coefficients are not an artifact of the BMA system since similar values were obtained for the piperidine/morpholine adducts of α-cyano-2,4-dinitrostilbene.[15]

The most "obvious" explanation of these results, namely, that k_H simply refers to unassisted protonation of T_A^- by H_3O^+ (k_3^H), has been ruled out in a previous section by showing that k_H is much higher than expected for k_3^H.

A possible cause for the extreme Brøsted coefficients is that the morpholine adduct displays enhanced reactivity akin to an α effect in nucleophilic reactions.[3,11] This effect could arise from a stabilizing interaction with a lone pair of the morpholine oxygen, possibly by hydrogen bonding if two water molecules were involved in the transition state (**8**). Note that with 2-methoxyethylamine, which also has an ether oxygen, such a transition state would be entropically disfavored because of the greater conformational flexibility of the noncyclic amine. A similar but more dramatic enhancement in reactivity by a ring oxygen has recently been reported by Bordwell and Hughes[48] in an S_N2 reaction of phenoxazine.

A more remote possibility is that our α_N (or β_N) values include a component for the solvation of the amine nitrogen. In the reaction of quinuclidines with phosphates Jencks[49] has attributed the extremely low or even negative β_{nuc} values to the requirement for desolvation of the amine before nucleophilic attack. If the same effect were operative in proton-transfer reactions, this would imply that the commonly reported Brønsted α values in the protonation direction overestimate the true α or the observed β values in the deprotonation direction underestimate the true β. The problem with this interpretation as applied to our k_H is that in both **2** and **4** the solvent is an active participant in the reaction; i.e., there is no need for solvation/desolvation of the amine nitrogen. We therefore disfavor this interpretation.

Effective Molarities. It is common practice to measure the effectiveness of an intramolecular reaction by its effective molarity (EM).[50] In our system EM is defined as $k_i/k_3^{AH}(pK_a^{\pm})$ with $k_3^{AH}(pK_a^{\pm})$ referring to a $RR'NH_2^+$ whose pK_a^{AH} is equal to $pK_a^{\pm}$. Since for a given amine $pK_a^{\pm}$ and pK_a^{AH} are very similar (Table II), the ratios k_i/k_3^{AH} obtained by using the experimental k_3^{AH} values are good approximations for EM. These ratios are included in Table II.

Except for the morpholine adduct the k_i/k_3^{AH} ratios are all in the range $\approx 10^{-2}$ to $\approx 5 \times 10^{-2}$ M. Such low EMs are typical for intramolecular proton transfers.[50] The fact that k_i/k_3^{AH} is much higher for the morpholine adduct than for all the others is a further indication that the morpholine adduct displays abnormally high reactivity with respect to the intramolecular process.

Experimental Section

All reagents were available in pure form from a previous investigation.[3] The kinetic experiments were performed in a temperature-controlled Perkin-Elmer 559A UV-vis spectrophotometer. In most cases the rates were measured at 255 nm, where $\epsilon_{products}$ (benzaldehyde and Meldrum's acid anion) is higher than $\epsilon_{T_A^-}$.[2] With the methoxyamine and semicarbazide adducts the decrease of [BMA] at 320 nm was monitored, since conversion to $T_A^{\pm}$ or T_A^- was not extensive.

A typical kinetic run was initiated by injecting 3-10 μL of a 0.05 M stock solution of BMA in Me_2SO (which contained traces of HCl to suppress hydrolysis) into a spectrophotometric cuvette that contained the thermally equilibrated amine buffer. First-order plots were linear over at least 3-4 half-lives.

With the piperidine adduct the rates were very slow, with half-lives up to 20 h or more. Here the reaction was only followed to 2-5% completion, and τ_2^{-1} was obtained by the method of initial rates, i.e., by dividing dOD/d*t* by $[BMA]_0(\epsilon_{products} - \epsilon_{T_A^-})$.

Acknowledgment. This research was supported by Grant CHE-8315374 from the National Science Foundation.

Registry No. T_A^- (RR'N = piperidine), 103150-39-6; T_A^- (RR'N = morpholine), 103191-55-5; T_A^- (RR'N = $BuNH_2$), 103150-40-9; T_A^- (RR'N = $MeO(CH_2)_2NH_2$), 103150-41-0; T_A^- (RR'N = $H_2NCOCH_2NH_2$), 103191-56-6; T_A^- (RR'N = $NCCH_2NH_2$), 103150-42-1; T_A^- (RR'N = $MeONH_2$), 103191-57-7; T_A^- (RR'N = semicarbazide), 103150-43-2.

Supplementary Material Available: Kinetics of conversion of the amine adducts into benzaldehyde, Tables S1-S7 (7 pages). Ordering information is given on any current masthead page.

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Liquid-Crystalline Solvents as Mechanistic Probes. 21. Control of Norrish II 1,4-Biradical Reactivity by the Phase and Molecular Dimensions of an Ordered Solvent[1]

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Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057. *Received January 27, 1986*

Abstract: The fates of four triplet 1,4-biradicals (produced as Norrish II intermediates during the irradiations of *n*-decanophenone, 2-cyclohexyl-1-(4-ethylphenyl)-1-ethanone, 4-cyclohexyl-1-phenyl-1-butanone, and 5-cyclohexyl-1-phenyl-1-pentanone) have been explored in crystalline-, smectic B-like-, nematic-, and isotropic-phase solutions of *trans,trans*-4'-*n*-butyl[1,1'-bicyclohexyl]-4-carbonitrile (BCCN). The experimental probe is the ratio of elimination to cyclization products. The results indicate that the ordered phases of BCCN behave as a molecular ruler with regard to solute conformations; the micromorphology of each phase imposes a different set of constraints upon the shapes of the 1,4-biradicals. A rationalization for the seemingly bizarre phase-dependent changes in product ratios, based upon the shapes and labilities of the 1,4-biradicals, is presented.

During the last several years, others and we have observed that the rates and reactivities of a wide variety of solutes can be influenced by the solvent order of liquid-crystalline phases.[2-17] In spite of the considerable attention given the effects, few conclusions of general applicability have emerged. This is largely a conse-

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[1] For Part 20, see: Ramesh, V.; Weiss, R. G. *J. Org. Chem.*, in press.
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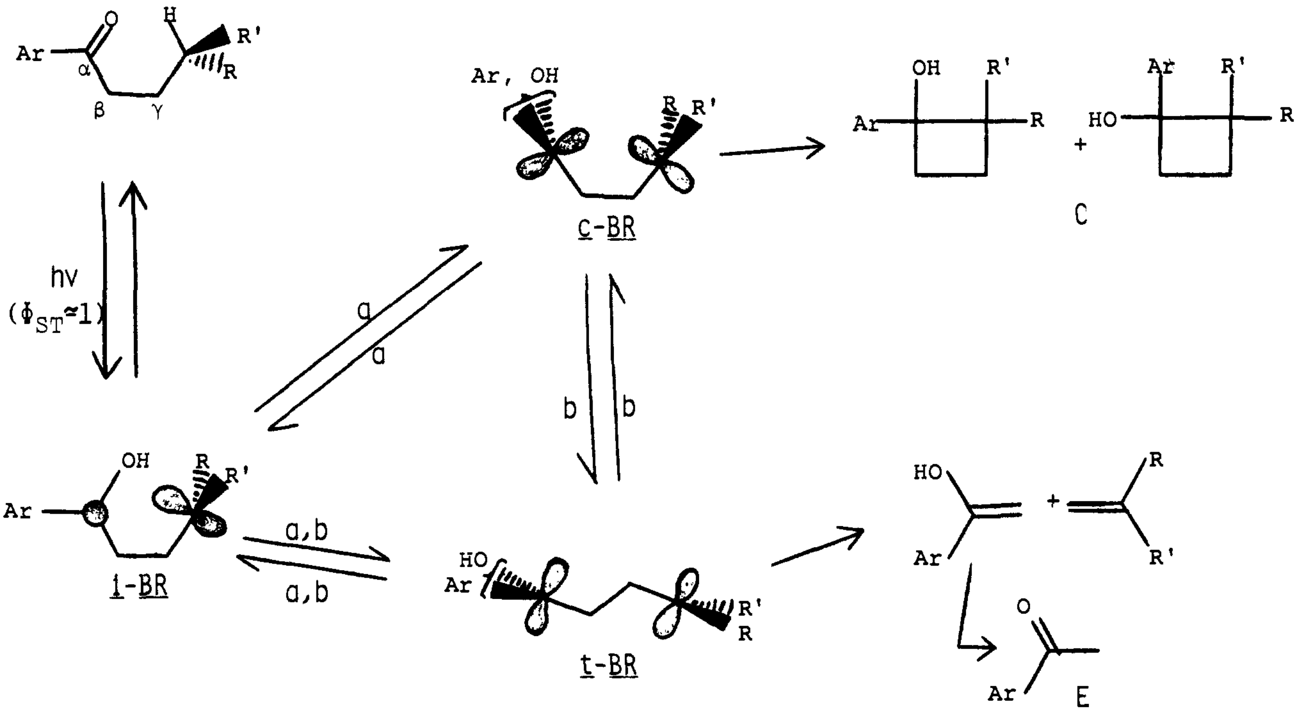
0002-7863/86/1508-5264$01.50/0

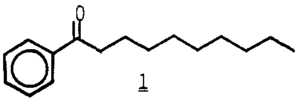
Scheme I. Simplified Conformational Representation of the Norrish II Reactions of Aryl Ketones. (a) 90° Rotation about C_α–C_β; (b) 180° Rotation about C_β–C_γ



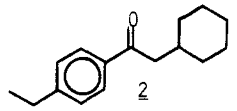
quence of the nonsystematic nature of most of the investigations. Frequently, a wide spectrum of reactants rather than several molecules of one family (each differing subtly from the others) has been surveyed. When systematic studies have been performed,[3,6,16,17] they have usually allowed mechanistically important conclusions to be reached.

Our recent studies indicate that the degree to which solvent order can control solute reactivity depends critically upon the length and shape similarities of a solvent and a solute and upon the specific nature of solvent phase order.[1,16,17a,18] To explore these relationships further, we have investigated the Norrish II (Scheme I) photoproduct ratios from four alkylphenones in the crystalline, smectic B-like, nematic, and isotropic phases of an enantiotropic solvent, *trans,trans*-4'-*n*-butyl[1,1'-bicyclohexyl]-4-carbonitrile (BCCN). The solutes—*n*-decanophenone (**1**), 2-cyclohexyl-1-(4-ethylphenyl)-1-ethanone (**2**), 4-cyclohexyl-1-phenyl-1-butanone (**3**), and 5-cyclohexyl-1-phenyl-1-pentanone (**4**)—were chosen because of their varying relationships to the size and shape of BCCN. Using the elimination/cyclization product ratios (E/C, where E is taken as the relative concentration of acetophenone or ethylacetophenone and C is the sum of the relative concentrations of cyclobutanol diastereomers; vide infra) as an experimental marker, we find that slight structural modifications of the alkylphenones and their triplet 1,4-biradical intermediates (BR) are sensed acutely by the solvent matrices (sometimes in unexpected ways).

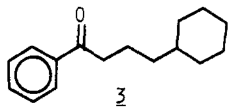
BCCN



1



2



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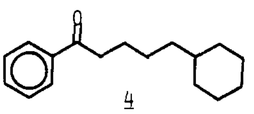

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An explanation of the results, based upon three primary considerations, is presented. They are the conformational lability of the BR in each phase, the arrangement of solute and solvent molecules in each phase, and the optimal space alotted a solute by the different solvent matrices.[19]

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Experimental Section

Ultraviolet–visible absorption spectra were recorded on a Perkin-Elmer 552 spectrophotometer. Infrared absorption spectra were obtained on either a Perkin-Elmer 457 or a Sargent-Welch 3100B spectrophotometer. A Varian EM 390 90-MHz spectrometer was employed for proton magnetic resonance spectra ($CDCl_3$; Me_4Si as internal standard).

Melting points and transition temperatures, measured on a Kofler hot-stage microscope fitted with polarizing lenses, are corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Column chromatography on silica was by the flash method.[20]

Decanophenone (1) (Aldrich, 95%) was recrystallized several times to give white crystals, mp 36.0–36.5 °C [lit. mp 35–36 °C,[21a] 36 °C[21b]] which showed one peak by gas chromatography. UV (hexane): λ_{max} 323 (ϵ 45), 275 nm (ϵ 550).

2-Cyclohexyl-1-(4-ethylphenyl)-1-ethanone (2). Cyclohexylacetyl chloride (1.6 g, bp 180 °C) in 3 mL of dry ethylbenzene was added slowly to a mixture of 1.6 g of dry $AlCl_3$ in 20 mL of ethylbenzene at 70 °C. The mixture was refluxed for 1 h, stirred overnight at room temperature under a dry atmosphere, and poured into 100 mL of water. Standard workup gave a yellow oil, bp 120–125 °C (0.15 torr), which contained a small amount of the ortho isomer in addition to the desired product. Purifications by column chromatography, preparative gas chromatography ($^1/_4$-in. × 5.2-ft 15% SE-30 on 60/80 Chromosorb W column), and recrystallization (hexane) resulted in crystals, mp 37.5–38.5 °C. IR: 1685 cm^{-1}. UV (hexane): λ_{max} 322 nm (ϵ 68). NMR: δ 0.6–2.0 (m, 14 H, with t at 1.27, J = 7 Hz, CH_3CH_2Ar), 2.70 (q, J = 7 Hz, 2 H, CH_3CH_2Ar), 2.80 (d, 2 H, J = 7 Hz, $COCH_2$), 7.60 (AA′BB′, 4 H, J = 8 Hz, $\Delta\nu$ = 56 Hz). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.68. Found: C, 83.54; H, 9.57.

4-Cyclohexyl-1-phenyl-1-butanone (3). 4-Cyclohexylbutanoyl chloride (from 2.5 g of 4-cyclohexylbutanoic acid and oxalyl chloride) was added as a benzene solution (20 mL) to a flask containing 2.0 g of anhydrous $AlCl_3$ in 30 mL of dry benzene under a dry atmosphere. The mixture was heated to 70 °C for 30 min and cooled to room temperature, and its contents were poured into 100 mL of water. Standard workup, purification by column chromatography, and fractional vacuum distillation gave a pale-yellow oil, bp 134–140 °C (0.4 torr), which yielded a white solid, mp 39–40 °C, after recrystallization from hexane. IR: 1690 cm^{-1}. UV (hexane): λ_{max} 324 (ϵ 46), 269 nm (ϵ 350). NMR: δ 0.5–1.9 (m, 15 H, alkyl), 2.95 (t, J = 7 Hz, 2 H, $COCH_2$), 7.3–8.0 (m, 5 H, aromatic). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.68. Found: C, 83.59; H, 9.43.

5-Cyclohexyl-1-phenyl-1-pentanone (4). 1-Bromo-4-cyclohexylbutane (a colorless oil, bp 85 °C (1.5 torr)) was prepared from 4-cyclohexyl-1-butanol and concentrated HBr in the presence of concentrated H_2SO_4. Under a N_2 atmosphere, 500 mg of magnesium twinings in 5 mL of dry ether was stirred while the crude 1-bromo-4-cyclohexylbutane, 2.2 g, in 20 mL of dry ether was added slowly. The mixture was refluxed for 15 min, 2.5 g of benzonitrile (Baker) was added, and the mixture was refluxed for another hour. After workup, purification by column chromatography, and three recrystallizations from hexane at −20 °C, white needles, mp 25–26 °C, were obtained. IR: 1680 cm^{-1}. UV (hexane): λ_{max} 324 (ϵ 48), 264 nm (ϵ 400). NMR: δ 0.5–1.9 (m, 17 H, alkyl), 2.92 (t, J = 7 Hz, 2 H, $COCH_2$), 7.2–8.1 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.45; H, 9.67.

trans,trans-4′-*n*-Butyl[1,1′-bicyclohexyl]-4-carbonitrile (BCCN), from Merck (Licristal ZLI-1538), was used in most experiments as received.[22] Its transition temperatures are k28s54n80i [lit.[23] k29s54n79i].

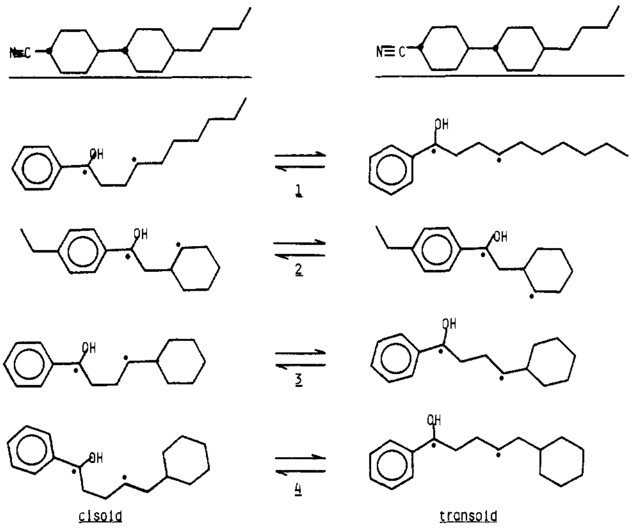
Irradiation and Analytical Procedures. Irradiations of thermostated samples in BCCN were performed in sealed Kimax capillary tubes under nitrogen by using a Hanovia 450-W medium-pressure Hg lamp whose output was filtered through water and Corning 0-54 and 7-54 filters (300 nm < λ < 400 nm). Each tube contained BCCN, 1.0–2.1% (by weight) of ketone, and a small amount of *n*-hexadecane (internal standard). Samples of ketones in either *tert*-butyl alcohol or benzene were deoxygenated by nitrogen bubbling for 20 min prior to irradiations.[24] Irradiations were conducted in capped Pyrex tubes, and GC analyses were performed at least in triplicate immediately thereafter. Conversions in all experiments, as determined from comparison with unirradiated samples were <30% and were usually <20%.

Table I. Transition Temperatures of BCCN Doped with **1–4**

ketone	concn, % w/w	transition temp, °C		
		k–s	s–n	n–i
none		28	54	79
1	2.1	27–28.5	44.5–51	75–76
2	2.1[a]	27.5–28.5	46–50.5	75.5–76.5
3	1.03[b]	25.5–26.5	50–53	79
	2.01[c]	25.5–26.5	49–52	79
4	1.67	28–28.5	46–52	75–76

[a] 0.13% *n*-hexadecane. [b] 0.17% *n*-hexadecane. [c] 0.25% *n*-hexadecane.

Scheme II. Representative Cisoid and Transoid 1,4-Biradicals of **1–4**. BCCN Is Included for Length and Width Comparisons



Analyses were performed on a Perkin-Elmer 3920 B flame-ionization, dual-column gas chromatograph. Samples containing **1** were analyzed with a $^1/_8$-in. × 8-ft 2% DC 550 on 80/100 Chromosorb W-DMCS column. A $^1/_8$-in. × 7-ft 10% OV-17 on 80/100 Chromosorb W-DMCS column was employed to analyze samples with **2** and **3**. With samples of **4**, a 0.53-mm × 10-m Alltech RSL 300 (poly(methylphenyl-siloxane)) open tubular column was used. Product peaks were quantified by integration on a Perkin-Elmer M2 calculating integrator and by cutting and weighing the peaks of a chart recording. Both methods gave the same results within the limits of experimental error. No secondary products, specifically the alcohols formed upon reduction of **1–4** (by independent treatment with lithium aluminum hydride in ether), were detected by GC. Retention times of acetophenone and 4-ethylacetophenone were ascertained by injection of authentic samples (Aldrich). Alkene elimination products were not analyzed.

Cyclobutanols were isolated from benzene solutions of the ketones, irradiated to ca. 100% conversion. They showed strong infrared absorptions near 3600 cm^{-1} ($CHCl_3$). NMR data for the cyclobutanols are presented below. From **1**: δ 0.6–2.8 (m, 19 H, alkyl and hydroxyl), 7.2–7.6 (m, 5 H, aromatic). From **2**: δ 0.9–2.9 (m, 17 H, including t, 3 H at 1.27, J = 7 Hz, CH_3CH_2–; m, 2 H at 2.70, J = 7 Hz, CH_3CH_2–), 7.1–7.5 (m, 5 H, aromatic). From **3**: δ 0.7–2.7 (m, 17 H, hydroxyl and alkyl protons), 7.1–7.6 (m, 5 H, aromatic). From **4**: 0.6–2.7 (m, 19 H, hydroxyl and alkyl protons), 7.1–7.5 (m, 5 H, aromatic).

Results and Discussion

Solubilization of 1–4 in BCCN. Generally, solutes whose size and shape are similar to those of the solvent disturb mesophase order least.[19] A measure of the ease of incorporation within a BCCN matrix is given by the solute-induced depression of phase transition temperatures. From the data in Table I, it is clear that **1–4** disturb the solvent order somewhat. Although the most flexible ketone, **1**, has the largest disturbing influence, the magnitude of the s–n depression is less than expected from shape compatability considerations. A possible explanation is that conformations like **1a** and **1b** are formed, allowing **1** to fit reasonably well into the crystalline and smectic matrices; even when

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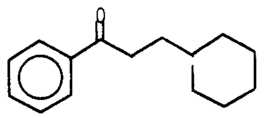
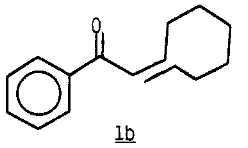
(22) A very small BCCN impurity had the same GC retention time as the cyclobutanols from **4** on several columns. It could not be removed by recrystallizing thrice from ethanol and water. k = crystal; s = smectic; n = nematic; i = isotropic.

(23) (a) Eidenschink, R.; Krause, J.; Pohl, L.; Eichler, J. In *Liquid Crystal Proceedings, International Conference*; Chandrasekhar, S., Ed.; Heyden: London, 1980; p 515. (b) Data supplied by E. Merck.

(24) No difference in the product ratios of nitrogen-saturated and air-saturated samples was observed. The ratios are not corrected for differing detector responses by the products.



1a



1b

fully extended, **1** is only ca. two bond lengths longer than BCCN. Scheme II presents some conformations of the ketone biradicals and compares their sizes and shapes to those of BCCN; the dimensions of the ketones and their biradicals are similar. At first glance, then, none of the ketones is grossly different in size and shape from BCCN.

General Aspects of the Photochemistry of 1–4. The photoreactions of **1–4** appear to occur almost exclusively via the Norrish II routes (Scheme I). No evidence for the formation of benzaldehyde (a Norrish I product) or 1-phenyl-1-nonadecanol (a reduction product of **1**) was obtained. During irradiations taken to high percent conversions of the solute ketones, no new product peaks could be discerned. If solvent adduct products were formed, they would have escaped detection. The structures of the cyclobutanols from **1–4** are based primarily upon their infrared spectra and the similarity of their NMR spectra to those of related compounds.[25-27]

E/C Product Ratios in Isotropic Media. To calibrate the effect of solvent order, a comparison must be made between solute reactivity in the anisotropic phases and a clearly recognizable isotropic phase. The isotropic phase of BCCN is most appropriate for our purposes and it will be used throughout. However, since it is formed only at elevated temperatures, solute reactions which are sensitive to heat and solvent anisotropy may behave differently in the meso and isotropic phases of BCCN for reasons which are unrelated to solvent order. Available data indicate that this is not the case: BR lifetimes are somewhat solvent dependent but show virtually no temperature dependence over the range investigated here.[28]

Table II contains the E/C ratios from **1–4** in benzene (a relatively nonpolar isotropic solvent) and *tert*-butyl alcohol (a relatively polar solvent) at room temperature and in isotropic BCCN at >80 °C. The isotropic BCCN data correspond more closely to that in *tert*-butyl alcohol than in benzene. This may reflect the increased tendency of a BR to yield elimination products at elevated temperatures[29] rather than the polarity of the local environment.[26,30] Data in the ordered and isotropic phases of BCCN are displayed graphically in Figures 1–4 and will be discussed later. The data for **1** in benzene and *tert*-butyl alcohol agree qualitatively with the results obtained previously for valerophenone and nonanophenone.[26]

Experimental Measures of Ordered Solvent Control over Ketone Reactivity. As mentioned, the primary experimental observable we have employed to monitor the influence of solvent order on solute reactivity is the E/C product ratios. Several other measures—ratios of cyclobutanol (cyclization product) diastereomers,[17] quantum yields,[17b] and triplet BR lifetimes[17]—are available in principle. Our choice was based upon experimental practicality and available instrumentation.

Table II. E/C Product Ratios from **1–4** in Isotropic Solvents

	E/C		
ketone	in benzene (25 °C)	in *tert*-butyl alcohol (25 °C)	in BCCN (80–90 °C)[a]
1	1.4 ± 0.3	2.6 ± 0.3	2.7
2	0.48 ± 0.05		0.8
3	1.4 ± 0.1	4.2 ± 0.2	3.8
4	1.6 ± 0.3		2.8

[a] Averages of several runs at several isotropic temperatures (see supplementary material for specific data).

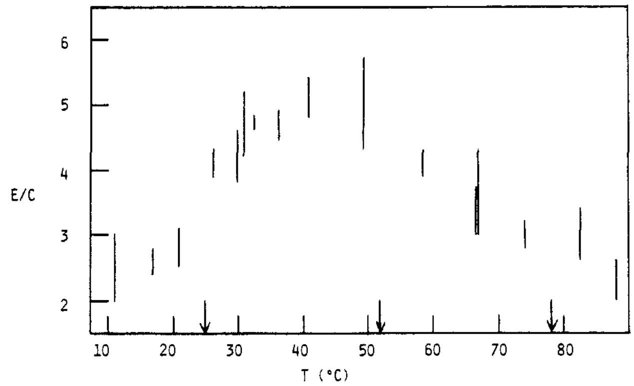


Figure 1. Elimination/cyclization ratios from **1** in BCCN vs. temperature. The arrows show solvent-phase transition temperatures. Vertical lines show one standard deviation of average values.

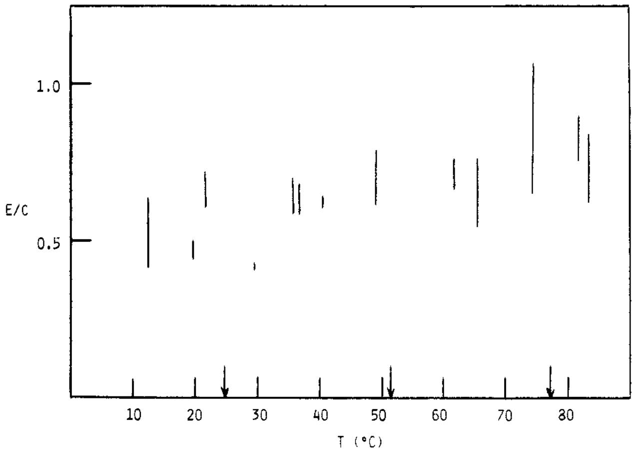


Figure 2. Elimination/cyclization ratios from **2** in BCCN vs. temperature. The arrows show solvent-phase transition temperatures. Vertical lines show one standard deviation of average values.

Only for **3** were the diastereomeric cyclobutanols analytically separable on our gas chromatographic columns. Other columns were tried but resulted in no separation. Even under conditions for which more than one diastereomer is known to be formed (e.g., **1** and **2** in isotropic solvents[25,27]), we were able to find only one peak. Thus, the absence of more than one cyclobutanol peak from **1**, **2**, and **4** is not an indicator of the number and distribution of diastereomers being formed.

The ratio of cyclobutanols from **3** was approximately independent of the BCCN phase. The cis and trans isomers were not identified, but the longer retention time peak was always the larger. The peak ratios varied from 3.2 in the crystalline phase to 3.8 in the smectic and nematic phases and 3.0 in the isotropic phase. In benzene and *tert*-butyl alcohol solutions at room temperature, the ratios were 3.7 and 1.3, respectively. Turro et al.[27] found 4.7 and 1.1 for octanophenone in the same solvents. The BCCN ratios seem reasonable for a slightly polar solvent which exerts little or no steric influence on cyclobutanol formation.

Due to a combination of solvent birefringence, light reflection, and low optical densities at the excitation wavelengths, we re-

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(25) (a) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 6959. (b) Ariel, S.; Omkaram, N.; Scheffer, J. R.; Trotter, J. Abstracts from the 68th Annual Conference of the Chemical Institute of Canada, Kingston, Ontario; June 1985; No. PC-A1-4, PC-C1-3. (c) Goswami, P. C.; de Mayo, P.; Ramnath, N.; Bernard, G.; Omkaram, N.; Scheffer, J. R.; Wong, Y.-F. *Can. J. Chem.* **1985**, *63*, 2719.

(26) Wagner, P. J.; Kelso, R. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, J. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

(27) Turro, N. J.; Lui, K.-C.; Chow, M.-F. *Photochem. Photobiol.* **1977**, *26*, 413.

(28) (a) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819. (b) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126. (c) Johnston, L. J.; Scaiano, J. C.; Sheppard, J. W.; Bays, J. P. *Chem. Phys. Lett.* **1986**, *124*, 493.

(29) (a) Guillet, J. E. *Pure Appl. Chem.* **1977**, *49*, 249. (b) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985; Chapter 10.

(30) (a) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495. (b) Wagner, P. J.; Kelso, R. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500. (c) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

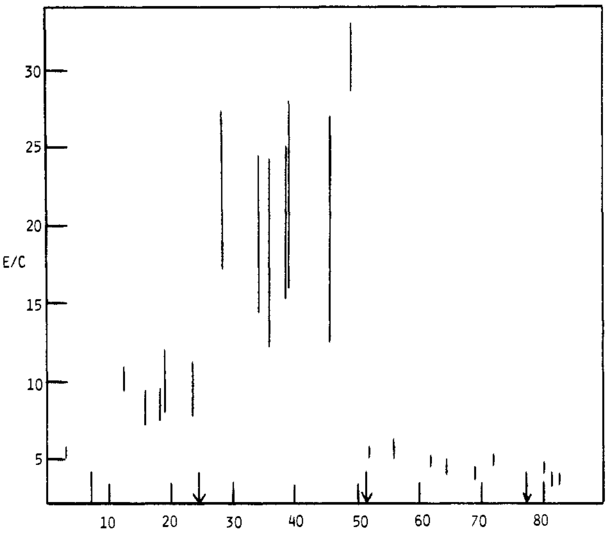


Figure 3. Elimination/cyclization ratios from **3** in BCCN vs. temperature. The arrows show solvent-phase transition temperatures. Vertical lines show one standard deviation of average values.

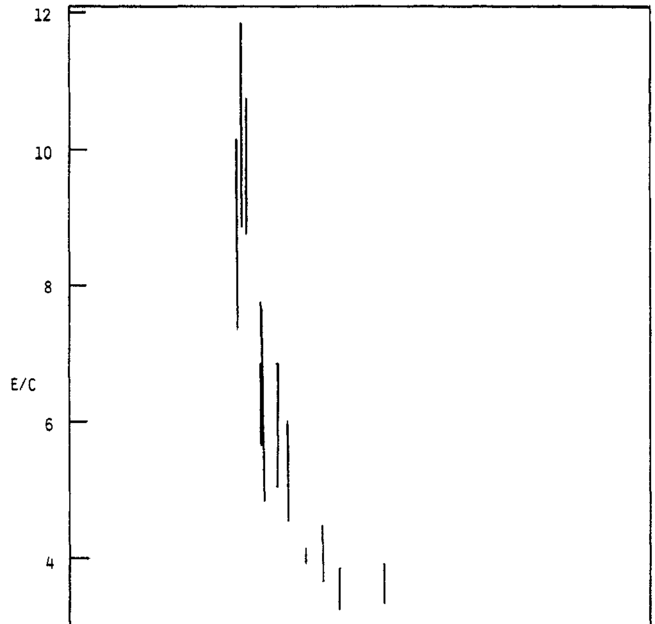
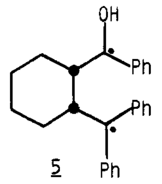


Figure 4. Elimination/cyclization ratios from **4** in BCCN vs. temperature. The arrows show solvent-phase transition temperatures. Vertical lines show one standard deviation of average values.

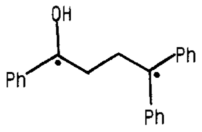
frained from attempting to measure quantum yields for loss of **1–4** in the ordered phases of BCCN. Quantum efficiencies would have been a useful indicator of the accessibility of abstractable γ-hydrogens[31] (Scheme I). Both Whitten et al.[32] and Guillet[29a] have shown that the Norrish II efficiency for alkylphenones can be attenuated significantly in very ordered and restrictive environments. Qualitatively, we find that the irradiation time required to attain a predetermined percent conversion is greatest in the solid phase and least in the isotropic phase of BCCN.

Correlation between Conformations and Lifetimes of BRs and Products in the Norrish II Reaction. The Norrish II reaction has been studied in detail,[26,30,33] and the salient features of its mechanism for alkylphenones are expressed in Scheme I. Intersystem crossing of the initially excited singlets occurs rapidly with unit efficiency. Abstraction of a γ-hydrogen by the carbonyl oxygen proceeds from a reactant conformation like that shown to yield an initial triplet 1,4-biradical, i-BR. Relaxation of this geometry in isotropic media can result in conformers like t-BR and c-BR from which elimination (E) and cyclization (C) products arise with the lowest expenditures of energy. Both t-BR and c-BR represent families of conformers whose average structures are shown in Scheme I. Additionally, i-BR can return to the starting ketone by retransferring the hydroxyl hydrogen.[30c,31] Since we wish to link the E/C ratio to the ratio of t-BR/c-BR, it is important that the evidence for and limitations of this relationship be explored.

Few examples which relate ketone conformation (or configuration) and Norrish II products are found in the literature. In what is perhaps the clearest study to date, Caldwell et al.[34a] showed that the conformationally locked cisoid biradical **5** yields predominantly cyclization products;[35] the conformationally labile (and presumably) transoid biradical **6** forms cleavage products. Turro and Wan have demonstrated that a very large preference for elimination products obtains from irradiations of octanophenone in zeolites when the host channel diameter precludes efficient formation of cisoid biradicals.[36] Furthermore, the E/C ratio from nonadecanophenone in smectic *n*-butyl stearate (which should favor transoid biradical conformations) is much larger than the ratio in the isotropic phase (which should accept cisoid biradical conformations much more readily).[17a] On these bases, we believe that the vast majority of elimination products eminate from transoid-BR conformations and cyclization products arise from cisoid conformations: E/C ≃ t-BR/c-BR.



5



6

In hydrocarbon-like solvents, the Norrish II triplet BR lifetimes from alkylphenones are 70–80 ns.[28b,33] The lifetime of **5** is somewhat shorter than for **6** in *n*-heptane but is longer in methanol. In spite of the vastly differing product distributions, the lifetime of the BR from nonadecanophenone is the same within experimental error in the smectic and isotropic phases of BS.[17a]

Several factors point to intersystem crossing as the rate-limiting step between the triplet BR and product formation. Singlet BRs similar to those expected from **1–4** have never been observed spectroscopically and their lifetime is estimated to be 10–500 ps.[28a] Even in low viscosity isotropic solvents, the activation energy for β–γ-bond rotation (which interconverts cisoid and transoid biradicals) is >4–5 kcal/mol in simple alkylphenones.[28b] With $E_a = 4$ kcal/mol[37] and $\log A = 11.5$,[37a] the rate constant for bond rotation at room temperature is calculated to be 4×10^8 s^{-1}, much

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(31) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

(32) Winkle, J. R.; Worsham, P. R.; Schanze, K. S.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 3951.

(33) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, Chapter 5.

(34) (a) Caldwell, R. A.; Dhawan, S. N.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 6454. (b) The lifetime of **5** is significantly longer than that of **6** in methanol.

(35) Very strained cyclopropyl ketones which must yield cisoid 1,4-biradicals have been shown by Scaiano[28a,c] to cleave. We do not feel that these are a representative example for ketones like **1–4**.

(36) Turro, N. J.; Wan, P. *Tetrahedron Lett.* **1984**, *25*, 3655.

(37) (a) Golden, D. M.; Furuyama, S.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 57. (b) Pitzer, K. S. *Disc. Faraday Soc.* **1951**, *10*, 66. (c) Lide, D. R., Jr. *J. Chem. Phys.* **1958**, *29*, 1426. (d) Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1958**, *29*, 914. The reported values in these references for potential barriers to internal C–C rotation of simple *n*-alkanes vary from 2.9 to 4.3 kcal/mol.

slower than the expected rate of decay of singlet biradicals[38] (but not necessarily of triplet biradicals).

A viscosity of 10^3 P is typical for smectic phases,[39] and crystalline phases are even more "viscous". Thus, an E_a of 8 kcal/mol (or more) for cisoid-BR $\rightleftarrows$ transoid-BR interconversion is not unreasonable in the smectic and crystalline phases of BCCN. Leigh has measured E_a = 16.7 kcal/mol for intramolecular triplet quenching of 7 in smectic BCCN.[40] Assuming the maximum frequency of rotation to be 10^{11}–10^{12} in these phases (i.e., when the solvent entropy of activation is not included), the rate of interconversion of biradicals becomes slower than their rate of intersystem crossing. In effect, equilibrium among the BR conformers will not be established prior to their intersystem crossing, and conformers similar to i-BR (e.g., c-BR) will have a larger reactive population than those more different from it (e.g., t-BR). This case appears to obtain when **1**, **3**, and **4** are the reactant ketones (vide infra) and must be considered as a kinetic factor additional to the thermodynamic ratio of t-BR/c-BR in determining the E/C product ratios. It may also explain why the ketones yield products less efficiently in the solid than in isotropic solutions: the probability of i-BR returning to starting ketone rather than proceeding to c-BR and t-BR is greatest in the solid; product formation may occur from BR conformations which do not minimize the activation energies.

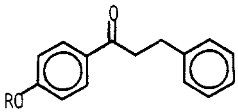
Order of BCCN Phases. X-ray diffraction studies on the meso and crystalline phases of the *n*-propyl, *n*-pentyl, and *n*-heptyl analogues of BCCN (PRCN, PECN, and HCCN, respectively) have been reported.[41] Although they pack differently in their crystalline phases, all exhibit cyclohexyl rings in chair conformations, fully extended chains, and head-to-tail orientations between neighboring molecules. PRCN[42] and PECN form bilayered smectic B phases with interdigitation of alkyl tails and cyano end groups. The characteristic ordering of a smectic B phase is that the molecules are hexagonally packed in layers and with their long molecular axes parallel to one another and normal to the layer planes.[43]

In the nematic phases of PECN and HCCN, the molecules appear to prefer slightly pairwise interactions (presumably dipole–dipole induced) in which they overlap by ca. 50% of their total length.[41b] This special order is additional to the typical nematic properties in which the long axes of the constituent molecules are, on average, parallel to one another.[43] In both nematic and smectic phases, solvent molecules rotate rather freely about their long axis.[43c] The order of the nematic phase is less than that of the smectic.

There is further evidence that BCCN exhibits a B-like smectic phase. Its microscopic texture under crossed polarizers is that of a B phase,[44] and it is miscible[45] (according to optical microscopy) with *n*-butyl stearate, a known smectic B.[46] However, the careful miscibility and calorimetry results of Leigh[47a] with BCCN and PRCN mixtures offer conclusive evidence that the smectic phase of BCCN differs slightly from that of PRCN. Thus, we believe that BCCN forms a B-like smectic phase, a partially associated nematic phase, and a crystalline phase with fully extended molecules which pack in anti-parallel pairs. The most recent X-ray studies on BCCN[47b] confirm the B-like packing of smectic BCCN: the molecules are slightly interdigitated and are hexagonally packed within a bilayer.

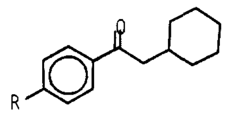
Phase-Dependent Solute Reactivity. Others and we have observed that many solute reactions are influenced by some forms of solvent anisotropy but not others.[1–17] In general, the effects are more dramatic with smectic mesophases than with nematic or cholesteric ones. However, important exceptions which demonstrate the complexity of ordered solvent–solute interactions have been reported.[12,13]

That small solute shape changes can have large dynamic consequences has been shown by Leigh[40a] for the conformationally dependent triplet lifetimes of 7.[40b] The difference between the activation energy for intramolecular triplet quenching of **7a** in the smectic and nematic phases of BCCN is 10 kcal/mol. The triplets of the slightly longer **7b** exhibit activation energies which are phase invariant.



7

a: R = CH_3-
b: R = *n*-C_5H_{11}-



8

R = CH_3-
R = CH_3O-
R = Cl-

Topochemical control of reactivity should be most demanding in the least mobile phase, the solid. Reactant conformations are best defined by a crystalline matrix, and deviations are very limited. Thus, many examples of solid-state catalysis or inhibition, including Norrish II processes,[48] have been reported.[49] Very few examples, however, have compared the influence of solid and mesophase matrices of one solvent upon a solute reaction. Recently, Scheffer, Trotter, et al.[25] examined the neat solid and isotropic (acetonitrile) solution behavior of some aromatic ketones (**8**) undergoing the Norrish II reaction. The E/C and *cis*/*trans*-cyclobutanol ratios vary little with phase *or* phenyl substituent.

In marked contrast, Turro's group and we[17] have found that the Norrish II E/C ratio from nonadecanophenone is greatest in the solid phase of *n*-butyl stearate (a solvent whose extended length is very close to that of the solute), lower but nearly constant throughout the smectic B phase, and lowest in the isotropic phase. Decanophenone (**1**), which is much shorter than *n*-butyl stearate, exhibits product ratios which do not change between the isotropic and smectic phases. We have now demonstrated that sensitive relationships exist between Norrish II product ratios from symmetrical di-*n*-alkyl ketones, their extended molecular lengths, and the phase of solvent *n*-butyl stearate.[18] Thus, even within the confines of one parameter of one photochemical reaction, the crystalline phase can exert little or substantial control over product selectivity.

E/C Ratios from 1–4 in BCCN. The data from irradiations of **1–4** in BCCN are displayed graphically in Figures 1–4 and are presented as tables in the supplementary material. At first glance, it is surprising that the E/C ratios from **1**, **3**, and **4** are lower in the (more ordered) crystalline phase than in the smectic phase of BCCN. However, as mentioned previously, the entropically more demanding transition state for cyclization is more favored

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(38) Doubleday, C.; McIver, J.; Page, M. *J. Am. Chem. Soc.* **1986**, *107*, 7904.

(39) See for instance: Jochan, J. M.; In *Liquid Crystals: The Fourth State of Matter*; Saeva, F. D.; Ed.; Marcel Dekker: New York, 1979; Chapter 7.

(40) (a) Leigh, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6114. (b) Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 628.

(41) (a) Haase, W.; Paulus, H. *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 111. (b) Brownsey, G. A.; Leadbetter, A. J. *J. Phys. (Les Ulis, Fr.)* **1981**, *42*, L-135.

(42) (a) Three smectic phases are formed by PRCN.[42b] The highest temperature one is the B type.[41b] (b) Pohl, L.; Eidenschink, R.; Krause, J.; Weber, G. *Phys. Lett.* **1978**, *65A*, 169.

(43) (a) Gray, G. W. *Molecular Structure and Properties of Liquid Crystals*; Academic: New York, 1962. (b) Saeva, F. D. *Liquid Crystals. The Fourth State of Matter*; Marcel-Dekker: New York, 1979. (c) de Vries, A. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, Cl-1.

(44) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.

(45) (a) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Weinheim, 1980; pp 380 ff. (b) Arnold, H.; Sackmann, H. *Z. Phys. Chem. (Leipzig)* **1960**, *213*, 137, 145.

(46) (a) Krishnamurty, K. S.; Krishnamurti, D. *Mol. Cryst. Liq. Cryst.* **1970**, *6*, 407. (b) Dryden, J. S. *J. Chem. Phys.* **1957**, *26*, 604. (c) Jeffrey, K. R.; Wong, T. C.; Tulloch, A. P. *Mol. Phys.* **1984**, *52*, 289, 307. (d) Krishnamurti, D.; Krishnamurthy, K. S.; Shashidar, R. *Mol. Cryst. Liq. Cryst.* **1969**, *8*, 339.

(47) (a) Leigh, W. J., private communication. (b) Rahimzadeh, E.; Tsang, T.; Yin, L. *Mol. Cryst. Liq. Cryst. Bull.* **1986**, *1*, 165.

(48) Schmidt, G. M. J., et al. *Solid State Photochemistry*; Ginsburg, D., Ed.; Verlag Chemie: Weinheim, 1976.

(49) Aoyama, H.; Hasegawa, T.; Omote, Y. *J. Am. Chem. Soc.* **1979**, *101*, 5343.

at lower temperatures. Additionally, the conformations available to the 1,4-biradicals may be dependent upon the initial ketone conformations.

From Scheme I, only conformers which allow γ-hydrogen abstraction can lead to product.[26,30,33] These initial conformations yield i-BR which are near the geometry of c-BR required for cyclization. Relatively benign shape changes can interconvert the two. The larger shape changes which attend cisoid → transoid or initial → transoid-BR transformations are hindered by the rigid crystalline matrix of BCCN and, therefore, should occur more slowly (competitively with intersystem crossing).[28a] A large volume is swept out by the cyclohexyl rings of **3**, as the conformational interconversions to t-BR occur. Crankshaft motions available to **1** and **4** (vide infra) allow conformational interconversions among its BRs to occur with smaller, but not inconsequential, shape changes.

If crystalline solvent control over t-BR formation is severe, some of the elimination product may arise from conformers in which the singly occupied p orbitals and the β–γ-bond are not completely parallel. The increased activation energy for these processes would attenuate elimination and lead to lower E/C ratios than observed in the smectic phase. In fact, **1**, being the most fluxional of the four reactants, should experience the least hindered cisoid-BR $\rightleftarrows$ transoid-BR equilibration in crystalline BCCN. However, if **1** packs somewhat like **1a** and **1b** in order to minimize its disruptive influence on the surrounding solid matrix, it too would experience difficulties in reaching a BR conformation.

Alternatively, the similarity between the solid and isotropic E/C ratios may be taken as evidence for a complete *lack* of solvent control by the former. Our previous experiences with Norrish II reactions in a solid phase[17a] and the very large influence that the less ordered smectic phase of BCCN exerts on product selectivity make this possibility unlikely. The same factors which would force a solute ketone into a crystalline defect site should make the cybotactic region in the smectic phase completely disordered, also. We believe that the crystalline sites at which solutes reside are defective since a ketone cannot occupy the exact space of a BCCN which it has displaced. Nevertheless, the crystalline structure near a solute should approximate that of the bulk.

Ketone **2** is uniquely unaffected by BCCN phase changes. Its BR is also the only one for which cisoid $\rightleftarrows$ transoid interconversion can be accomplished with minimal shape changes and for which the two conformers can be nearly identical in shape.[50] Since the van der Waals thickness of a cyclohexyl or phenyl ring is very near its width,[41,51] interconversion of these two BRs should be relatively facile even in the crystalline phase of BCCN: at all points along the potential energy surface leading from c-BR to t-BR, the molecular shape can remain almost constant in length and width. The lack of solvent phase influence on the product ratio from **1** is reminiscent of the Norrish II results obtained with neat crystalline and isotropic solutions of **8**.[25] It was noted that the t-BR from **8** can cleave only with great difficulty. The constraints imposed by the molecular framework make the p orbitals of the radical centers point at an angle which is more conductive to cyclization. Thus, the Norrish II reactions of **1** are controlled more by internal energetic constraints than by solvent anisotropy.

The precipitous increase in the E/C ratios of **1**, **3**, and **4**[52] between the crystalline and smectic phases of BCCN is consistent with the greater lability of i-BR in the less viscous medium. Since the smectic phase is very ordered but not as immobile as the crystalline phase, more interconversion of c-BR and t-BR should be possible during their triplet lifetimes. Individual differences between the comportment of the ketones must involve how well they fit within the smectic matrix.

Fully extended **3** and **4** are, respectively, ca. two and one bond lengths shorter than BCCN. However, the optimal available space in BCCN for **3** and **4** (due to their lack of an alkyl tail) is less than or equal to one-half of an interdigitated smectic bilayer. The increased elimination in the smectic phase is a clear indication that this solvent matrix prefers the extended, transoid conformations of the BRs from **3** and **4** to a greater extent than do the isotropic and nematic phases.

Some noteworthy differences between the Norrish II selectivities of **3** and **4** are easily discerned from Figures 3 and 4. Whereas the E/C ratio from **3** is about constant throughout the smectic region, the ratio from **4** decreases as the nematic phase is approached. In fact, both **1** and **4** exhibit this behavior, but it is more pronounced in the less flexible **4**. The BRs from both ketones have available "crankshaft" motions about the γ-radical centers which permit cisoid $\rightleftarrows$ transoid equilibration without large translocations of ancillary molecular parts. Interconversion of the BR from **3** requires an unavoidable, large shape change which will be inhibited by smectic order: a large volume is swept out by the rotating cyclohexyl ring and the molecular length changes. We assume that t-BR of **3**, once formed in smectic BCCN, will return to the *cisoid* conformer with difficulty. By contrast, the lower barrier for transoid $\rightleftarrows$ cisoid interconversion of the BRs from **1** and **4** (which can occur with inversion-like motions of ancillary groups) should allow them to interconvert much more rapidly. As a result, the E/C ratios will correspond more closely to the thermodynamic preference of the solvent matrix to accept a cisoid-BR or transoid-BR.

The comportment of **1** in smectic BCCN merits further attention. The long alkyl chain of **1** is capable of adapting its molecular shape to a greater extent than the other ketones. The changes in the E/C ratio are consistent with conformers like **1a** and **1b** being less preferred (and with greater conformational mobility of their solute chain) in the smectic phase than in the crystalline phase. The slight increase in the E/C ratio from **1** within the smectic phase as temperature is increased should be compared with the comportment of **4**, especially.

Solvent molecules in a nematic phase exhibit little or no longitudinal order.[24b,50] Thus, to be well-incorporated into the nematic matrix, a solute must be of similar diameter to BCCN but not necessarily of similar length. This latitude means that many conformers of the biradicals from **1**, spanning a large difference in total molecular length, will be comparably accepted by the solvent matrix. We believe that the gradual decrease in E/C in the nematic and isotropic phases arises as the BR from **1** "relax" to their thermodynamically more-favored conformations. Presumably, this relaxation is complete in the isotropic phase of BCCN.

Since the nematic is also "looser" in its order than the crystalline or smectic phase,[53] a wider variety of biradical conformations from **3** and **4** are accomodated. The shape differences between cisoid-BRs and transoid-BRs which are felt very acutely by the smectic phase of BCCN, are sensed to a much smaller extent by the nematic phase. In fact, the looseness of the nematic phase should allow the BRs even from **3** to interconvert rapidly. Consistent with this hypothesis, little or no break in the E/C ratios

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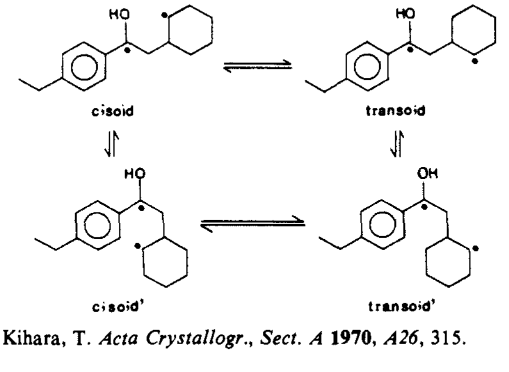
[50] (a) A different set of rotations about C_α–C_β and C_β–C_γ of **2** can convert cisoid-BRs and transoid-BRs. However, they require shape changes which should be sensed and resisted by the crystalline and mesophase matrices of BCCN. These motions are somewhat similar to those experienced by spectroscopic triplets of **7** which lead to intramolecular quenching.[40]



[51] Kihara, T. *Acta Crystallogr., Sect. A* **1970**, *A26*, 315.

[52] The large errors associated with the E/C ratios from **3** in smectic BCCN are a consequence of our inability to measure precisely the very small quantities of cyclization products formed. Elimination was the overwhelmingly favored Norrish II mode of reaction.

[53] Reference 45a, Chapter 3 and pp 231 ff.

from **3** or **4** occurs between the nematic and isotropic phases.

Conclusions. The constraints imposed by the crystalline and mesophase matrices of BCCN on 1,4-biradicals from ketones **1–4** are very different. Whereas both the crystalline and smectic phases restrict solute breadth and length, the consequences of the specific interactions are vastly different due to the differing solute shapes and mobilities in the two phases. In the smectic and nematic mesophases, the difference between strong and weak (or no) solvent control over solute length and breadth has a marked influence on the fate of the initially formed BRs as they equilibrate with their environment before yielding either elimination or cyclization products.

The governing factors—mobility of solutes during their reactive lifetimes and solvent control over their shapes—should be operative in many other reactive solutes. Indeed, we have found that some lyotropic phases exhibit control over solute reactivity which is remarkably sensitive to solute–solvent shape matches.[18] Although the specific manner in which all of the ordered solvent–solute interactions express themselves is not understood, it is clear that they influence both structural and dynamic aspects of the reactions.

Our results indicate that liquid-crystalline order may play an even more important role in biological reactivity (and structure) than that which has been recognized.[54]

In future work we intend to investigate how modifications of other structural features of aromatic ketones influence the ways in which BCCN and related ordered solvents control solute reactivity.

Acknowledgment. We thank Dr. Werner Becker of E. Merck, Darmstadt, FRG, for a generous sample of BCCN and Dr. F. V. Allan of EM Chemicals for valuable discussions concerning BCCN. The National Science Foundation is acknowledged for its support of this work (Grants CHE 83-01776 and CHE 85-17632). R.G.Z. thanks NATO for a postdoctoral travel grant. We thank Prof. Willie Leigh, especially, for sharing his data on the structure of the phases of BCCN prior to publication.

Supplementary Material Available: Five tables of data for E/C and cyclobutanol ratios from irradiations of **1–4** in BCCN (3 pages). Ordering information is given on any current masthead page.

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Complexation of Crown Ethers with Neutral Molecules. 2. Comparison of Free Macrocycles and Their Complexes with Malononitrile in Solution

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Abstract: Thermodynamic parameters for the complexation of a neutral guest (malononitrile) with crown ethers having ring sizes of 15 to 33 ring atoms and various functionalities were obtained. The results give useful information about the conformations of the free crown ethers and their interactions with solvent molecules. 18-Membered macrocycles form the most stable complexes with malononitrile. Crown ethers in which the uncomplexed form strong intraannular interactions are present form weaker complexes while macrocycles in which additional binding sites (e.g., C═O) are available for complexation form more stable complexes with malononitrile than expected. A compensating effect of $T\Delta S^\circ$ and ΔH° of complexation was found for all complexes. The crystal structure of 2,6-pyrido-18-crown-6·$CH_2(CN)_2$ (1:2) was determined; it shows a hydrogen bond to the pyridyl nitrogen atom.

Although most of the work on crown ethers has been focussed on their complexation with metal ions,[1] more recently also the complexation of neutral polar guest molecules has been studied.[2] The complexation of CH-acidic neutral molecules was first reported by Cram et al.,[3] who suggested the complexation of 18-crown-6 and acetonitrile as a method for the purification of 18-crown-6. Up to now, several complexes of crown ethers and CH-acidic polar neutral molecules[4–15] (e.g., $CH_2(CN)_2$,[4–8] CH_3CN,[3,7,9–12] and CH_3NO_2,[4,7,10–12]) have been reported. X-ray data[5–8,13,15] show that the nature of the host–guest binding in the solid state seems to be dominated by hydrogen bonds between the acidic hydrogen atoms of the guest and the crown ether oxygen atoms. Hydrogen bonding in solution was confirmed by ^1H NMR[4,7–9] and IR[8,9] measurements.

Only in a few cases, the thermodynamic stabilities of complexes of crown ethers and neutral molecules have been determined. We have reported thermodynamic constants for complexes of 18-crown-6 with CH_3NO_2, CH_3CN, and $CH_2(CN)_2$ and of 1,3-xylyl-18-crown-5 with CH_3NO_2 in C_6D_6.[7] Besides, association constants of the complexes of 18-crown-6 with CH_3CN (in CCl_4,[9]

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