Length- and Direction-Specific Solute–Solvent Interactions As Determined from Norrish II Reactions of *p*-Alkylalkanophenones in Ordered Phases of *n*-Butyl Stearate[1]

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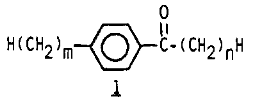
Abstract: The photochemistry of a series of *p*-alkylalkanophenones (**1**) has been investigated in the ordered and isotropic phases of *n*-butyl stearate (BS). By varying the total length of the ketones and the relative position of the benzoyl group within ketones of constant length, the solvent-related factors responsible for Norrish II product selectivity and reactivity have been identified. Specifically, the location of the hydroxy 1,4-biradical intermediates from **1** with respect to the carboxyl groups of neighboring BS molecules and the orientation of the biradical centers within a BS layer appear to control the nature and efficiency of product formation. Infrared spectra of models of the hydroxy 1,4-biradicals in BS and eicosane support the hypotheses. Differential scanning calorimetric data indicate that the ketones exhibiting the lowest product selectivity or least reactivity are not incorporated well within the BS anisotropic phases.

The general ability of the ordered phases of *n*-butyl stearate (BS) to influence the reactive course of electronically excited aliphatic and aromatic ketones undergoing Norrish II processes (Scheme I) has been amply demonstrated.[2-4] However, the specific nature of the responsible solute–solvent interactions is still a matter of conjecture. For instance, selectivity in the ratio of elimination to cyclization products (E/C) is greatest when the lengths of *sym*-alkanones and BS are nearly equal *or* when the lengths of 2-alkanones and only the stearate portion of BS are similar.[3] This suggests that product selectivities from *sym*-alkanones are controlled by their ease of fit into a solvent matrix while those from 2-alkanones are dominated by an additional factor, perhaps interactions between hydroxyl groups of intermediate 1,4-biradicals and carboxyl groups of neighboring solvent molecules. Unfortunately, the complex nature of Norrish II product mixtures expected from *n*-alkanones whose carbonyls are positioned at intermediate points between the 2- and *sym*-positions makes them inappropriate to investigate these effects.

Such complexity does not attend irradiations of *p*-alkylalkanophenones (**1**) since their γ-hydrogen abstractions are limited to the alkyl chain remote from the aromatic ring: changes in Norrish II parameters can be followed rationally with **1** as a function of solute length, position of the locus of reactivity within a BS layer, and orientation of the locus of reactivity with respect to neighboring BS molecules. Thus, we examine here the E/C and trans/cis cyclobutanol (t/c) product ratios and the relative quantum yields (Φ_{rel}) from two series of **1**. In one series, the total molecular length is constant ($m + n = 21$) but the position of the benzoyl group is moved systematically along the chain. In the second series, the total molecular length is varied but the distance of the benzoyl group from one molecular end is constant ($m = 5$, $n = 11-18$). The results show that *bulk* solvent order is a very poor indicator of control over solute reactivity: both the location of the hydroxyl 1,4-biradical intermediates from **1** and the orientation of the biradical centers within a BS layer must be considered to explain the dramatic changes in photoreactivity and selectivity that occur. In extreme cases of BS control over solute selectivity, E/C ratios >100 have been observed.



1

	m	n		m	n
a	0	21	f	6	15
b	2	19	g	8	13
c	3	18	h	10	11
d	4	17	i	12	9
e	5	16	j	15	6

Results and Discussion

General Solvent Considerations. Above 26 °C, BS molecules exist in an isotropic liquid phase.[5] Between ca. 15 and 26 °C, a "hexatic" smectic B phase forms:[5d] individual molecules are in extended conformations and pack hexagonally in layers with their long axes perpendicular to the layer planes; rotation about the long molecular axes is somewhat encumbered, but it does occur. Below 15 °C, BS is a solid with orthorhombic packing within layers.[5a,b] The regions of least order (most gauche defects) in the layered phases are around the carboxyl groups (near a layer end) and those of greatest order are at a layer middle.[5c] There is ample evidence that rod-like solutes like **1** prefer to enter the layers as surrogates for BS molecules.[2-4] That is, each solute molecule occupies roughly the place of a solvent molecule in the BS matrices. The fit depends primarily upon the comparative lengths of **1** and BS.

Norrish II Reactions. As shown in Scheme I, cyclization products derive from collapse of cisoid biradicals. Depending upon the steric constraints imposed upon them and the presence or absence of alkyl substituents at the γ-carbon, cisoid biradicals may also yield elimination products.[6] However, in the absence of intramolecular steric constraints, several studies indicate that the vast majority of elimination products arise from transoid biradicals.[6e,f,7] Similarly, two families of diastereomeric cisoid biradicals can lead to their respective cis and trans cyclobutanols (c and t).

The factors influencing the singlet and triplet lifetimes of hydroxy 1,4-biradicals and related biradicals have been discussed extensively. Although no theory has emerged that relates quantitatively biradical lifetimes to structure, it is clear that solvent

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[1] Part 38 in our series, Liquid-Crystalline Solvents as Mechanistic Probes. For part 37, see: Lin, Y.-C.; Kachar, B.; Weiss, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 5542.

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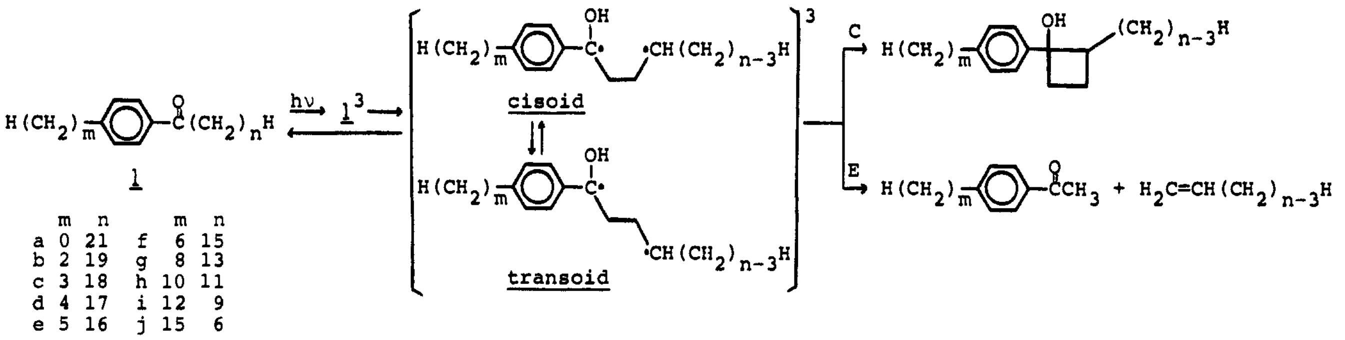
Scheme I. A Representation of the Norrish II Reactions of **1**



	m	n		m	n
a	0	21	f	6	15
b	2	19	g	8	13
c	3	18	h	10	11
d	4	17	i	12	9
e	5	16	j	15	6

interactions,[8] singly occupied orbital orientations and their separation,[9,10] and singlet–triplet energy gaps are important contributors.[9,10] From the estimated rates of C–C bond rotations[11] and the relatively long triplet lifetimes of hydroxy 1,4-biradicals from **1** in BS (64 ns at 30 °C and 70 ns at 20 °C for **1** (m = 0, n = 19) in BS[2]), one infers that equilibrium conformational distributions may be established in the isotropic and hexatic B phases of BS prior to intersystem crossing to singlets. This is probably not the case in solid BS. By contrast, available information indicates that in very viscous media like those employed here, interconversion of the *singlet* biradical conformers in Scheme 1 will be much slower than their collapse to products.[12] Thus, the E/C and t/c ratios from **1** reflect the relative populations of triplet transoid and cisoid biradicals at the time of their intersystem crossing to extremely short-lived singlets.

It is also important to differentiate the mechanistic steps that determine product ratios and Φ_{rel}. Whereas the E/C and t/c ratios depend solely upon the fraction of triplet biradicals that eventually give products, Φ_{rel} is a function of all steps subsequent to ketone excitation. As shown in Scheme I, intersystem crossing of excited singlets is assumed to occur with unit efficiency since this is the case for aromatic ketones in a wide variety of isotropic media.[13] Then, the magnitude of Φ_{rel} is given by the product of the fraction of ketone triplets that undergo hydrogen abstraction and the fraction of those biradicals that do not back hydrogen transfer (yielding ground-state ketone).[14]

Product Ratios from 1 (m = 5, n = 11–18). In Figure 1, the E/C ratios from **1** in which m = 5 and n = 11–18 are presented for three phases of BS. For comparison purposes, smectic phase data for **1** with m = 0 and n = 17, 19, or 21[2] are plotted also so that their total lengths correlate with those of **1** containing the *p*-pentyl groups. Clearly, the effect on the E/C ratios of increasing total molecular length in the two series of **1** is very different: E/C ratios from **1** with m = 0 maximize at lengths at least 4 C–C bonds shorter than in **1** with m = 5; for both BS ordered phases, the maximum E/C ratios were obtained from **1** with m = 5 and n near 16. These E/C changes are clearly not intrinsic to **1** alone since the ratios are nearly invariant to n in the isotropic phase of BS. Also noteworthy is the large E/C increase in the BS solid phase (10 °C) for **1** (m = 5) with n = 13 and 14. Both of these are near in length to BS, demonstrating the rough correlation between solute length and E/C selectivity: the degree to which the more rod-like transoid biradical will be favored over the bulkier cisoid depends upon *local* solvent order; in turn, local solvent order increases as the solutes' disturbing influence on neighboring BS molecules decreases.

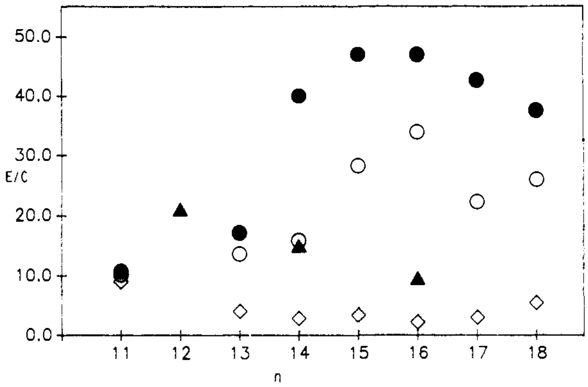


Figure 1. E/C ratios from irradiation of 2% (w/w) **1** (m = 5) as a function of n chain length in the solid (10 °C, ●), hexatic B (20 °C, ○) and isotropic (30 °C, ◇) phases of BS. Data from **1** (m = 0) in the hexatic phase of BS[2] (20 °C, ▲) are plotted as n - 5 in order to allow direct length comparisons with the m = 5 series.

Thermodynamic evidence for the above explanation is found in differential scanning calorimetry (dsc) measurements performed on 2 wt % ketone in BS samples. Figure 2a presents the heating and cooling curves of neat BS. BS solutions of all of the **1** with m = 5 except n = 11 gave similar dsc curves. As seen in Figure 2b, new exotherms are present in the cooling cycle of **1** (m = 5, n = 11). The product ratios from this ketone (Figure 1) are consistent with reaction occurring in a rather disorganized environment.

The t/c ratios displayed in Figure 3 for the same *p*-pentylalkanophenones vary only slightly, but the solid-phase extremum matches that of the E/C ratios. The similarity between the t/c ratios from isotropic and smectic phase experiments indicates that the shapes of the two cisoid hydroxy 1,4-biradicals are too similar to be differentiated within the hexatic matrix. Somewhat surprisingly, the t/c ratios in solid BS are very low and, for the most ordered ketones, *cis*-cyclobutanols are the dominant isomer.

Wagner et al.[13] have noted that t/c ratios from irradiation of alkanophenones are reduced by greater solvent polarity (Lewis bases), and we[15] have found t/c ratios less than 1 from irradiations of some 2- and *sym*-alkanones in aqueous phases of potassium stearate whose order is smectic B-like. Since the polarity conditions necessary to obtain t/c < 1[16] are lacking in BS, another factor must be responsible. Considering the very large magnitude

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(14) This analysis assumes that only Norrish II processes occur upon irradiation of **1** in BS. In fact, chromatograms of reaction mixtures do show very small amounts of other products that may be from intermolecular processes.[14a,b] Although introducing small errors in Φ_{rel}, as defined, they would not influence the Norrish II product ratios. Specifically, we were unable to detect **2c** and **2g** from protracted irradiations of **1c** and **1g** in the solid, hexatic, and isotropic phases of BS. (a) Breslow, R.; Kitabatake, S.; Rothbard, J. *J. Am. Chem. Soc.* **1978**, *100*, 8156. (b) Porter, N. A.; Lehman, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 4731.

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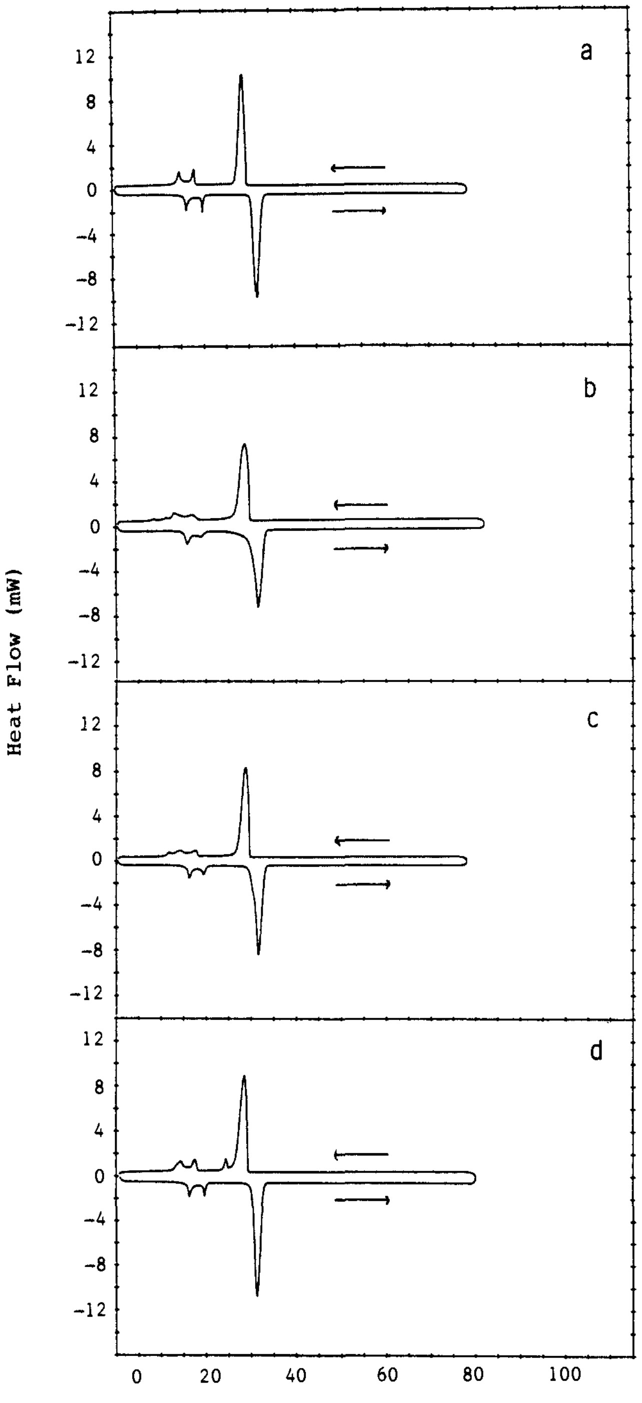

Figure 2. Differential scanning calorimetry heating and cooling cycles for (a) neat BS and 2 wt % of (b) **1** ($m = 5$, $n = 11$), (c) **1g** and (d) **1h** in BS.

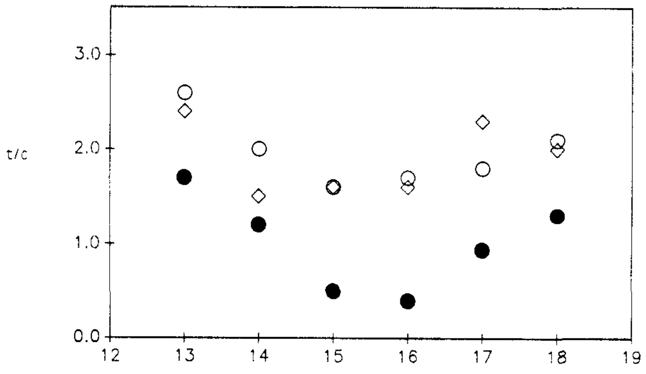

Figure 3. Ratios of *trans*- and *cis*-cyclobutanol from irradiation of 2% (w/w) **1** ($m = 5$, $n = 13$–18) in solid (10 °C, ●), hexatic B (20 °C, ○), and isotropic (30 °C, ◇) phases of BS versus solute length.

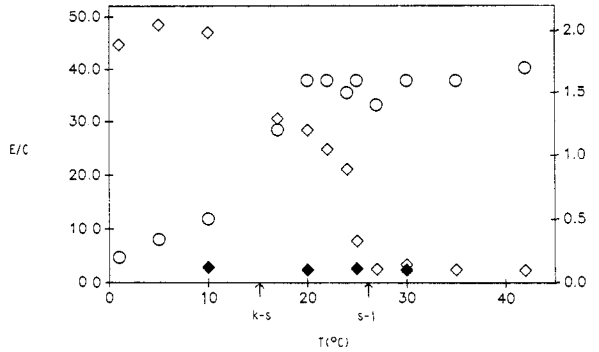

Figure 4. Temperature dependence of E/C (◇) and t/c (○) ratios from irradiation of 2% (w/w) **1** ($m = 5$, $n = 15$) in BS. E/C ratios from irradiation in benzene (◆) are included for comparison. The solid-hexatic B (k–s) and hexatic B–isotropic (s–i) transitions are marked with arrows.

of the E/C ratios, the fraction of biradicals that yield cyclobutanols is very small (ca. 2% of the total from **1** ($m = 5$, $n = 14$–17)). Since the requirements for incorporation of **1** into the BS solvent matrix become more severe as temperature is reduced (and order is increased), a possible explanation for the low t/c ratios is that much, if not all, of the cyclobutanols arise from hydroxy 1,4-biradicals residing in defect sites. Such sites may force biradicals into coiled conformations (and promote their hydrogen bonding to carboxyl groups of nearby solvent molecules[13]) from which *cis*-cyclobutanols can form relatively easily.

To explore this possibility further, a detailed mapping of the temperaure dependence of product ratios from **1** ($m = 5$, $n = 15$) was undertaken (Figure 4). Although the E/C selectivities are somewhat higher in Figure 4, the nature of the temperature dependence is very similar to that reported previously for **1** ($m = 0$, $n = 19$) in BS.[2] Throughout the isotropic and most of the hexatic B phase, the t/c ratios remain 1.5–2.0 (like those from isotropic solvents of low polarity[2]). However, at lower temperatures that include the solid phase of BS, the t/c ratios decrease rapidly while the E/C ratios reach a plateau near 45. Over the same temperature range, the E/C ratios and t/c ratios from irradiations conducted in benzene (supplementary Table 2) are virtually invariant. The increasing E/C ratios and decreasing t/c ratios in BS as temperature is lowered are fully consistent with our hypothesis that cyclization of hydroxy 1,4-biradicals aligned in layers becomes increasingly more difficult as local order increases and solvent mobility decreases.[4] At the same time, the small fraction of biradicals from **1** trapped in defect sites of the BS lattice experiences greater difficulty in escaping from contorted conformations and gives rise to *cis*-cyclobutanols with greater probability.

Product Ratios from 1 ($m + n = 21$). On the basis of data in Figures 1 and 3, the photochemistry of a series of **1** with $m + n = 21$ was examined to determine the dependence of the product ratios on the location of biradicaloid centers along a solute chain of fixed length. Of specific importance are the absolute and relative distances of the benzhydryl and γ-radical sites from a layer boundary: the data presented demonstrate the consequences of the γ-radical site being nearer a layer boundary than the benzhydryl and vice versa. It is the positions of the loci of reaction (i.e., the biradical centers of the intermediates), and not the position of the precursor benzoyl group of **1** in a BS layer, that determine the selectivity of Norrish II reactions from **1**.

As seen in Figure 5, E/C ratios from this series of **1** in the ordered phases vary enormously, spanning >100 with **1c** and <10 with **1j** in solid BS. The variation of E/C ratios with m follows similar patterns in the hexatic B phase, but the magnitudes are larger in the more ordered solid, as expected. Elimination products from **1** ($m = 11$–14, $m + n = 21$) could not be separated ana-

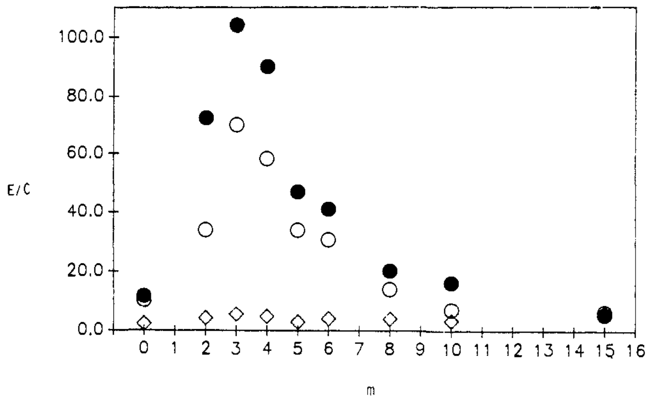

Figure 5. E/C ratios from 2% (w/w) **1** ($m + n = 21$) in the solid (10 °C, ●), hexatic B (20 °C, ○), and isotropic (30 °C, ◇) phases of BS. $n = 21 - m$ on the abscissa.

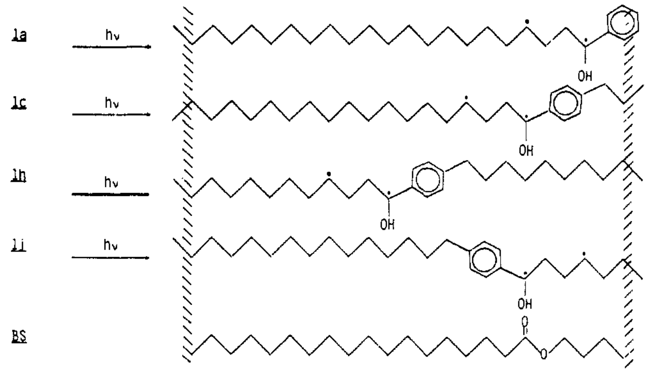

Figure 6. Representation of extended transoid hydroxy 1,4-biradicals from selected **1** ($m + n = 21$) and their orientations in a BS layer according to the surrogate solubilization model. Note the approximate depths of the hydroxyl groups of the biradicals and their relationship to the carboxyl of BS. The approximate layer boundaries are shown as shaded areas.

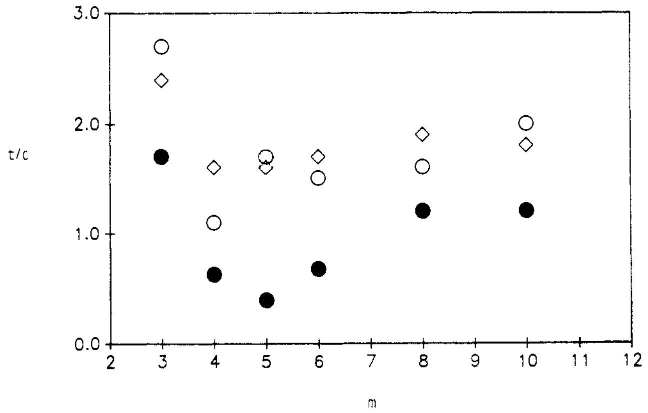

Figure 7. Ratios of *trans*- and *cis*-cyclobutanol from irradiation of 2% (w/w) **1** ($m + n = 21$) in the solid (10 °C, ●), hexatic B (20 °C, ○), and isotropic (30 °C, ◇) phases of BS as a function of benzoyl location along the solute chain. $n = 21 - m$ on the abscissa.

lytically from BS by GC with use of a Chrompack 10 m × 0.53 mm cp-sil-19 CB wide bore silica column or an Alltech RSL-300 10 m × 0.53 mm bonded fused silica heliflex column.

From the "surrogate" solubilization model for **1** ($m + n = 21$) in a layered phase of BS (Figure 6), the locus of reaction in **1c** is rather far from a layer center. *However, the hydroxyl of the 1,4-biradical from **1c** can hydrogen bond easily to carboxyl groups of neighboring BS molecules.* We believe that this interaction is a major source of the maximal product selectivity.[17] In essence, hydrogen bonding to a carboxyl of ordered BS can anchor the biradical locus along a layer and restrict its projections toward a layer middle. Prior to hydrogen abstraction, dipole–dipole forces are the strongest interactions available between any **1** and a BS molecule. Thus, ketones should not be fixed as firmly along a BS layer as their biradical intermediates when the latter can hydrogen bond to the solvent. It should be noted that each ketone will be surrounded by an average of 6 BS molecules in the layered phase matrix. Only one of them need be oriented so that its carboxyl group is near a carbonyl of **1** in order for the dipole–dipole interactions (and subsequent hydrogen bonding by the hydroxy 1,4-biradical) to occur.

Equally important to product selectivities is the projection of the biradical centers within a solvent layer. Whereas the loci of the hydroxy 1,4-biradical from **1c** point toward the more ordered layer middle, the loci from the **1j** intermediate point away from it and are located near the most disordered layer ends. As a consequence, the E/C ratios from **1j** in the ordered phases of BS are indistinguishable from the isotropic phase ratio. The biradicaloid loci from the intermediate of **1a** are about the same distance from a layer end as those from **1j**. However, they are again projected *toward* the more ordered layer middle. As a consequence, the E/C ratios from **1a** in the ordered BS phases are ca. twice those from **1j**. This difference is a true manifestation of differing selectivities imposed by solvent order since the E/C ratio from **1a** is 4–5 times smaller in the BS isotropic phase than in the hexatic B or solid phase. Thus, even if the hydroxyl groups from biradicals of both **1a** and **1j** are capable of some hydrogen bonding to neighboring carboxyl groups of BS, the consequences of the remainder of the reactive locus being projected toward or away from the least ordered portion of a solvent layer are paramount in controlling product selectivities.

The loci of reaction in **1g–i** are near the middle of the molecules and, therefore, should reside very near the highly ordered middle of a BS layer. Why the product ratios from **1g–i** are not the most selective of the $m + n = 21$ series will be discussed in the section on relative quantum yields.

The t/c ratios from irradiation of **1** ($m + n = 21$) are plotted as a function of the benzoyl location along the chain in Figure 7. Unfortunately, we were unable to separate the *cis*- and *trans*-cyclobutanols in several cases. However, the limited data include **1c**, the ketone whose E/C ratio is largest, and its contiguous relatives. Somewhat surprisingly, the t/c ratios from **1c** in the ordered phases of BS are the *largest* measured. This observation seems in conflict with the explanation used for the data in Figure 3. Since the isotropic phase t/c ratio from **1c** is also very high and the ratios from the other **1** in the ordered phases are consistent with previous arguments, we are reluctant to speculate about the origin of this anomaly: cyclobutanol formation represents less than 1.5% of the total **1c** reaction in the ordered phases and the analytical separation of products was not as clean as in many other cases; consequently, the mechanistic value of the apparent t/c ratio may be limited. Conversely, t/c ratios from **1** ($m = 5$, $n = 13$) in BS (Figure 3) are also larger than expected. This suggests that the biradicals responsible for cyclobutanols from the two ketones may be incorporated within BS layers rather than existing at defect sites. If true, their t/c ratios represent the ability of the BS layers to differentiate between the shapes of the diastereomeric cisoid and transoid hydroxy 1,4-biradical conformers.

Infrared Studies of Hydroxy 1,4-Biradical Models in BS. Alcohols **2c** and **2g** were synthesized from the corresponding ketones, and their infrared spectra were recorded in BS and in eicosane. By subtracting the spectra of the neat solvents from those of the solute-containing mixtures, details of the hydroxyl absorptions were revealed (Figures 8–11).

The structures of **2c** and **2g** differ only slightly from the hydroxy 1,4-biradicals derived from **1c** and **1g** and, therefore, they model interactions between the two biradicaloid intermediates and BS molecules in anisotropic phases. The choice of **2c** and **2g** is based upon our hypothesis that hydrogen bonding in the layered phases will occur between BS molecules and hydroxy 1,4-biradicals from

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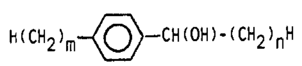
[17] The Lewis basicity of a carboxy should increase E/C ratios and decrease t/c ratios of nearby hydroxy 1,4-biradicals,[13] regardless of solvent order. However, the magnitude of the expected changes is much too small to explain our results.



2c m = 3, n = 18

2g m = 8, n = 13

1c, but not from **1g** (Figure 6).

In Figures 8b and 9b, the spectra of **2c** and **2g** in solid eicosane are similar and very weak. Both show a relatively sharp peak at 3602 and 3620 cm^{-1}, respectively, from free hydroxyl vibrations[18] and a very broad peak centered at <3400 cm^{-1} from hydroxyl vibrations of hydrogen-bonded alcohols in aggregation.[18] The isotropic phase spectra of the same samples (Figure 8a and 9a) are more intense. They contain a strong peak at 3620 cm^{-1}, indicating a larger mole fraction of isolated alcohol and the broad aggregation peak, now centered at ca. 3500 cm^{-1}. The isotropic phase spectrum of **2g** in BS (Figure 10a) shows only a small free hydroxyl absorption (3619 cm^{-1}) and a predominant absorption at 3534 cm^{-1} attributed to hydroxyls that we associate with carboxyl groups of BS molecules. At room temperature, **2c** and **2g** in ethyl acetate display intense broad peaks at 3526 and 3528 cm^{-1}, respectively. In the hexatic B phase of BS, the spectrum of **2g** (Figure 10b) indicates a small amount of free hydroxyl. The broad absorption appears to have two major components, one from carboxy-associated hydroxyl vibrations (ca. 3524 cm^{-1}) and the other from self-associated hydroxyl vibrations at lower frequencies. Although the exact proportions of each cannot be calculated, it is clear that the self-associated hydroxyls are the major component.

Figure 11 presents the absorption spectra of **2c** in BS. The isotropic phase spectra of **2c** and **2g** are very similar in shape. The absorption maxima of **2c** occur at 3619 and 3533 cm^{-1}. A major difference between the hexatic B phase spectra of **2c** and **2g** is obvious. In Figure 11b, the absorptions associated with free and self-associated hydroxyl vibrations are very weak. The one dominant feature of the spectrum is the absorption at 3528 cm^{-1} assigned to carboxy-associated hydroxyl vibrations.

The differences between Figures 10b and 11b are striking and expected from the surrogate solubilization model of Figure 6. The hydroxyl group of **2c** can lie near carboxyl groups of neighboring BS molecules in the layered phases; the hydroxyl of **2g** is removed from the carboxyl groups. That some carboxy-associated hydroxyl absorption is found with **2g** in smectic BS is not surprising given the large solute concentrations (5% by weight) employed to facilitate the recording of spectra. Regardless, a cursory comparison between Figures 10b and 11b supports the selective nature of ordered solvent interactions with hydroxy 1,4-biradicals from **1**.

Relative Quantum Yields for Disappearance of 1 ($m + n = 21$). In spite of the many experimental difficulties associated with measuring quantum yields in liquid-crystalline media,[19] we have accumulated a body of data from irradiation of **1** ($m + n = 21$) in the various phases of BS (Figure 12) that is self-consistent and reproducible. Also, in accord with the very similar lifetimes observed for the triplet biradical from **1** ($m = 0$, $n = 19$) in the isotropic and smectic phases of BS,[2] the corresponding relative quantum yields are within the limits of experimental error. Due to the potentially large experimental errors, small differences among the Φ_{rel} are considered inconsequential.

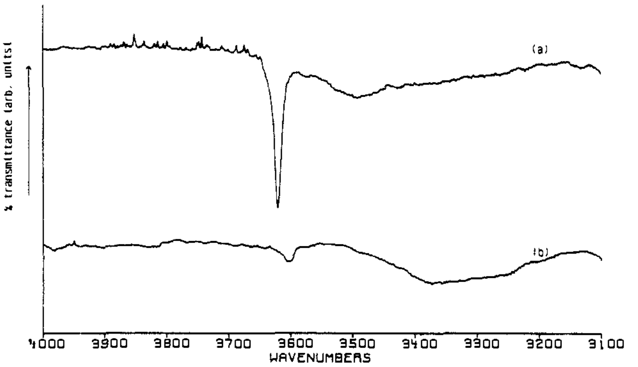


Figure 8. FTIR absorption spectra of 5% (w/w) **2c** in eicosane (after subtraction of the neat solvent spectrum; 1280 scans, 2-cm^{-1} resolution) at 42 °C (a, isotropic phase) and 28 °C (b, solid phase).

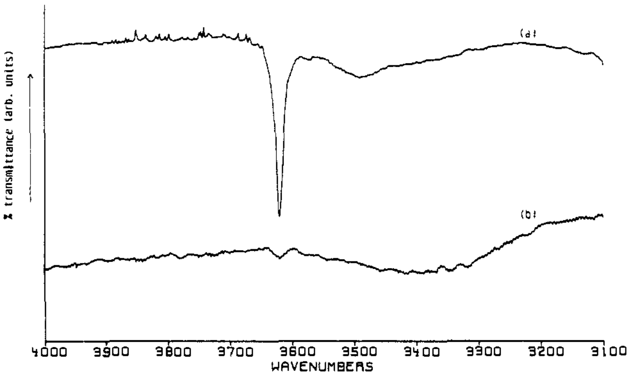


Figure 9. FTIR absorption spectra of 5% (w/w) **2g** in eicosane (after subtraction of the neat solvent spectrum; 1280 scans, 2-cm^{-1} resolution) at 42 °C (a, isotropic phase) and 28 °C (b, solid phase).

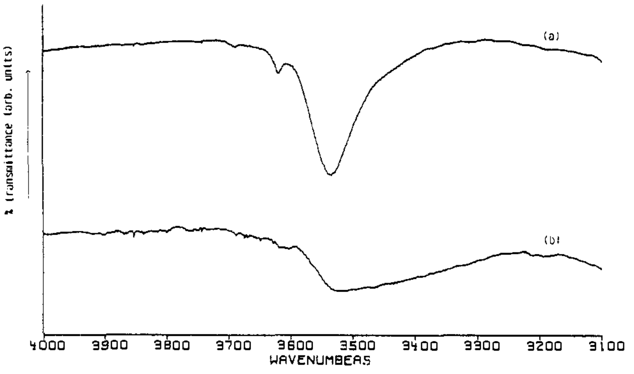


Figure 10. FTIR absorption spectra of 5% (w/w) **2g** in BS (after subtraction of neat solvent spectrum; 1280 scans, 2-cm^{-1} resolution) at 31 °C (a, isotropic phase) and 18 °C (b, hexatic phase).

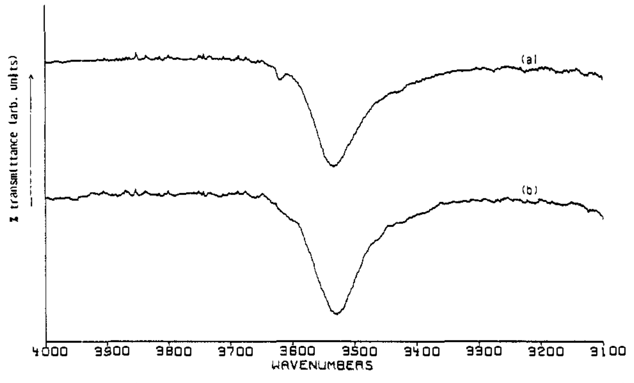


Figure 11. FTIR absorption spectra of 5% (w/w) **2c** in BS (after subtraction of neat solvent spectrum; 1280 scans, 2-cm^{-1} resolution) at 31 °C (a, isotropic phase) and 18 °C (b, hexatic phase).

The isotropic phase Φ_{rel} for all **1** ($m + n = 21$) are near the maximum value, as expected for long-chained alkanophenones that are able to undergo facile conformational changes. In the smectic and, especially, in the solid phases, two classes of behavior emerge for the Φ_{rel} of **1**: **1a–f** and **1j** exhibit $\Phi_{rel} > 0.6$ and **1g–i** have markedly lower efficiencies. The large Φ_{rel} from the former groups of **1** indicate that their excited triplet states are able to attain easily the bulky conformation necessary for γ-hydrogen abstraction and then adopt biradical conformations that yield products. Since neither hydrogen abstraction is attenuated nor back hydrogen transfer from the biradicals is promoted appreciably even in the solid phase of BS, these ketones and their intermediates must experience a somewhat mobile environment near their loci of reaction. On the other hand, the exceedingly large E/C ratios

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[18] Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley: Chichester, 1980; Chapter 6.

[19] (a) Nerbonne, J. M.; Weiss, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 402. (b) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413.

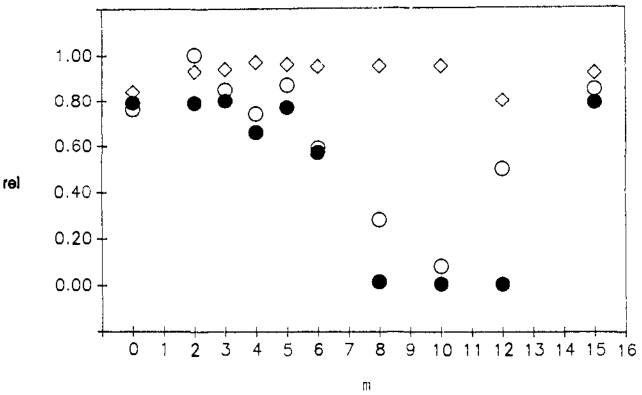

Figure 12. Relative quantum yields for conversion of 2% (w/w) **1** ($m + n = 21$) to less than 20% disappearance in the solid (10 °C, ●), hexatic B (20 °C, ○), and isotropic (30 °C, ◇) phases of BS. $n = 21 - m$ on the abscissa.

require that the immediate environment of the biradicaloid centers be very ordered.

These observations can be accommodated by the surrogate solubilization model illustrated in Figure 6. In all of the ketones with high Φ_{rel} in the ordered BS phases, the benzoyl groups (and, therefore, biradicaloid centers) are located near a somewhat disordered layer end. Prior to γ-hydrogen abstraction and hydroxy 1,4-biradical formation, the strongest interactions available to a ketone and neighboring BS molecules are from dipole–dipole forces. Since these are relatively weak and the bulky phenyl group causes a disturbance to its local environment, the carbonyl and nearby methylenes of **1** should be able to move somewhat freely in the vicinity of layer ends, allowing efficient hydrogen abstraction. Once formed, the biradicals localized near layer ends are capable of donating hydrogen bonds to nearby carboxyl groups. This stronger interaction causes more specific solvent–intermediate interactions (that lead to photoproduct selectivity) without increasing reversion to **1**: in isotropic media, Lewis bases *increase* the efficiency with which hydroxy 1,4-biradicals give products, and absolute quantum efficiencies for reaction of alkanophenones in very polar solvents approach unity.[8a,b,20]

The loci of reaction in **1g–i** are near the middle of the molecules and, therefore, should be very near the highly ordered BS layer middle if solubilized as shown in Figure 6. In spite of this, the E/C ratios from these ketones are far from the largest in the series (Figure 5), and their Φ_{rel} are exceedingly low in the ordered phases of BS. When viewed together, the E/C ratios and Φ_{rel} suggest that reaction of **1g–i** occur primarily from a small fraction of the total solute population that exists at solubilization sites different from those shown in Figure 6. The majority of **1g–i** may be incorporated within a BS layer and be almost photoinert.

Parts c and d of Figure 2 show that some phase separation does occur with 2 wt % **1g** and **1h** in BS. The dsc of **1i** is very similar to that of **1h**. The other ketones of the $m + n = 21$ series in BS yield dsc curves almost indistinguishable from those of the neat solvent. Thus, the **1** whose benzoyl groups are expected to lie nearest a BS layer middle are incorporated with the greatest difficulty. These results would indicate that the very ordered region of a layer experienced by **1** (that is, the portion capable of severely impeding the motions necessary for initial γ-hydrogen abstraction) is limited to a relatively small part of the total length. Essentially, triplet states of **1g–i** in BS layers are predicted to experience a great deal of difficulty in attaining the initial conformation necessary for γ-hydrogen abstraction.

Conclusions. These results indicate that initially excited triplets of **1** whose lengths are comparable to BS and whose carbonyl groups are near a BS carboxyl in a layered phase are relatively unconstrained in adopting conformations that can lead to γ-hydrogen abstraction. Their hydroxy 1,4-biradicals interact strongly with the carboxyl groups and the consequences of that interaction differ enormously depending upon whether the γ-radical center is projected toward a layer middle (significant control over product selection) or toward a layer end (less or negligible control over product selection). By contrast, **1** whose carbonyl groups and γ-carbons are initially near a layer middle experience an environment from which formation of bent conformations that are needed to form hydroxy 1,4-biradicals is exceedingly difficult. In the most ordered solvent matrices of BS, some molecules of **1** may be forced into defect sites in which higher energy conformations are imposed and from which product distributions not reflective of the environment of the vast majority of ketones can be produced.

The degree to which ordered phases of BS influence product selectivity also depends upon the fit of **1** into a solvent layer. Ketones whose length is near that of an extended BS molecule are less disruptive to their local environment than shorter or longer homologues. As such, they and their intermediates experience greater order along their reaction course and greater product selectivity.

Thus, a macroscopically ordered solvent like BS can provide environments to solutes like **1** that vary from being very restrictive to very permissive of nearly all deviations from fully extended conformations.

Finally, it should be reiterated that the crystalline and hexatic B phases of BS provide matrices that must allow very limited mobility to many of the ketones and their hydroxy 1,4-biradical intermediates. At the present time, little is known about the triplet biradical conformations and motions that facilitate intersystem crossing and allow ground-state product formation.[9a,21] The geometric constraints imposed by BS on the biradicals may be reflected in their triplet lifetimes if only a limited number of conformations facilitates intersystem crossing. We hope to explore this dependence in future studies.

Experimental Section

NMR spectra were recorded on a Bruker AM-300 WB spectrometer on a dedicated Aspect 3000 computer. Melting and transition temperatures (corrected) were obtained with a Kofler hot-stage microscope equipped with crossed polarizing lenses. Analytical gas chromatography employed a Perkin-Elmer 3920 B gas chromatograph (flame ionization detectors) with a Perkin-Elmer M2 integrator or a Perkin-Elmer 8500 gas chromatograph and a 10 m × 0.53 mm Chrompack CP-Sil-19 CB wide bore silica column. Unless noted otherwise, peak responses for photoproducts from each ketone were normalized. Infrared spectra were obtained on a Nicolet 170 SX FTIR spectrophotometer. Thermostated samples were placed between AgCl disks and 1280 scans were averaged. To obtain the reported spectra, an equal number of averaged scans from neat solvent were subtracted from the solution spectra. UV spectra were recorded on a Perkin-Elmer 552 spectrophotometer.

Differential Scanning Calorimetry. Heating and cooling curves were recorded (in that order) on ca. 5-mg samples sealed in two-piece aluminum pans with a Dupont 1090 scanning calorimeter. The rate of the temperature change was 2 deg/min. Samples were prepared as mentioned above for irradiations. All curves could be reproduced quantitatively durng second heating–cooling cycles.

Chemicals. BS (98% pure by GC) synthesized from stearic acid (Aldrich, 99%) and 1-butanol (Baker Reagent)[19a] was a gift from Jon Baldvins. It was free of both stearic acid and 1-butanol. Benzene (Baker Analysis Reagent) was used as received.

p-Alkylalkanophenones were prepared via a standard Friedel-Crafts procedure[2] employing commercially available alkylbenzenes and acyl chlorides either purchased or prepared from the carboxylic acids and thionyl chloride. Typically, ca. 1 mmol of acyl chloride and 1 mmol of alkylbenzene were dissolved in 100 mL of dry methylene chloride. In a dry atmosphere at 0 °C, 1.5 g of anhydrous $AlCl_3$ were added and the mixture was stirred at 0 °C for 30 min. After workup (sequential extractions with ice water, 10% aqueous $NaHCO_3$, and saturated aqueous NaCl solutions), the dried (anhydrous $MgSO_4$) organic liquid was evaporated to residue on a rotary evaporator. The crude product was recrystallized from methanol–ether. Except for **1a**, the ^{1}H NMR spectra of the *p*-alkylalkanophenones in the low-field region are very similar. The intensity of the high-field resonances depends upon the alkyl chain lengths. For example, the spectrum of 1-(4-pentylphenyl)hexadecan-1-one (**1** with $m = 5$, $n = 15$) is assigned as follows ($CDCl_3$, TMS): δ 7.57 (AB pattern, $J = 8.2$ Hz, 4 H, aromatic), 2.93 (t, $J = 7.4$ Hz, 2 H, $-COCH_2-$), 2.65 (t, $J = 7.7$ Hz, 2 H, $ArCH_2-$), 1.6–1.75 (m, 4 H, $ArCH_2CH_2-$ and $-COCH_2CH_2-$), 1.26 (~s, 28 H, methylenes), 0.88 (m, 6 H, methyls). The UV absorption spectra of **1** are also very similar.

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[20] Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

Table I. Alkylalkanophenone Syntheses

1		yield,[a]	purity,	
m =	*n* =	%	%[b]	mp, °C
5	11	69	98	36.0–37.0
5	13	70	98	40.5–42.5
5	14	*c*	98	42.0–43.0
5	15	68	98	50.5–52.0
5	16	50	98	48.5–49.5
5	17	65	98	53.0–54.0
5	18	60	99	54.0–55.5
0	21	60	99	73.0–74.0[d]
2	19	68	97	64.5–66.5
3	18	65	98	54.5–55.5
4	17	70	97	53.0–54.5
6	15	74	99	52.0–52.5
8	13	71	99	57.0–58.0
10	11	68	99	65.5–67.5
12	9	62	99	59.5–60.5
15	6	63	>99	45.0–46.0

[a] After purification. [b] By GC analysis. [c] Prepared by Dr. Richard Treanor. [d] Lit.[2] mp 73.5–75 °C.

For **1** (*m* = 5, *n* = 15) (cyclohexane), λ_{max} 250 nm (ϵ 1.8 × 10^4) and 312 nm (ϵ 71). Further data are collected in Table I.

p-Alkylacetophenones, one of the expected photoelimination products, were synthesized by the same Friedel-Crafts procedure with alkylbenzenes and acetyl chloride. 1-Alkenes, the other elimination products, were obtained commercially when available. In their absence, the corresponding alkanes were used since the GLPC retention times are nearly identical with the alkenes on the column employed. The alcohol reduction products, 1-(4-propylphenyl)-1-nonadecanol (**2c**, 95% pure, mp 38.5–40.0 °C) and 1-(4-octylphenyl)-1-tetradecanol (**2g**, 98% pure, mp 32.5–33.5 °C), were prepared by treatment of **1** (*m* = 3, *n* = 18) and **1** (*m* = 8, *n* = 13), respectively, with sodium borohydride in 2-propanol. Eicosane (99% pure, mp 37.1–38.1 °C) was a gift from Dr. Alberto Nunez.

Usually, cyclization products were not isolated. They exhibit characteristic chromatographic properties that allow their identity to be inferred.[2,13] However, the cyclization products from **1** (*m* = 5, *n* = 17) were isolated after its irradiation (300 mg in 20 mL of N_2-saturated 1/9 2-propanol–hexane; Pyrex filter) to a high percent conversion. After evaporation on a rotary evaporator, the residue was eluted through a 3.5 cm × 21 cm column of silica (Aldrich, 230–400 mesh) with 1/10 ethyl acetate–hexane. The longer retention time cyclobutanol peak by GC eluted first on the silica column. The second isomer was isolated with 4-pentylacetophenone, an elimination product. The proton NMR spectrum of the first eluting isomer ($CDCl_3$/TMS) showed peaks at δ 7.26 (AB pattern, *J* = 8.2 Hz, 4 H aromatic) and at δ 2.59 (t(+m), *J* = 7.7 Hz, 3 H, benzylic plus cyclobutyl), 2.38 (q, *J* $\simeq$ 9 Hz, 1 H, cyclobutyl), 2.15 (m, 1 H, cyclobutyl), 1.95 (m, 1 H, cyclobutyl), 1.80 (m, 1 H, cyclobutyl), 1.74 (m, 2 H, $ARCH_2CH_2$), 1.59 (s, 1 H, hydroxyl), 1.25 (~s, 30 H, methylenes), and 0.88 (2 s, 6 H, methyls). When 20% (v/v) CD_3OD was added to the $CDCl_3$, the singlet at δ 1.59 disappeared and a new singlet appeared at δ ~4.3. The spectrum of the contaminated isomer was qualitatively similar to that of the pure one, but its resonances could not be separated satisfactorily from those of 4-pentylacetophenone. On the basis of its greater yield from irradiations in hydrocarbon solvents[13,16b,22] and isotropic BS,[2] the first eluting (pure) isomer was designated as trans. In all other cases, the cyclobutanol isomer obtained in greater yield from isotropic phase irradiations was taken to be trans.

Irradiation Procedures. An alkylalkanophenone (2% by wt) was dissolved in isotropic BS and the solution was bubbled with N_2 for 10 min. Aliquots were transferred to Pyrex capillary tubes and purged again with N_2, and the tubes were flame-sealed. The sample was heated to the isotropic phase and placed in a thermostated water bath for 10 min prior to irradiation. Tubes were irradiated with a 450-W medium-pressure Hg arc for periods that allowed <20% conversion (usually 2–4 min in isotropic and 4–10 min in smectic or solid phases) for determination of E/C ratios and for longer periods (60–90% conversion) for t/c ratios. Small differences were found between t/c ratios from experiments with small and large percent conversion. After irradiation, the tubes were broken and their contents dissolved in hexane. Data reported are the average of at least one determination from 3 or more tubes.

The same procedure was employed in measurements of relative quantum yields except that the tubes were mounted in the bath as radical spikes on a rotating wheel that allowed each sample to experience the same amount of radiation over a fixed period of time.

Experiments in different phases were normalized by irradiating one (or more) ketone at 10, 20, and 30 °C on the same day without altering the configuration of the apparatus. However, experiments conducted on different days agreed well with those conducted on the same day.

Irradiations in benzene were conducted by placing 2% (w/w) of **1** (*m* = 5, *n* = 15) in the solvent and deoxygenating the solution for 5 min with bubbling N_2. The Pyrex tube holding the sample was sealed with a flame and placed in a thermostated water bath. Irradiations were conducted with a 450-W medium-pressure Hg arc as before.

Although the precision of Φ_{rel} measurements is good, absolute errors are large (probably ±50%) due to reflection and diffraction of radiation by the anisotropic phases; E/C and t/c ratios are more accurate (±20% or less) since they depend only upon internal comparisons.

Data presented graphically are included with precision error limits in supplementary tables.

Acknowledgment. We thank Jon Baldvins and Drs. Alberto Nunez and George Hammond for helpful discussions. The National Science Foundation (Grant CHE 88-18873) is thanked for its support of this work.

Supplementary Material Available: Tables of product ratio and relative quantum yield data (3 pages). Ordering information is given on any current masthead page.

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(22) (a) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 6959. (b) Casal, H. L.; de Mayo, P.; Miranda, J. F.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5155.