Tetrahedron Vol. 43, No. 7, pp. 1371 to 1391, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

LIQUID-CRYSTALLINE SOLVENTS AS MECHANISTIC PROBES. 23. NORRISH II REACTIONS OF 2- AND SYM-ALKANONES IN THE ISOTROPIC, SMECTIC B, AND CRYSTALLINE PHASES OF n-BUTYL STEARATE.[1]

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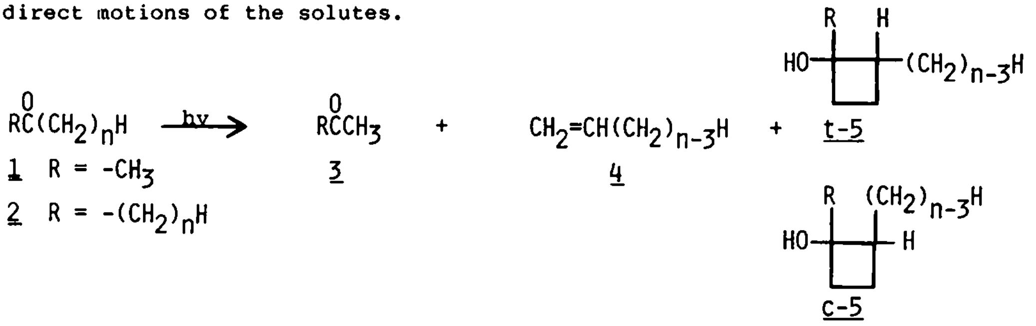
(*Received in UK* 16 *February* 1987)

n-Alkanones with the carbonyl group at the 2 or central positions (1 and 2, respectively) have been irradiated in the isotropic, smectic B, and two solid phases of n-butyl stearate (BS). The lengths of the ketones were varied from 11 to 31 carbons. The ratios of elimination/cyclization products and diastereomeric cyclobutanol products were measured for each as a function of temperature and BS phase. The effect of 1 and 2 on the phase transition temperatures of BS has been correlated with changes in the product ratios. The experiments demonstrate that a very sensitive cooperative relationship exists between the ease with which 1 and 2 fit into the ordered phases of BS and the degree to which the solvent matrices influence ketone photochemistry. The influence of solvent order on the product ratios is distinctly different for 1 and 2, and for the two product ratios from one ketone.

INTRODUCTION

We describe results from a comprehensive study of the influence exerted by the isotropic, smectic B, and solid phases of n-butyl stearate (BS) on the Norrish II photoreactions of a series of 2- and sym-alkanones (1 and 2; eq. 1). The Norrish II reaction has several favorable characteristics for following solute-solvent interactions: The photoprocesses linking reactants and products are well understood; the reactions are relatively free of side products; the ratios of elimination to cyclization products (3 or 4)/5 (E/C) and of diasteromeric cyclobutanols t-5/c-5 (t/c) can be measured simultaneously. Each product ratio provides different information concerning how solvent molecules direct motions of the solutes.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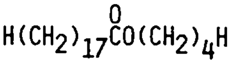

$\mathrm{H(CH_2)_{17}\overset{O}{C}O(CH_2)_4H}$

BS

Others have recognized the utility of Norrish II processes to monitor the influence of ordered solvents on solute reactions. For instance, Scheffer, Trotter, et al.[2a,b] have irradiated crystals of many α-cycloalkylacetophenones and then attempted to correlate product distributions with lattice structures. The photochemistry of similar ketones has been examined in clathrate complexes.[2c] Scaiano, de Mayo, et al.[3] have shown that 5-nonanone encapsulated in urea complexes yields only the trans cyclobutanol although comparable amounts of the cis and trans are formed upon irradiations in methanolic solutions. Whitten et al.[4] have demonstrated that the quantum efficiency for the Norrish II reaction of the surfactant keto acid, 16-oxo-16-(p-tolyl)hexadecanoic acid, can vary from near unity in hydroxylic solvents to near zero in monolayer assemblies. Turro et al.[5] have explored the influence of micelles on the efficiency of formation and distributions of products from irradiations of some n-alkylphenones.

Our recent studies have shown that the degree to which solvent order can affect solute reactivity depends critically upon the length and shape similarities of the solute and solvent molecules and upon the specific nature of the solvent phase.[6-11] Small, seemingly innocuous modifications of solute shape (far from the locus of reactivity) can result in drastically different product selectivities or rates of conversion, even when the same reactants behave similarly in isotropic solvents. A common feature of our unimolecular examples is that they involve large shape changes as a solute procedes to its transition state. Such changes, conceptually, should be most easily sensed by ordered solvents. Fortunately, formation of Norrish II products involves distinctly different shape changes along the several reaction coordinates.

It has become increasingly obvious that meaningful interpretations of data are facilitated when the ordering of the undoped solvent molecules is well understood and analogous reactions of a series of solutes (each differing slightly from the others) are studied as a group. Using this approach, we have investigated the Norrish II reactions of α-diketones in several liquid crystals,[12] of *n*-alkylphenones in the isotropic, smectic B, and solid phases of *BS*,[13] and of alkylphenones in the isotropic, nematic, smectic and solid phases of *trans,trans*'-4-*n*-butylbicyclohexyl-4'-carbonitrile (*BCCN*).[14] Leigh has performed pertinent experiments on the triplet lifetimes of β-phenylpropiophenones in *BCCN*.[15]

Previously, Turro and we[13] had shown that *n*-alkylphenones in *BS* undergo phase dependent Norrish II photoprocesses when the lengths of the solute and *BS* are approximately the same. Less extensive results with two *n*-alkanones demonstrated that *BS* ordered phases can direct their product ratios, also. It appeared to us that the influence of *BS* on the photoreactions of 2- and *sym*-alkanones merited much closer scrutiny for several reasons: (1) the reactive chromophore in **1** or **2** is much smaller and, therefore, less disruptive to local solvent order than the benzyl group of *n*-alkylphenones; (2) the carbonyl group can easily be placed so that it will be near the more ordered interior of a smectic or solid layer (as in **2**) or near the more disordered layer boundaries (as in **1**). The advantages of employing alkanones as reactive solutes (including their availability and the ease with which their photoproducts can be characterized) seemed to outweigh their major mechanistic disadvantage: aromatic ketones undergo Norrish II reactions almost exclusively from their $^3(n,\pi^*)$ states; alkanones undergo reaction from both their $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states.

RESULTS

Solubility and Transition Temperature Studies. In an attempt to discern empirically the disturbing influence of **1** and **2** on *BS*, *macroscopic* phase transition temperatures were measured as a function of solute concentration. Solid→smectic phase transitions were very difficult to observe precisely by optical microscopy and their temperatures are not reported. None of the smectic phase solutions containing 1.4% (w/w) of a ketone shorter than 31 carbons gave evidence of microcrystal formation over periods much longer than the irradiation times. In the isotropic phase (30°C), all of the solutions containing **1** appeared to be thermodynamically stable. This included 2-heneicosanone whose photochemistry could not be followed due to analytical problems (*vide infra*). Similarly, *BS* solutions of 1.4% (w/w) of **2** with <25 carbons were stable indefinitely at 30°C.

Symmetrical ketones longer than 13-pentacosanone crystallized from isotropic *BS* over periods which correlated with their length. The approximate periods for which solutions remained visibly clear of crystals were 1 h (14-heptacosanone), 40 min (15-nonacosanone), and 1 min (16-hentriacontanone). Complete solution could not be obtained with 1.4% of 18-pentatriacontanone in *BS* at 30°C; the ketone dissolved completely above 55°C. The microscopic texture of 16-hentriacontanone doped *BS* below 25°C changed from smectic to microcrystals dispersed in a smectic matrix after *ca*. 1 min. (as determined by optical microscopy). All transition temperatures were recorded during heating progressions and are based upon pattern changes viewed microscopically with plane polarized light. For *BS* samples with > 25% by weight ketone, "smectic"-biphasic (s→b) transition temperatures were detected from pattern fluctuations as pressure was applied manually to the sample cover plates.

BS phase transitions are very dependent upon the lengths of the dopants, *1* and *2*. At the ketone concentrations used for the irradiation studies, the depression in the *BS* smectic to isotropic phase transitions (s→i) is <1° regardless of the ketone length or carbonyl position.

Thus, high weight percents of ketone (25-50%) were utilized to obtain observable phase depressions which could be associated with the disturbing influences of the solutes on solvent order. The optical pattern of the highly doped mesomorphic materials appeared smectic; the transitions measured are for smectic mesophase to isotropic liquid (most by *BS*) and solid (ketone). At concentrations where the biphasic region exists, (> 10% by weight) the s→b transition temperatures seem to be for ketone saturated *BS* with excess (solid) ketone not influencing the mesophase: the transition temperatures are nearly constant for any one ketone at both 25% and 50% concentrations; the b→i clearing points approach the ketone melting points, as expected.

Very important differences between the effect of *1* and *2* on *BS* do exist. Between 1% and 10% concentrations, where the biphasic region was undetected, all of the *1* cause a small, nearly constant depression of the s→i phase transition temperature. In the same concentration range, the effect of *2* is somewhat larger and depends upon the ketone chain length. These data are consistent with *2* being more disruptive than *1* to *BS* phase order. A carbonyl in the center of a solute is sensed as an alien object by nearby solvent molecules more than one near the end of a solute.

Further differences can be seen in Figure 1. The smallest disturbance to the s→b transition temperature occurs, as expected, with 12-tricosanone, the *2* whose length most closely matches *BS*: 22 carbons and one oxygen are linked in the *BS* chain *1*. The *1* series profile shows that 2-heptadecanone affects the s→b phase transition temperatures least and 2-heneicosanone, the 2-alkanone (of those measured) closest in length to BS, causes a large depression! Omitted from Figure 1 is the s→b transition temperature of 2-heptacosanone. It appeared at 0-1°C. A preference for the carboxyl of BS and carbonyl of 1 (regardless of its length) to remain near one another in the ordered phases may be responsible for these observations (*vide infra*).

Photolyses of 1 and 2 in BS and in Isotropic Liquids. Irradiation of 1 and 2 (<1.4% w/w) in BS produces truncated ketones (3), alkenes (4), and cyclobutanols (c-5 and t-5). Conspicuously absent from all of the reaction mixtures were alkanes from α-cleavage (Norrish I) processes.[16] A small yield of these products could have escaped our detection and some α-cleavage followed by efficient radical-radical recombination may have occurred. The diastereomeric ratios of cyclobutanols (t/c) were constant at all ketone conversions. The elimination/cyclization (E/C) product ratios (4/5 for 1; 3/5 for 2) remained the same within the limits of our experimental error up to 65% and 30% conversions of 1 and 2,

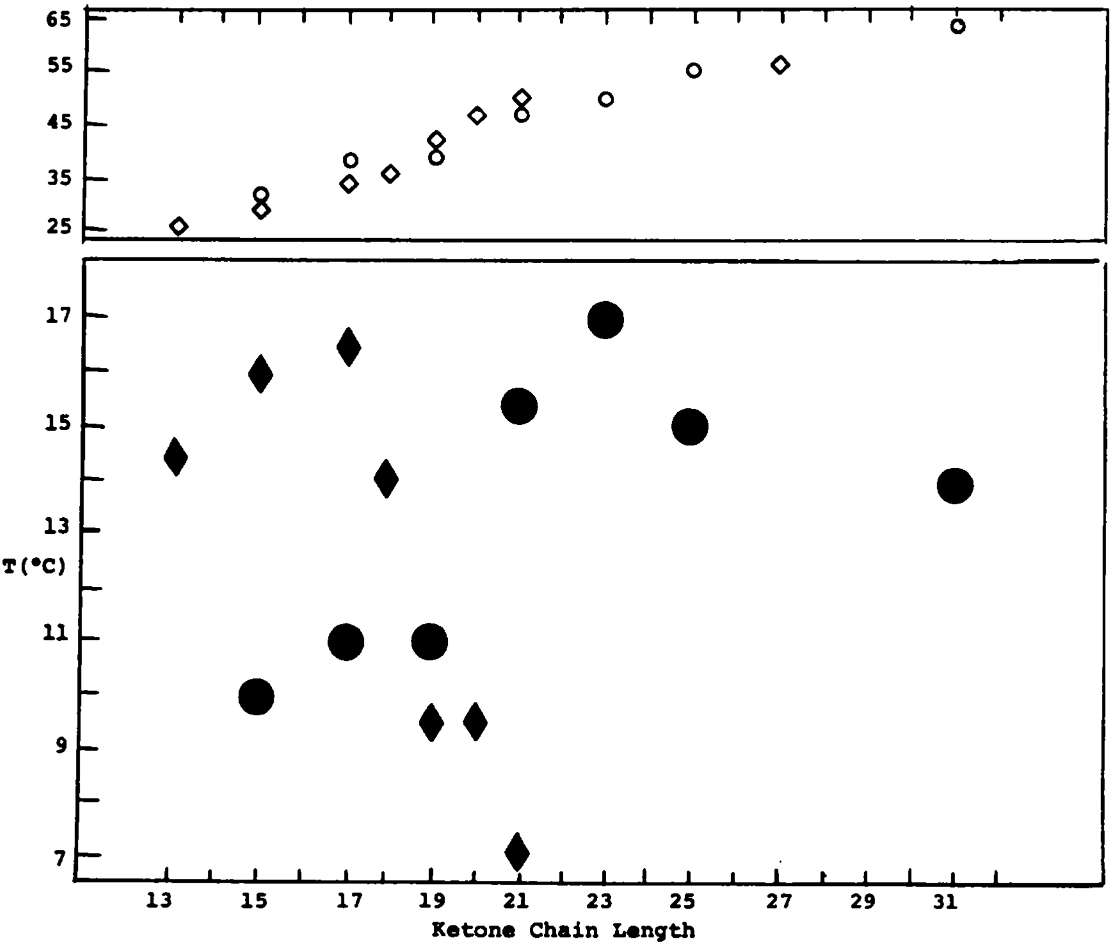


Figure 1. Smectic→ biphasic (filled symbols) and clearing temperatures (unfilled symbols) for 50% by weight 1 (diamonds) or 2 (circles) in BS

respectively. All of the E/C results are taken from experiments where reaction was less than these percentages.

In *t*-butyl alcohol or hexane, the product ratios varied little with ketone chain length. Previous studies with similar ketones have shown that the product ratios do not vary appreciably over the temperature range of our experiments in these and other isotropic solvents.[13,14]

Table 1. Norrish II product ratios from **1** in *BS*.

1 Carbon Chain Length	Temperature (°C)	E/C	t/c
11	RT[a,b]	2.3±0.3	2.0±0.2
	30	2.9±0.3	1.3±0.1
	20	3.1±0.3	1.2±0.1
	10	2.6±0.3	1.2±0.1
	0	3.6±0.6	1.2±0.1
13	RT[a,b]	2.8±0.1	1.5±0.1
	30	3.5±0.4	1.5±0.1
	20	4.0±0.3	1.4±0.1
	10	4.2±0.4	1.3±0.1
	0	8.1±1.2	1.3±0.2
15	39[a]	2.9±0.1	1.2±0.1
	39[c]	3.3±0.2	2.8±0.1
	30	3.6±0.2	1.3±0.1
	20	11.7±1.7	1.3±0.3
	10	19.8±1.7	1.8±0.1
	0	20.5±2.5	1.6±0.2
17	39[a]	2.7±0.3	1.3±0.1
	39[c]	3.9±0.5	3.1±0.2
	30	3.7±0.4	1.5±0.1
	20	15.1±2.7	1.9±0.3
	10	27.4±3.2	1.9±0.3
	0	40.0±6.2	2.0±0.3
18	30	3.7±0.4	1.1±0.1
	20	14.8±2.3	1.6±0.2
	10	31.3±3.3	1.3±0.2
	0	42.3±7.0	1.7±0.2
19	39[a]	2.9±0.2	1.3±0.1
	30	4.1±0.2	1.3±0.2
	23.5	10.7±0.6	1.8±0.2
	22	14.3±1.2	2.1±0.2
	20	16.5±1.6	2.4±0.1
	10	22.8±3.8	2.5±0.1
	0	29.4±4.6	2.5±0.3
20	RT[b,c]	5.0±0.2	2.4±0.1
	30	3.9±0.5	1.0±0.1
	20	10.4±1.7	1.5±0.1
	10	18.5±3.0	1.5±0.2

a) *t*-butyl alcohol as solvent
b) at ambient room temperature
c) hexane as solvent

Table 2. Norrish II Product Ratios from 2 in BS.

2 Carbon Chain Length	Temperature (°C)	E/C	t/c
11	30	2.0±0.4	1.8±0.5
	20	1.8±0.4	1.5±0.5
	10	2.0±0.3	1.6±0.3
	0	2.0±0.3	2.0±0.4
15	RT^{a,b}	1.4±0.1	1.2±0.1
	30	1.9±0.5	2.4±0.6
	20	2.3±0.3	2.8±0.5
	10	3.2±0.6	3.5±0.4
	0	3.6±0.5	3.5±0.6
17	RT^{a,b}	1.8±0.1	1.3±0.1
	35	2.6±0.3	2.3±0.2
	30	2.2±0.6	2.2±0.6
	28	2.3±0.4	2.6±0.4
	26.5	2.0±0.1	2.3±0.1
	25.2	2.6±0.3	5.8±0.4
	24.5	3.2±0.8	7.0±0.5
	22.5	—	8.2±0.2
	20.0	3.2±0.8	10.8±1.6
	17.5	3.5±0.1	13.5±0.1
	13.5	4.4±0.5	11.1±0.3
	10	7.0±1.0	11.5±2.3
	8	—	9.9±0.3
	4.5	10.1±0.4	7.2±1.0
	0	10.0±2.5	6.8±0.3
19	RT^{a,b}	1.8±0.1	1.3±0.1
	36	2.1±0.6	1.6±0.1
	30	2.0±0.3	1.8±0.2
	25	3.6±0.3	6.9±0.4
	23.5	4.4±0.8	11.6±0.3
	20	6.2±0.9	13.3±0.3
	16.5	8.5±1.5	12.1±1.4
	12	9.1±0.6	11.3±0.7
	10	10.0±2.3	11.3±0.9
	8	10.6±2.2	10.4±0.9
	5.5	15.7±0.5	8.4±0.4
	2.5	13.1±3.5	6.2±0.2
	0	15.9±1.8	4.2±0.2
21	RT^{a,b}	1.8±0.2	1.2±0.1
	35	2.2±0.4	2.5±0.3
	30	2.0±0.2	2.5±0.6
	20	5.5±1.0	14.1±0.1
	10	15.0±5.0	12.0±3.0
	0	>15	6.0±2.0
27	RT^{a,b}	2.0±0.1	1.3±0.1
	30	2.8±0.5	2.2±0.3
	20	3.2±0.5	7.2±0.5
	10	6.3±1.3	6.1±0.7
	0	7.5±1.3	4.0±0.3
29	30	2.7±0.7	2.2±0.3
	20	3.6±0.5	5.9±0.1
	10	2.9±1.1	7.0±0.3
	0	2.3±0.6	2.5±0.3
31	RT^{b,c}	2.8±0.3	3.7±0.1
	42^{c}	2.8±0.2	3.6±0.3
	42	3.9±0.5	2.1±0.1
	20	3.0±0.5	5.5±0.5
	10	2.3±0.5	5.0±0.1
	0	1.7±0.6	3.1±0.3

a) *t*-butyl alcohol as solvent
b) at ambient room temperature
c) hexane as solvent

Figure 2. Elimination/cyclization ratios from 9-heptadecanone as a function of temperature. Vertical lines represent one standard deviation from average. Transition temperatures of BS are noted for reference.

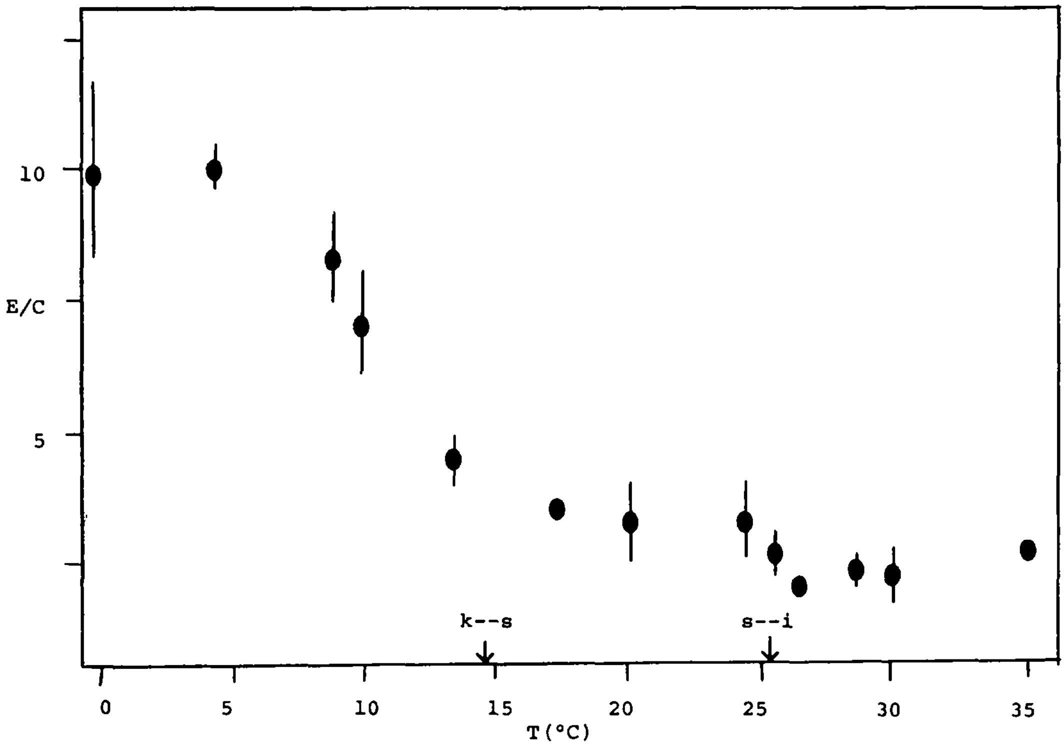
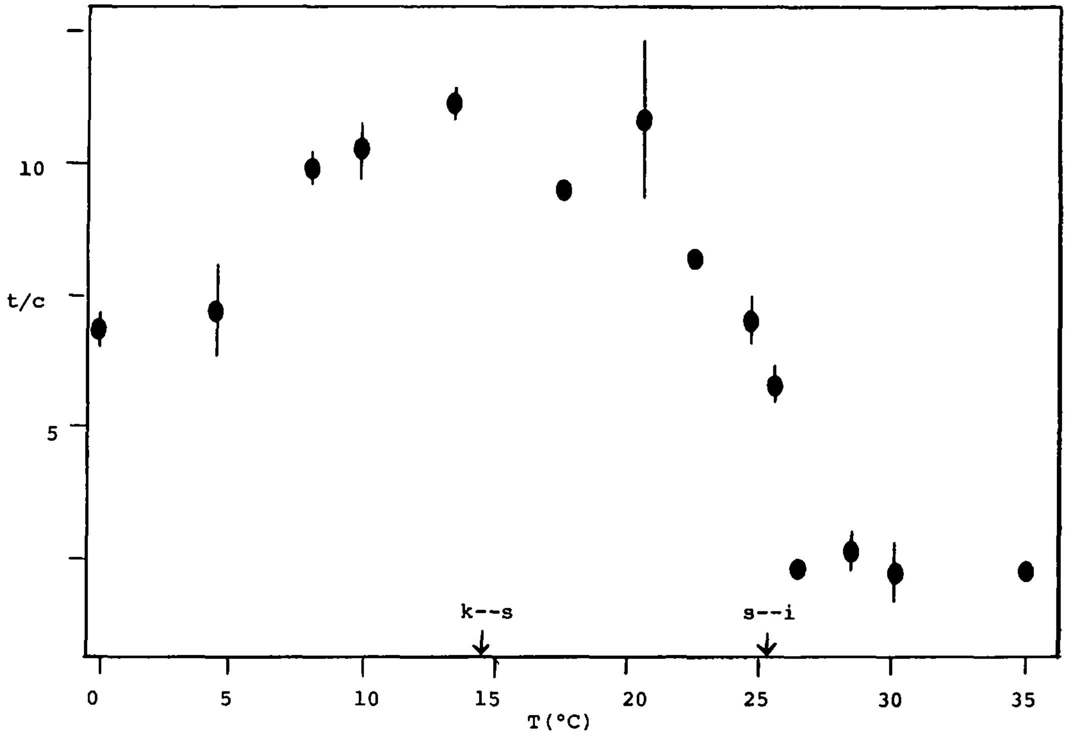


Figure 3. Trans/cis cyclobutanol ratios from 9-heptadecanone as a function of temperature. Vertical lines represent one standard deviation from average. Transition temperatures of BS are noted for reference.



As seen in Table 1, the E/C ratios from several 2-alkanones respond to temperature changes when BS is solvent. The same ketones exhibit t/c ratios which are impervious to BS phases. The data in Table 2 demonstrate that both the E/C and t/c product ratios from several sym-alkanones in BS are influenced by temperature. Qualitatively, the 2 whose molecular lengths are near that of BS have product ratios most sensitive to temperature changes. 2-Heptadecanone and 2-octadecanone, ketones of the 1 series significantly shorter than BS, exhibit the largest temperature dependent E/C ratios in the ordered phases. These data correlate qualitatively with the influence of the ketones on BS phase transition temperatures. Unfortunately, peak overlaps in the gas chromatographic analyses did not allow us to study the photochemistry of the ketones whose molecular lengths are closest to that of BS: the BS solvent peak engulfed completely the cyclobutanol peaks from 1 with 21 carbons and 2 with 23 and 25 carbons, as well as the alkene peaks from 2-heptacosanone and 2-octacosanone.

Although the E/C ratios from 1 or 2 increase with decreasing temperature, members of the 2 series (which are sensitive to temperature in BS) display t/c ratios which rise between 30°C and 10°C and then decrease thereafter. These effects are displayed in detail for 9-heptadecanone in Figures 2 and 3. The two product ratios do not correlate completely. The major discontinuities in the curves near 25°C correspond closely to the s→i phase transition temperature of BS (vide infra). The t/c maximum and the beginning of the second E/C increase occur near the solid to smectic B phase transition temperature. At slightly lower temperature than the reported solid-solid phase transition of neat BS, we observe the onsets of second plateau regions. Similar comportment has been noted for E/C product ratios from eicosanophenone in BS.[13] Clearly, the two product ratios (and, ergo, the motions which link their immediate precursors and their transition states) are controlled by different aspects of BS solvent order.

Perhaps the best evidence that 1 and 2 are not crystalline in solid BS lies in their photoreactivity. Solid alkanones are nearly impervious to uv irradiation. Guillet has shown that solid, neat 7-tridecanone is photostable,[17] and we observe that neat samples of 16-hentriacontanone and 18-pentatriacontanone are >98% unreacted after irradiation for 5h at room temperature. Thus, the ketones for which product ratios are presented are dispersed in the solid and smectic phases of BS.

Only the data for 16-hentriacontanone need be interpreted with caution. As mentioned, 1.4% (w/w) of this ketone in BS at 20°C appears to contain microcrystals. Irradiation of the sample for 3.5 h resulted in less than 10% of reaction. By contrast, an equal concentration of 10-nonadecanone in smectic BS was 30% reacted after 20 min of irradiation under the same conditions. We believe that the small amounts of photoproducts from 16-hentriacontanone in smectic BS derive from dissolved ketone (at the solubility limit), but have no direct evidence for this assertion. No secondary photolysis is observed.

DISCUSSION

Order of BS Phases and their Solutions. The ordered phases of BS have been investigated carefully.[18,19] Neat BS exhibits an enantiotropic smectic B liquid-crystalline phase at ca. 15-26°C.[20] The exact phase transition temperatures are dependent upon the amount and type of impurities present. X-ray crystallographic studies show that the individual BS molecules in the smectic phase prefer fully extended conformations and are orthogonal to the layers which their hexagonal close packing define.[18] NMR and IR studies further indicate that the molecules rotate rapidly about their long molecular axes and methylenes near the molecular ends are less ordered than those near the center.[18-21]

The first crystalline phase (α_2) exists between ca. 10-15°C. It shares many characteristics of the smectic phase. In addition to the ordering described above, rotations about the long axes of molecules are restricted and the closest packing arrangement within a layer collapses to orthorhombic.[19] The nature of the lower temperature crystalline phase (α_3) is less clear. Its existence has been established by differential scanning calorimetry (cooling curves only), NMR, X-ray diffraction, and dielectric absorption studies.[18,19] The crystalline packing in the two phases must be very similar since no perceptable differences were noted between their optical textures[19] and only very small differences between their X-ray patterns.[19] In fact, the NMR data are consistent with the second crystalline phase being like the first, but with further dampened rotational oscillations for the methylene groups.[19]

In its isotropic phase, BS behaves like any other long-chained ester. Repeatedly, we have found that the reactivities of solutes in it and in nonmesogenic solvents of similar polarity are very similar.[1,6,7,9,12] The ease with which isotropic BS solubilizes guest molecules depends almost exclusively upon their functional groups and polarity.

Solubilization and reactivity of solutes in smectic (or solid) BS depend upon the aforementioned properties and, additionally, the size and shape of the guest molecules and their transition states. Thermodynamic studies have shown that the heats of mixing of isomeric guest molecules with liquid crystals vary with the structure of the solvent and solute.[22] In general, globular guests are incorporated with greater difficulty than long, cylindrical ones which mimic the shape and size of the constituent solvent molecules. On this basis, we expect that 1 and 2 will prefer fully extended conformations and will be aligned with their long molecular axes parallel to neighboring solvent molecules in smectic and solid BS.

Furthermore, ketones which are significantly shorter or longer than BS should disturb their local solvent environment to a greater extent than 1 and 2 which are near the length of BS. Since shorter ketones cannot fill completely the equivalent space of a BS, neighboring solvent molecules will bend to compensate and rotations of their methylenes will be less constrained than in undoped ordered phases. Longer ketones will be compressed within one layer (and, therefore, bulge at one point) or will extend partially into a second layer (and, therefore, disrupt the layer boundary and order of solvent molecules near it).

Ketones which are not well-suited to lie within a solvent layer can, in principle, reside between layers. Our studies with 1 and 2 in aqueous gel phases (which preclude this possibility)[1] lead us to believe that the location in BS of 1 and 2 (at least those for which the influence of solvent ordering is large) is within a layer. The consequences of a solute reacting between smectic BS layers has been documented.[7]

Our interest in measuring the phase transition temperatures was two fold: to obtain information about the *microscopic* influence of individual ketone molecules upon their immediate solvent environments; and to test the validity of the previous arguments. Microscopic phase transitions can occur several degrees lower in temperature than macroscopically observed transitions.[4,8,10,13-15,23] At low percent loadings, even very disruptive solutes may have little or no effect upon macroscopic properties of the solvent.

Regardless, the ability of a ketone to bend into bulkier conformations will be facilitated if it disrupts the order of its local environment. Solutes which are well-ordered initially in a meso or solid phase will encounter greater difficulty from nearby solvent molecules in altering their shape. Thus, 1 and 2 which depress the BS phase transition temperatures least should experience the greatest resistance to attaining conformations necessary for c-BR (and cyclobutanol) formation in the ordered phases. Ketones which depress the phase temperatures most should be held less rigidly by the ordered solvent matrix and should be able to change from t-BR conformations with greater ease.

It is gratifying that these hypotheses are borne out by experiment: Figures 4 and 5 show that at a constant weight % of ketone, $X_K = 50\%$, the shape of the curve described by plotting phase transition temperatures versus ketone chain length is qualitatively similar to the E/C (or t/c) versus chain length plots. The maximum selectivities occur with ketones that depress the s→b phase transitions least.

Figure 4. Elimination/cyclization ratios (●) from 1.4% (w/w) of 1 in BS at 10°C and s → b phase transition temperatures (♦) from 50% (w/w) of 1 in BS versus ketone chain length.

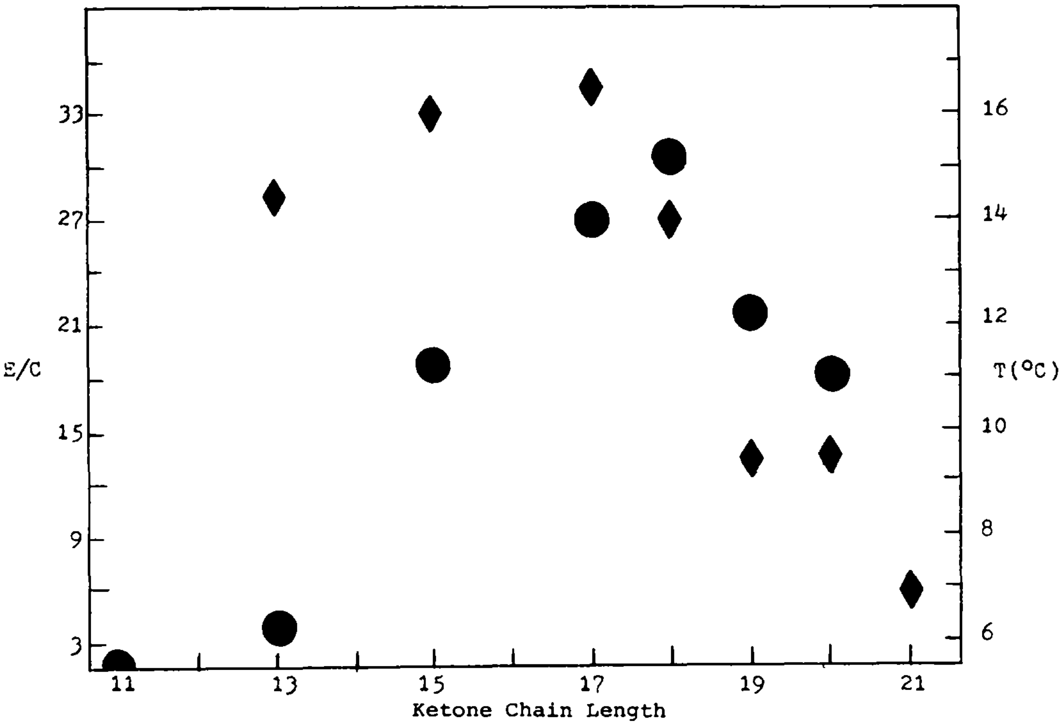
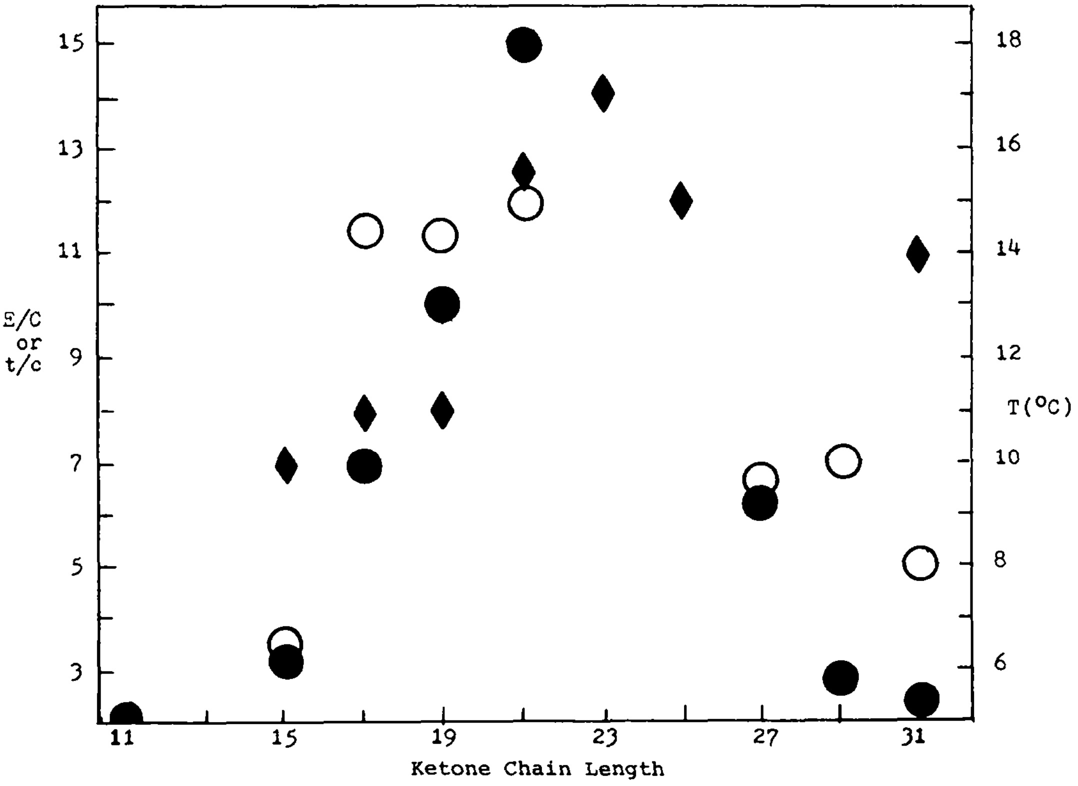
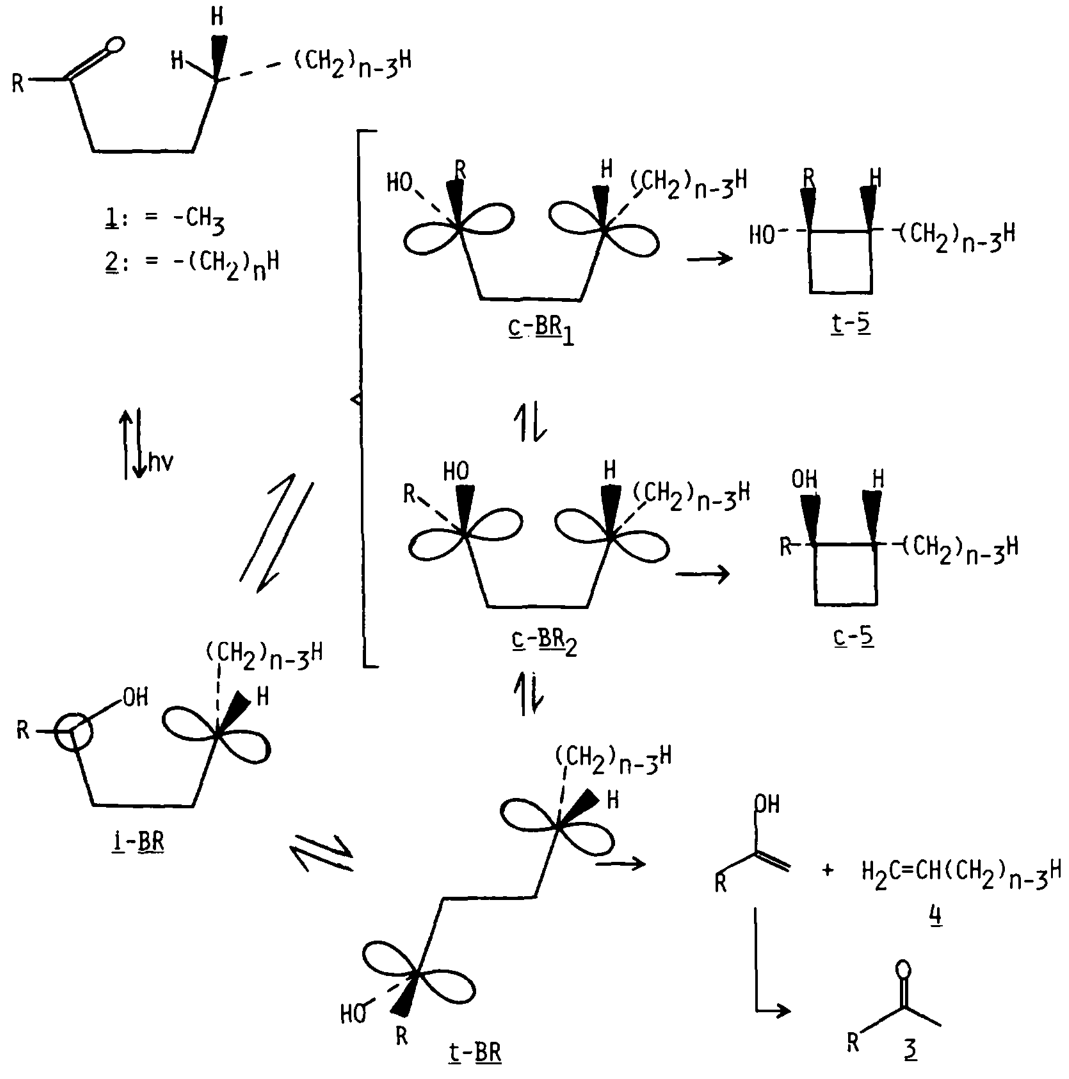


Figure 5. Elimination/cyclization ratios (●) and trans/cis cyclobutanol ratios (○) from 1.4% (w/w) of 2 in BS at 10°C and s → b phase transition temperatures (♦) from 50% (w/w) of 2 in BS versus ketone chain length.



Scheme 1. Representation of the Norrish II pathways leading to elimination and cyclization products. Each structure represents a family of closely related conformers which undergo the same process.



Norrish II Photoprocesses of Alkanones in BS and Other Solvents. The mechanisms of the photoreactions of n-alkanones have been investigated in detail in isotropic solutions.[24] The vast majority of products arise from Norrish II processes (Scheme 1) whose first chemical step is formation of i-BR via abstraction of a γ-hydrogen by the carbonyl oxygen. Subsequent product formation depends upon both the multiplicity of the BR and its conformation. Each BR represents a family of similarly structured conformers which lead to one product or undergo a characteristic process.

Germane to this study are the interconversions of c-BR and t-BR and of the two c-BR precursors to the cis and trans cyclobutanols. The i-BR either returns to starting ketone (via back hydrogen transfer) or undergoes C-C bond rotation to c-BR or t-BR. Conformational effects within the families of c-BR and t-BR geometries are important in determining the rates of reactions.[2,3,13,14,25] Usually, t-BR can cleave to 4 and the enol of 3. The fate of c-BR is less clear: when steric constraints inhibit overlap of the singly occupied orbitals[26] or when ring strain makes cyclization unfavorable,[27] elimination can dominate; when c-BR is unencumbered by steric constraints, appropriate orbital alignment for cleavage is difficult, or orbital overlap is possible, cyclization dominates.[2,25,28] The biradicals from 1 and 2 in isotropic media are unencumbered and able to adopt conformations which lead facilly to elimination or cyclization products. They should be very susceptible to intermolecular influences.

Both chemical evidence[29] and (attempted) spectroscopic observations[27b] are consistent with lifetimes much shorter than 1 ns for a singlet BR (^{1}BR). Naito[30] found 25 ns for the lifetime of the triplet BR (^{3}BR) from 2-hexanone in dichloromethane. This is significantly shorter than the ^{3}BR lifetimes from alkylphenones,[27b,31] but sufficient to ensure equilibration between c-BR and t-BR in isotropic solvents of low viscosity.[14,32]

Guillet[16b] has shown that the fraction of singlet reaction is independent of ketone chain length in isotropic solvents. A reasonable rate limiting step for formation of product from ^{3}BR is conversion to ^{1}BR.[25,27b] The very short lifetime of the ^{1}BR ensures that products reflect the conformation of the ^{3}BR at the moment of its intersystem crossing.[29] Thus, the yields of products and the concentrations of BR conformers are related as shown in eqs. 2 and 3.

$$\frac{[\mathrm{E}]}{[\mathrm{C}]} \propto \frac{[t\text{-}\mathrm{BR}]}{[c\text{-}\mathrm{BR}]} \tag{2}$$

$$\frac{[t]}{[c]} \propto \frac{[c\text{-}\mathrm{BR}_1]}{[c\text{-}\mathrm{BR}_2]} \tag{3}$$

These can be elaborated as shown in eqs. 4 and 5 (where α_n is the fraction of reaction emanating from ketone singlets of carbon chain length n). Unfortunately, the values of α_n[16b,33] cannot be taken directly from isotropic solutions of low viscosity. The singlet contributions should be diminished, if anything, in the ordered phases of BS since α_n decreases for n-alkanones in isotropic solvents as the temperature is lowered[33] and the ketones encounter greater difficulties to attain the bulky conformations needed for γ-hydrogen abstraction (Scheme 1) in ordered media:[12,14,34] intersystem crossing of the short-lived $^1(n,\pi^*)$ states (<5 ns[35]) will compete more effectively with hydrogen abstraction in very viscous, highly ordered media which favor extended conformations.[36]

$$\frac{[\mathrm{E}]}{[\mathrm{C}]} \approx \alpha_n \frac{[^1(\underline{\mathrm{t}}\text{-}\underline{\mathrm{BR}})]}{[^1(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}})]} + (1 - \alpha_n) \frac{[^3(\underline{\mathrm{t}}\text{-}\underline{\mathrm{BR}})]}{[^3(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}})]} \tag{4}$$

$$\frac{[\underline{\mathrm{t}}]}{[\underline{\mathrm{c}}]} \approx \alpha_n \frac{[^1(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}_1})]}{[^1(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}_2})]} + (1 - \alpha_n) \frac{[^3(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}_1})]}{[^3(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}_2})]} \tag{5}$$

The much longer $^3(n,\pi^*)$ lifetimes (~1 us in solution[24b,37]) give the ketones a much better opportunity to attain a conformation from which ^{3}(i-BR) can form. Thus, eqns. 6 and 7 hold approximately in the ordered phases of BS. In the isotropic phase, where the singlet component is larger, the E/C ratios do not provide a reasonable approximation to ^{3}(t-BR)/^{3}(c-BR) since ^{1}BRs are known to yield mainly elimination products.[29,38] Therefore, the E/C ratios observed in the isotropic phases reflect the maximum ^{3}(t-BR)/^{3}(c-BR) ratio which can be expected.

$$\frac{[\underline{\mathrm{t}}\text{-}\underline{\mathrm{BR}}]}{[\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}}]} \approx \frac{[^3(\underline{\mathrm{t}}\text{-}\underline{\mathrm{BR}})]}{[^3(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}})]} \tag{6}$$

$$\frac{[\underline{\mathrm{c}}\text{-}\mathrm{BR}_1]}{[\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}_2}]} \approx \frac{[^3(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}_1})]}{[^3(\underline{\mathrm{c}}\text{-}\underline{\mathrm{BR}_2})]} \tag{7}$$

Furthermore, the E/C and t/c ratios do not represent the equilibrium ^{3}(t-BR)/^{3}(c-BR) and ^{3}(c-BR_1)/^{3}(c-BR_2) populations in the solid phases of BS. It is unlikely that the initially formed ^{3}(i-BR) can relax among the species in Scheme 1 during its lifetime.[14] The severe constraints imposed by the solid phases must attenuate the rates of some of the motions which interconvert the BR which lead directly to products. Since i-BR can form c-BR with less motion than it can t-BR, the plateauing of the E/C and t/c ratios from 9-heptadecanone in the α_3 solid phase may arise from a balancing of opposing thermodynamic (increased stability of t-BR over c-BR) and kinetic (decreased ability of i-BR to relax to t-BR during its triplet lifetime) factors. Unfortunately, we lack the quantitative information necessary to test this hypothesis.

Differences in the Photoreactions of 1 and 2 in BS. Figs. 4 and 5 show that the order "seen" by a BR is a very sensitive function of the disruption that its presence (and the presence of its parent ketone) causes to the local environment. Although the correspondence between product selectivities and phase transition temperatures is remarkable, the Figures do not explain why a carbonyl group near the middle of a solvent layer is more disruptive than one which is near a layer end.

The sizes of a carbonyl (the sum of the covalent radii of unsaturated carbon and oxygen plus the van der Waals radius of oxygen), *ca.* 2.7 A°, and a methylene (approximated as the van der Waals radius of a methyl group plus the covalent radius of saturated carbon), *ca.* 2.8 A°,[39] do not differ sufficiently to account for the gross disturbances to ordered BS which occur when they are interchanged from the 2 position to a middle carbon of an *n*-alkanone.[40] The electronic properties of a methylene and a carbonyl *are* very different: their group dipoles are 0.45 D and 2.3 D, respectively, and are projected oppositely with respect to carbon.[41] In principle, carbonyls of 1 can be stabilized through dipole-dipole interactions with carboxyls of neighboring BS molecules. No such intermolecular interaction is available to the carbonyls of 2. These factors and the intrinsically greater order of methylenes near the middle of a smectic layer must contribute to the differences noted between 1 and 2 in BS.

Of interest, also, is why the t/c ratios of 2 are sensitive to BS order but those of 1 are not. The answer cannot lie in the magnitudes of the changes in the E/C ratios of 1 and 2: as demonstrated by Figs. 2 and 3, the *c*-BR$\rightleftharpoons$*t*-BR and *c*-BR$_1$$\rightleftharpoons$*c*-BR$_2$ interconversions are sensitive to different aspects of BS order; the magnitude of change in the E/C ratios from 1 (whose products arise from reactions near the less ordered part of a BS layer) are larger than those from 2.

An important consideration is the shape of the two diastereomers of *c*-BR from 1 and 2. How do *c*-BR$_1$ and *c*-BR$_2$ from one ketone appear to vicinal solvent molecules? The two *c*-BR from 1 differ only in the placement of a methyl and a hydroxyl (groups of similar size). Even in ordered BS, the two *c*-BRs must be sufficiently similar to allow the t/c product ratios to be controlled primarily by intramolecular exigencies.

The shapes of the two *c*-BR from 2 are very different. Interchange of a hydroxyl and a long alkyl chain alters the *c*-BR shape in ways which should be easily detected by neighboring BS molecules. The *c*-BR$_1$ (with alkyl groups on opposite sides) and its *trans*-cyclobutanol product are capable of being incorporated into a solvent layer much more readily than *c*-BR$_2$ and its *cis*-cyclobutanol product.

Conclusions. Several key observations can be extracted from this study. The position of the reactive chromophore along the alkanone chains is very important in determining the type and degree of BS solvent control over the product-forming biradicals. Those ketones which disturb solvent order least, as determined from depressions in BS phase transition temperatures, exhibit Norrish II product ratios which are influenced most.

The Norrish II product ratios from the 2-alkanone which is closest in length to BS do not suffer the greatest influence by solvent order.

In toto, these results demonstrate the extreme dependence of solute-solvent shape and size relationships on the control of solute reactivity by solvent order.

EXPERIMENTAL

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. E.I. mass spectra were taken on a Kratos MS-30 double focusing dual beam spectrometer. NMR data were obtained on a Bruker AM-300 WB spectrometer. Melting points, from a Kofler hot-stage microscope equipped with polarizing lenses, are corrected. Analtyical gas chromatography was accomplished with a Perkin-Elmer 3920 B chromatograph equipped with flame ionization detectors and either an Alltech RSL-300 or a Chrompack CP-Sil-19 CB wide bore (0.53 mm x 10 m) fused silica open tubular column. Chromatograms were integrated with a Perkin-Elmer M2 calculating integrator. Preparative gas chromatography was done on a Varian Aerograph Model 920 chromatograph (thermal conductivity detector) and a packed column of 15% SE-30 on chromosorb W (1/4 in. x 5 ft.).

Materials. n-Butyl stearate was synthesized from stearic acid (Aldrich 99+%) and n-butanol (Baker reagent)[10] by S. Ganapathy and was 97% pure by gc analysis. In those cases where solvent impurities overlapped photoproducts, an especially purified sample of BS (>99% by gc analysis) was employed. Where necessary, ketones were purified by either repeated recrystallization or silica gel column chromatography (hexane/ether) and were >98% pure by gas chromatography. Melting points are reported for purified compounds. 2-Heptanone, 2-nonanone, 2-undecanone, 7-tridecanone (mp. 31-32 °C), 8-pentadecanone (mp. 42-43 °C), 9-heptadecanone (mp. 52-53 °C), 10-nonadecanone (mp. 56-57 °C), 1-nonene, 1-dodecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, and 1-heptadecene were all purchased from Aldrich. 6-Undecanone and 14-heptacosanone (mp. 73.5-74.5 °C) were from Wiley Organics. 2-Decanone, 2-pentadecanol, and 11-heneicosanone (mp. 63.5-64.5 °C) and 13-pentacosanone (mp. 72.4 °C) were from Lancaster Synthesis. 16-Hentriacontanone (mp. 82-83 °C) and 18-pentatriacontanone (mp. 84.5-85.5 °C) were from TCI. 2-Tridecanone (mp. 29.5-30.5 °C) was from Eastman. 2-Pentadecanone (mp. 38-39 °C) was prepared from 2-pentadecanol by chromic acid oxidation and purified by column chromatography (ether/hexanes). 2-Heptadecanone (mp. 46.5-47 °C), 2-octadecanone (mp. 50-51 °C) 2-nonadecanone (mp. 55-56 °C), 2-icosanone (mp. 58-59 °C) and 2-henicosanone (mp. 61-62 °C) were synthesized from n-alkanoic acids and methyl lithium in THF.[42] 12-Tricosanone (mp. 68 °C) and 15-nonacosanone (mp. 81.5-82.5 °C) were prepared from the acid chloride and triethylamine.[43] The 2- and sym-alkanols were purchased or were synthesized from the corresponding alkanones by lithium aluminum hydride reductions in ether or THF.

Sample Preparation and Photolysis. Ketones ($<$1.4% by weight) were dissolved in isotropic BS. The solutions were vortexed 5 min. and weighed aliquots were placed into 0.8 mm (i.d.) pyrex cells. The samples were degassed by three freeze-pump-thaw cycles and sealed at $<10^{-3}$ torr. Samples were heated to the isotropic phase, immediately quenched at the desired temperature, and thermostatted for at least one hour prior to irradiation. The photolysis lamp consisted of a 450 W Hanovia medium pressure mecury arc with a quartz cooling jacket immersed in a Haake temperature bath (±0.5 °C). Irradiation time varied from 2 minutes, for all ketones in isotropic BS, to 30 minutes for longer ketones in smectic and solid phases of BS. In some cases the t/c ratio was determined at high % conversions, with irradiation times $<$2 hrs. Hexane and tert-butyl alcohol solutions ($<$0.2 M) were deoxygenated with nitrogen.

Product Analyses. Product analysis was accomplished by gas chromatography and provided baseline resolution for all diasteromeric cyclobutanol products. Weighed aliquots of irradiated samples were analyzed immediately after being mixed with hexane and a standard. Product ratios are not corrected for differences in detector responses. Percent conversion determinations are ±10%. All data reported for 30°, 20°, 10°, and 0 °C are the averages of 2 samples, with three injections per sample. All other data are from three injections of a single sample. Errors are reported as one standard deviation. Elimination and reduction products were identified by coinjection with authentic materials. Ubiquitous Type I products, the truncated alkanes (available from Humphrey Chemicals), could not be detected in the reaction mixtures by gc. No nearby peaks which could be attributable to the corresponding alkenes were observed either.

The assignments of trans and cis cyclobutanols are based upon both the relative retention times and relative yields of the two diastereomers in isotropic solvents.[2a,3,5,44] The cyclobutanols of 8-pentadecanone were isolated by preparative gc and re-analyzed to check their thermal stability under the analytical conditions. 6-Undecanone, 2-undecanone, 9-heptadecanone, 2-heptadecanone, and 14-heptacosanone were irradiated to >99% conversion in _tert_-butyl alcohol or benzene. After solvent evaporation, ir spectra (neat smear) showed large hydroxyl stretches (3400 cm^{-1}) and the loss of the carbonyl stretch (1710 cm^{-1}). Mass spectra of the cyclobutanols from 9-heptadecanone showed masses at 253 $(M-H)^+$, 237 $(M-OH)^+$, 236 $(M-H_2O)^+$, 183 $(M-C_5H_{11})^+$, and 141 $(M-C_8H_{17})^+$.

Solubility Studies. Samples were prepared by weighing appropriate amounts of _BS_ and ketone. Each solution was heated to its clearing point, and thoroughly mixed, placed between glass plates, and heated on a hot stage microscope equipped with polarizing lenses. Pressure was applied at the edge of the glass plates during heating in order to determine better the smectic to biphasic transition temperature.

Acknowledgments. We wish to thank Dr. Jerry Liu for several helpful discussions at the inception of this work. The National Science Foundation (Grants CHE83-01776 and CHE85-17632) is acknowledged for its financial support.

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