorded in Table 1. The data were treated by the least-squares method. Each rate constant represents six to ten experimental determinations and a plot of the logarithm of the fraction of reactant consumed *versus* the reaction time gives a straight line.

For each reaction a plot of the logarithm of the rate constant as a function of the reciprocal of the absolute temperature gives a straight line, the slope of which defines, E_a, the energy of activation. Figure 1 shows such a plot for the rearrangement of allyl *p*-cyanophenyl ether. The frequency factor, A, was calculated from the Arrhenius equation and the entropy of activation, $\Delta S^{\ddagger}$ from the equation $A = k'T/h \cdot \exp \Delta S^{\ddagger}/R$. Heat of activation, $\Delta H^{\ddagger}$, for each reaction was calculated by standard methods.(3) The activation parameters for

TABLE 1 First order rate constant for Claisen rearrangement



Temperature	Compound	Nematic Solvent k × 10^6 sec^{-1}
160±.04°C	R equals CH_3	4.17±.02
185±.04°	,,	32.76±.60
200±.05°	,,	95.25±3.5
160±.04°	R equals Cl	3.41±.05
185±.04°	,,	26.96±.40
200±.05°	,,	83.55±1.2
160±.04°	R equals CN	1.38±.01
185±.04°	,,	12.05±.18
200±.05°	,,	40.85±.30
160±.04°	R equals NO_2	1.23±.02
185±.04°	,,	10.32±.25
200±.05°	,,	42.74±1.2

the rearrangement of a series of *para*-substituted allyl phenyl ethers to the phenols using a nematic solvent are given in Table 2. The activation energies are reliable to 1 kcal/mole and the entropies of activation to one entropy unit.

Reaction rates and activation parameters for the Claisen rearrangement found in the nematic phase of the solvent are compared with two different solvents in the isotropic phase: (a) di(*p*-methoxyphenyl)-*trans*-cyclohexane-1,4-dicarboxylate at 220° and 230°; (b) diphenyl ether at 160°, 185° and 200°.

The Arrhenius plot (Fig. 2) of the data for the rearrangement of allyl *p*-cyanophenyl ether in the solvent, di(*p*-methoxyphenyl)-*trans*-cyclohexane-1,4-dicarboxylate at five different temperatures, three in the nematic range and two in the isotropic range of the solvent shows no discontinuity and indicates that the influence of temperature on the rate of reaction is the same regardless of the state of the solvent. A similar plot for allyl *p*-nitrophenyl ether also describes a straight line.

The activation parameters (Table 3) for the Claisen rearrangement

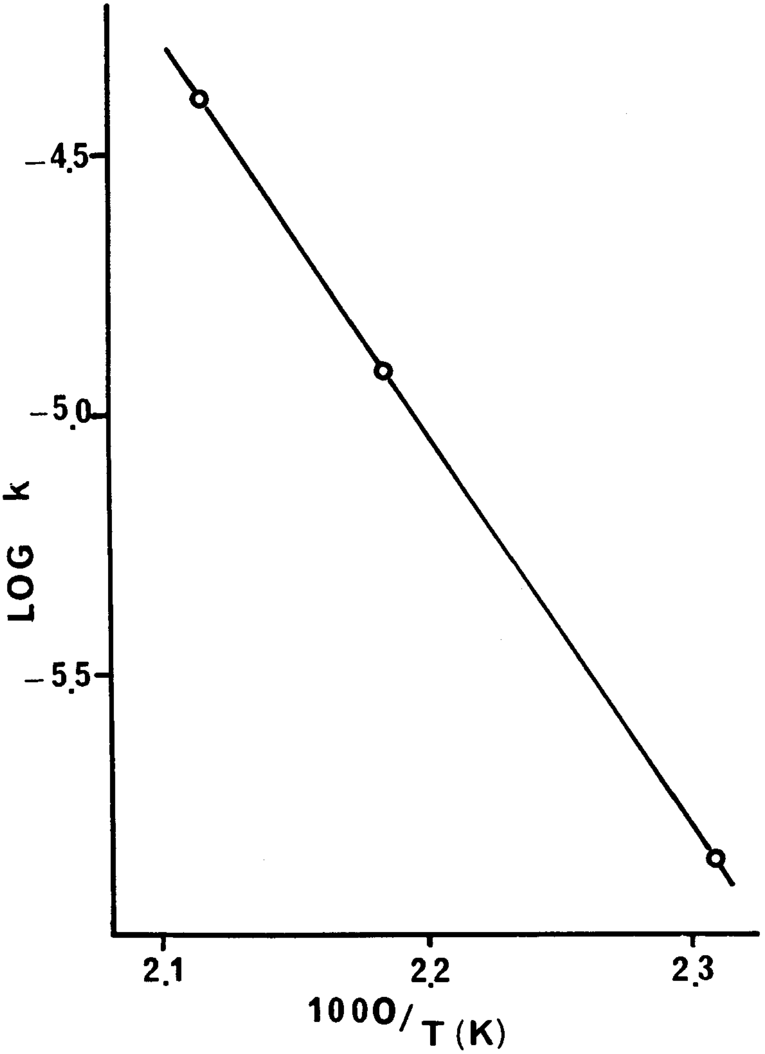
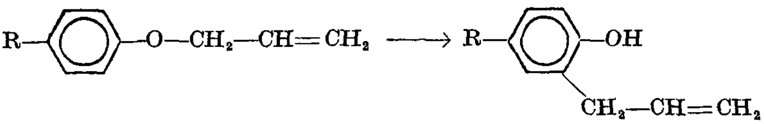


Figure 1. Arrhenius Plot for the rearrangement of allyl *p*-cyanophenyl ether in nematic solvent.

Table 2 *Activation parameters in* nematic solvent*



R	E_a†	$\Delta H^{\ddagger}$†§	Log A§	$\Delta S^{\ddagger}$§Φ
CH_3	31.9	29.8	10.76	-10.2
Cl	32.6	30.5	10.97	- 9.3
CN	34.7	32.6	11.66	- 6.1
NO_2	35.8	33.7	12.08	- 4.1

* Di (*p*-methoxyphenyl)-*trans*-cyclohexane–1, 4-dicarboxylate
† kcal/mole
§ Calculated at 185°
Φ Cal/deg/mole

dissolved in the isotropic solvent, diphenyl ether, indicates the similarity of the reactions in the different solvent systems.

Discussion

Electron-donating groups in the *para*-substituted allyl phenyl ethers produce an accelerating effect on the reaction rate while electron-withdrawing groups retard the rate of rearrangement. This effect is also reported in the rearrangement of these ethers in isotropic solvents,(4) suggesting some polar character of the transition state.(5) The rate constants for electron-donating groups in the nematic solvent are about three times those found for the electron-withdrawing groups in the series of *para*-substituted ethers. The data in Table 3, indicates that as the electron-releasing power of the *para*-substituent decreases, the energy of activation and the entropy of activation increase in both types of solvent. This conclusion is in contrast to the study reported previously in diphenyl ether as solvent,(6) and supports the trend reported for the rearrangement of *para*-substituted allyl phenyl ethers in the hydroxylic solvent, carbitol.(7)

The loss of entropy of activation (Table 2) accompanying the rearrangement may be explained by the ordered nematic solvent restricting molecular motion of the reaction intermediate or by the

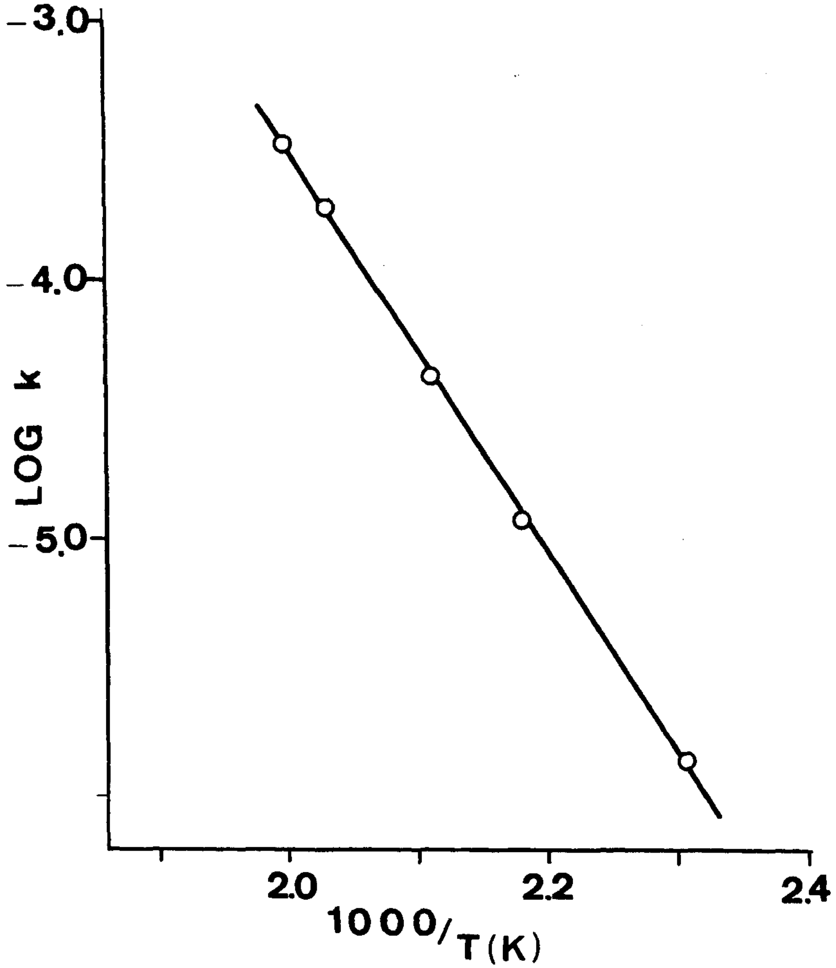


Figure 2. Arrhenius Plot for the rearrangement of allyl *p*-cyanophenyl ether in the nematic and isotropic phase of the liquid crystalline solvent.

increased ordering of the transition state due to solvation. Neither of these explanations seem appropriate since comparable entropy losses are found in isotropic solvents. The highly ordered cyclic transition state of the Claisen rearrangement appears to explain the loss in entropy.

The activation energy and other thermodynamic parameters for the Claisen rearrangement are the same in the nematic and isotropic phases of the dicarboxylate and in diphenyl ether (see Table 3). The

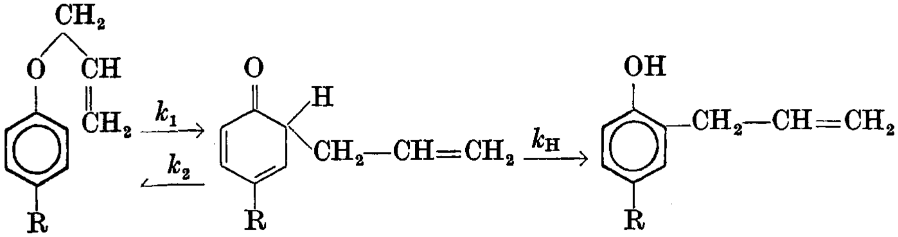
TABLE 3 Comparison of activation parameters

		Nematic Solvent	
R	E_a	$\Delta H^{\ddagger *}$	$\Delta S^{\ddagger *}$
$-CH_3$	31.9 kcal/mole	29.8 kcal/mole	−10.2 cal/deg/mole
$-Cl$	32.6	30.5	−9.3
$-CN$	34.7	32.6	−6.1
		Isotropic Solvent†	
R	E_a	$\Delta H^{\ddagger *}$	$\Delta S^{\ddagger *}$
$-CH_3$	31.9 kcal/mole	29.8 kcal/mole	−10.7 cal/deg/mole
$-Cl$	33.2	31.1	−8.6
$-CN$	34.3	32.2	−7.7

* Calculated at 185°

† Diphenyl ether

similarity of the reaction order and the activation parameters of the Claisen rearrangement in nematic and isotropic solvents indicates similar rate-determining steps for the reaction in both types of solvent. The reported first-order rate constants for the Claisen rearrangements in isotropic solvents are recognized to be composites of the rate constants of the individual steps:



In isotropic solvents the rate determining step is k_1, since the enolization step, k_H, is very rapid. The intramolecular nature of this reaction which proceeds through a cyclic intermediate is well documented in isotropic solvents(8,9) and the similarity of activation parameters and the order of the reactions in nematic solvents indicates a similar mechanism. The problem of measuring the influence of the nematic solvent upon the Claisen rearrangement is limited to the rate-determining step, that is, the formation of the cyclic intermediate state. The similar influence of the nematic and isotropic solvents in this reaction is expected because of the unimolecular nature of the reaction. The influence of isotropic solvents on reactions is more pronounced in higher order reactions,(10) and we are currently investigating nematic solvents for these reactions.

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