

Type II Photochemistry of Ketones in Liquid Crystalline Solvents. The Influence of Ordered Media on Biradical Dynamics¹

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Abstract: The Norrish type II photochemistry of five alkylphenones, PhCO(CH₂)_nH (**1a**, *n* = 4; **1b**, *n* = 10; **1c**, *n* = 17; **1d**, *n* = 19; **1e**, *n* = 21), 10-nonadecanone (**2**), and 2-undecanone (**3**) was studied in the isotropic, smectic, and solid phases of *n*-butyl stearate. The ratio of elimination-to-cyclization products for ketones **1c–e** and **2** exhibits a strong phase dependence with a 7–8-fold increase in the smectic phase relative to the isotropic phase. The ratio of isomeric cyclobutanols from **2** shows a similar change. Further increases in the elimination-to-cyclization ratio are observed for **1d** in the solid phase. The product ratios for ketones **1a**, **1b**, and **3** are the same in all the phases studied. Transient absorption studies on the intermediate 1,4-biradical produced from laser flash photolysis of **1d** yield lifetimes of 64 ± 5 and 70 ± 5 ns in the isotropic and smectic phases, respectively. These results are explained in terms of the structures of the various phases of *n*-butyl stearate and the accepted behavior of Norrish type II biradicals.

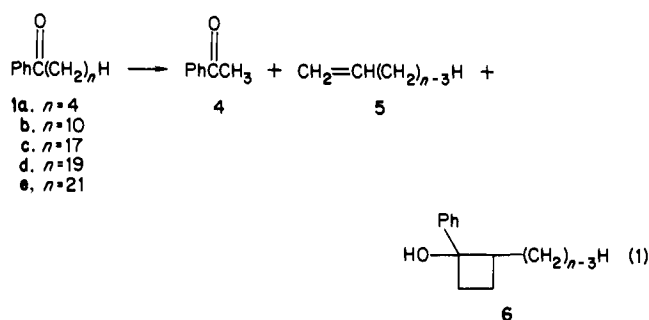
The Norrish Type II reaction is one of the most extensively studied and best understood photochemical reactions of ketones.^{2,3} The efficiency of the type II reaction is known to be a sensitive function of solvent polarity,^{2b} temperature,^{2c} and substitution.^{2d} The wealth of data available on this reaction in homogeneous solutions has made it a useful probe for the properties of a variety of unusual environments. Numerous studies have appeared involving type II ketone photochemistry in media such as micelles,^{4,5} monolayers,⁵ polymers,⁶ inclusion compounds,⁷ and crystalline solids.^{6,8}

It has previously been shown that the ordered structure in liquid crystalline solvents can influence the outcome of a variety of chemical reactions. Dimerization reactions,⁹ radical-pair dynamics,¹ and unimolecular isomerizations¹⁰ have been shown to depend on the phase of the liquid crystalline solvent. In particular, the efficiency of the type II reaction of α -diketones^{11a} and the ease of intramolecular excimer formation from α,ω -bis(1-pyrenyl)alkanes^{11b} have been shown to depend on the solvent molecular order.

Type II reactivity of ketones is known to be influenced strongly by conformational flexibility in the molecule.³ Since it is possible that the ordered structure of liquid crystalline mesophases may impart some control on the conformational dynamics of dissolved solute molecules,^{10,11} we have studied the type II photochemistry of five *n*-alkylphenones (**1a–e**) and two dialkyl ketones, 10-nonadecanone (**2**) and 2-undecanone (**3**), in isotropic and liquid crystalline solvents. The liquid crystal used was *n*-butyl stearate which exhibits an isotropic phase above 26.1 °C and a smectic phase between 15.0 and 26.1 °C. The smectic phase consists of discrete layers of fully extended, hexagonally close-packed molecules in which the long axes are parallel to one another and perpendicular to the layer plane.¹²

Results

Photolysis of Ketones 1a–e. Photolysis of ketones **1a–e** (0.02 M) in *n*-heptane, *n*-butyl acetate, *n*-heptadecane, and *n*-butyl stearate (1.0 mol %) at 30 °C resulted in the formation of acetophenone (**4**), alkenes **5a–e**, and cyclobutanols **6a–e** as shown in eq 1. The ratios of elimination products (**4**) to cyclization products (**6**) for each ketone are listed in Table I. The increase observed upon changing the solvent from *n*-heptane to *n*-butyl acetate is consistent with an increase in the solvent polarity.^{2b} When ketones **1a–e** were photolyzed at 20 °C in *n*-heptane or *n*-butyl acetate no change in the product ratio was observed. These results are consistent with previous reports regarding the insensitivity of the product ratio to temperature over the range 22–55 °C.^{2c} In fact, even when the photolysis was carried out at 20 °C



in solid *n*-heptadecane (mp 22.5 °C), no significant change was observed in the product ratio.

Surprisingly, when ketone **1d** was photolyzed in the smectic phase of *n*-butyl stearate at 20 °C an 8-fold increase in the product ratio (**4/6d**) was observed. It was also observed that the percent conversions were not significantly altered when the ketones were photolyzed in either the isotropic or smectic phases of *n*-butyl stearate. Thus, relative to the situation in isotropic solvents at 20 °C, a decrease in the yield of **6d** as well as an increase in **4** was observed. Ketones **1c** and **1e**, both of similar dimensions to **1d**, exhibited analogous type II behavior in *n*-butyl stearate. While the product ratios for ketones **1c–e** were dramatically affected by the smectic phase, no significant change in the product ratio was observed for either ketone **1a** or **1b**.

(1) This paper is Part 14 in the Georgetown series, Liquid Crystalline Solvents as Mechanistic Probes. For Part 13 see: Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.*, **1984**, *106*, 5291.

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Table I. Product Ratios^a (4/6) for the Type II Reaction of Ketones 1a-e

ketone	solvent	solvent			
		<i>n</i> -heptane	<i>n</i> -butyl acetate	<i>n</i> -hepta-decane	<i>n</i> -butyl stearate
1a	30 °C	2.3	4.2	1.9	3.2
	20 °C	2.6	4.1	2.9	3.3
	20 °C/30 °C	1.2	1.0	1.5	1.0
1b	30 °C	0.8	2.0	1.3	1.7
	20 °C	0.7	1.9	1.7	2.0
	20 °C/30 °C	0.9	0.9	1.3	1.2
1c	30 °C	1.1	2.0	1.0	3.0
	20 °C	1.1	2.2	1.2	21
	20 °C/30 °C	1.0	1.1	1.2	7.0
1d	30 °C	1.8	2.0	1.0	1.9
	20 °C	1.5	2.0	0.7	15
	20 °C/30 °C	0.8	1.0	0.7	7.9
1e	30 °C				1.3
	20 °C				9.5
	20 °C/30 °C				7.5

^a Values are not corrected for differences in detector response (error $\pm 10\%$).

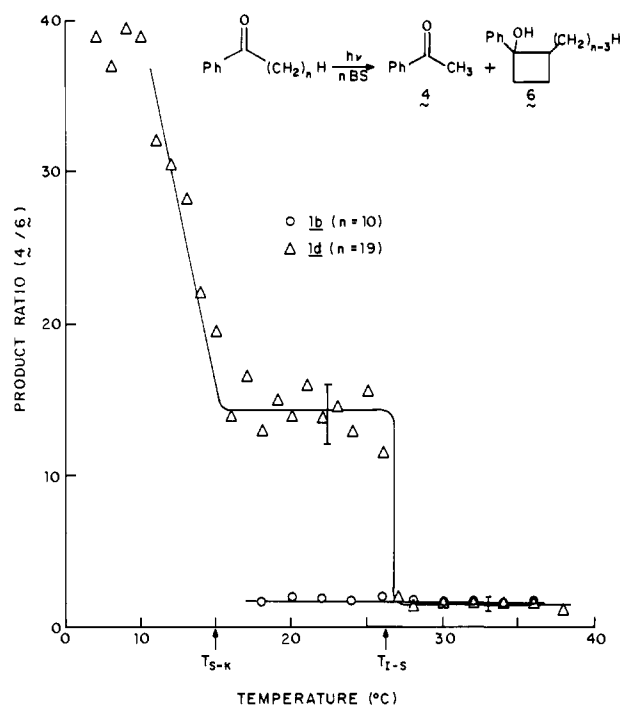


Figure 1. Temperature dependence on the ratio of elimination (4) to cyclization (6) products for photolysis of ketone 1d (\blacktriangle) and 1b (\circ) in *n*-butyl stearate. The lines are drawn through points to show the trends in the data only.

Temperature Dependence on the Product Ratio in *n*-Butyl Stearate. To clarify the origin of this liquid crystal effect the product ratio for ketone 1d was measured over a temperature range encompassing the isotropic, smectic, and solid phases of *n*-butyl stearate (Figure 1). The average value for the product ratio (4/6d) was 1.7 ± 0.2 for temperatures greater than 26 °C and 14 ± 2 for temperatures between 16 and 26 °C. Similar behavior was observed for 1c over the same temperature range. However, the average value for the product ratio (4/6b) for ketone 1b was 1.8 ± 0.2 in both the isotropic and smectic phases.

The discontinuities in Figure 1 correspond to the temperatures reported by Krishnamurti et al.¹² for the isotropic-smectic ($T_{i-s} = 26.1$ °C) and smectic-solid ($T_{s-k} = 14.8$ °C) transitions obtained by examination of the changes in phase textures under a polarizing microscope. The discontinuities observed at the isotropic-smectic (T_{i-s}) and smectic-solid (T_{s-k}) transition temperatures and the

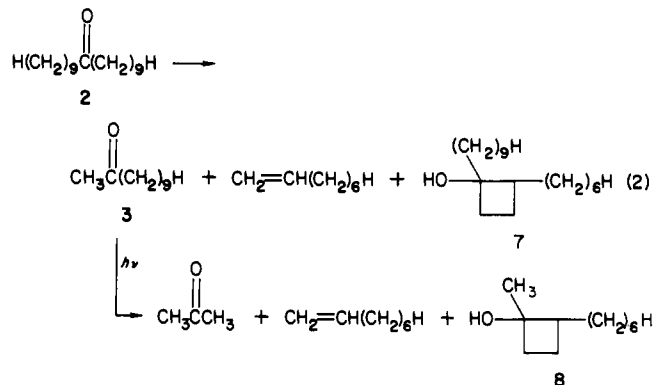
Table II. Product Ratios^a for Type II Reactions of Ketones 2 and 3

ketone	solvent			
	<i>n</i> -hexane ^e	<i>tert</i> -butyl alcohol ^e	<i>n</i> -butyl stearate	
			31 °C	20 °C
2 (3/7)^c	2.4 ± 0.4	1.9 ± 0.2	1.3 ± 0.1	9.4 ± 1.2
2 (7t/7c)^f	2.6 ± 0.4	1.7 ± 0.2	2.4 ± 0.3	$>10^b$
3 (8t/8c)^{d,f}	1.5 ± 0.1	1.0 ± 0.0	1.2 ± 0.2	1.3 ± 0.2

^a Errors are calculated as the standard deviation of GC analyses with 2–5 injections per sample. ^b The minor isomer peak was too small to make an accurate calculation of the ratio by GC. ^c The conversions were kept low, <5%, to avoid secondary photolysis. ^d The ratios were determined at higher conversions (30%). ^e Room temperature. ^f See ref 16.

constant values for the product ratio (4/6d) in both phases confirm the phase-dependent origin of the effect. While a correlation between the product ratio and the isotropic-smectic and smectic-solid phase transitions is apparent, the reason for the continued increase in 4/6d below 15 °C is not. However, Krishnamurti et al.¹² and Dryden¹³ report further solid-phase transitions below 15 °C. Further study is needed to determine whether this is in fact the cause for this unusual behavior.¹⁴

Photolysis of 10-Nonadecanone (2) and 2-Undecanone (3). Although the molecular order in the smectic phase appears to be a primary influence, the lack of an effect on the product ratios for ketones 1a and 1b in the smectic phase indicates that the observed effects are dependent on solute structure as well. To further probe this solute structure dependence the dialkyl ketone, 10-nonadecanone (2), was photolyzed in *n*-butyl stearate (eq 2). This ketone is expected to be easily incorporated into the smectic phase as evidenced by only a small depression (0.5 °C) in the isotropic-smectic phase transition temperature upon addition to *n*-butyl stearate.¹⁵ The elimination-to-cyclization ratios for photolysis of 2 in standard isotropic solvents are listed in Table II. The change in the product ratio for ketone 2 and the *trans*-/*cis*-cyclobutanol ratio for both ketones 2 and 3 results from a change in solvent polarity. However, as found for ketones 1c-e,



a 7-fold increase in the ratio of elimination-to-cyclization products (3/7) was obtained when the photolysis was carried out in the smectic phase relative to the isotropic phase of *n*-butyl stearate. In addition to the increase in this ratio, a concomitant increase in the ratio of *trans*-cyclobutanol to *cis*-cyclobutanol was obtained.¹⁶ In fact, within the detection limits of the analysis, only the *trans*-cyclobutanol was formed (Table II). In contrast, the photolysis of the shorter ketone, 2-undecanone (3), in *n*-butyl

(13) Dryden, J. S. *J. Chem. Phys.* **1957**, *26*, 604.

(14) Unusual behavior was also observed in this temperature range for the recombination of benzyl radicals in *n*-butyl stearate (see ref 1).

(15) For studies on the effect of solute structure on phase stability see: Oweimreen, G. A.; Martire, D. E. *J. Chem. Phys.* **1980**, *72*, 2500. Oweimreen, G. A.; Lin, G. C.; Martire, D. E. *J. Phys. Chem.* **1979**, *83*, 2111.

(16) The GC retention times of similar *trans*-cyclobutanols on similar GC columns^{16a} are known to be shorter than those of the corresponding *cis* isomers. The *trans*- to *cis*-cyclobutanol ratios are usually >1 .^{7,8,16a} On the basis of these considerations, the stereochemistries, of the isomers of 7 and 8 are tentatively assigned. (a) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

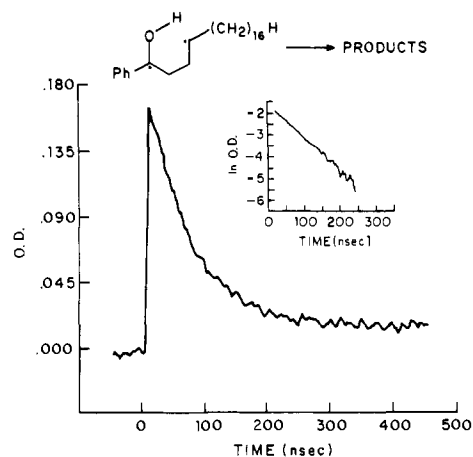


Figure 2. Representative transient absorption decay at 317 nm after laser flash photolysis of **1d** at 20 °C in the smectic phase of *n*-butyl stearate.

stearate resulted in absolutely no enhancement in the *trans*-/*cis*-cyclobutanol ratio when photolyzed in the smectic relative to the isotropic phase. The results confirm that the influence of the liquid crystalline phase on solute reactivity is strongly dependent upon solute-solvent interactions which are, themselves, a sensitive function of solute shape.

Laser Flash Photolysis of **1d.** The identity and kinetic behavior of the intermediate 1,4-biradical obtained from the Norrish type II reaction of alkyl phenones has been well established by using laser flash photolysis-transient absorption techniques.^{17,18a,b} Typically, lifetimes for type II derived triplet biradicals are on the order of $\sim 10^{-8}$ to $\sim 10^{-7}$ s and are dependent on solvent polarity. In particular, the lifetime of the triplet biradical obtained from laser flash photolysis of valerophenone (**1a**) increases from ~ 30 to ~ 100 ns upon changing the solvent from heptane to methanol.^{17b} Laser flash photolysis of ketone **1d** in the isotropic (30 °C) and smectic (20 °C) phases of *n*-butyl stearate yielded biradical lifetimes of 64 ± 5 and 70 ± 5 ns, respectively (Figure 2). The value obtained in a standard isotropic solvent, *n*-butyl acetate, was 68 ± 5 ns. These values indicate that the biradical derived from **1d** resides in a moderately polar environment in both *n*-butyl acetate and *n*-butyl stearate. The similarity in the lifetimes of the biradical in the isotropic and smectic phases of *n*-butyl stearate supports the suggestion that the benzoyl group resides in the ester region of the smectic layers.

Discussion

Description of *n*-Butyl Stearate Phase Structure. The origin of the phase effects described above is a direct result of the molecular packing in the smectic and solid phases of *n*-butyl stearate. X-ray diffraction studies on thin films of *n*-butyl stearate¹² indicate a molecular arrangement in which the long axes of the molecules are aligned parallel within a layer of width ~ 32 Å (i.e., length of *n*-butyl stearate, fully extended). Furthermore, within the layers the molecules are arranged in a hexagonal close-packed structure. Although there are considerable conformational constraints imposed on the individual molecules in the smectic phase, IR and NMR results indicate that the methylene units are free to rotate resulting in axial symmetry about the long axes of the molecules. However, upon entering the solid phase the rotational motion of the methylene units is severely hindered due to intermolecular interactions. This decreased mobility results in a loss of the axial symmetry of the molecules and an overall change in the crystal structure from hexagonal close packed to orthorhombic.

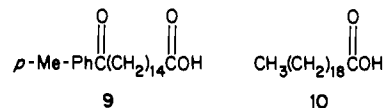
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It is well-known that dissolved solute molecules can be incorporated within liquid crystalline mesophases. Furthermore, the more similar the solute molecule is to the liquid crystal molecule, in size and shape, the easier it will be for the solute to become incorporated into the liquid crystalline phase.¹⁵ Therefore, if the outcome of a chemical reaction depends on solvent order, the largest effects are expected for those solute molecules which fit best into the liquid crystal structure. It is obvious that the structures of ketone **1c** and *n*-butyl stearate are identical except for the terminal phenyl and butoxy groups. Furthermore, molecular models indicate that ketones **1d** and **1e** are approximately the same length as *n*-butyl stearate itself. Since the main structural similarity is the alkyl portion of the molecules, it is reasonable to expect that the ketones will be incorporated into the liquid crystalline lattice so that the alkyl chains are aligned. The resulting lattice interactions should cause the alkyl chain of the ketones to be fully extended. As a result of the alignment of the alkyl chains the benzoyl portion of the ketone should reside in the ester region of the smectic layer. However, to keep the solvent disturbances to a minimum the benzoyl group should acquire a geometry in which it is aligned parallel to the surrounding ester head groups of *n*-butyl stearate.

Type II γ H-Abstraction in the Smectic Phase of *n*-Butyl Stearate. It is known from NMR and IR studies¹² that there is greater disorder and motion in the ester region than elsewhere in the smectic layer. This fact, coupled with the inherent static disturbing influence of the benzoyl group itself, results in a decrease in the solvent order in this region. A consequence of this decrease in solvent order is that the nearby methylene units will experience a less anisotropic and more fluid environment. The resulting enhancement in chain mobility allows the molecule to attain, with relative ease, the six-membered cyclic transition state necessary for efficient γ H-abstraction without requiring significant movement of the benzoyl group from its equilibrium position.

The fact that the percent conversions for the same irradiation time are similar in both the isotropic and smectic phases of *n*-butyl stearate can be contrasted to the behavior of similar ketones in monolayer assemblies.⁵ When 16-oxo-16-*p*-tolylhexadecanoic acid (**9**) was photolyzed in benzene solution the quantum yield obtained for type II reaction was 0.27. However, when **9** was photolyzed



in a monolayer with arachidic acid (**10**) the quantum yield for type II reaction decreased to $\sim 10^{-3}$ – 10^{-4} . The decrease in the quantum yield was attributed to the inability of the ketone to attain the proper geometry for γ H-abstraction due to the rigid environment imposed on the ketone by the monolayer structure. It is apparent from these results that the presence of the benzoyl group alone is not sufficient to cause a significant amount of disorder in its local environment. However, since the benzoyl group of **9** resides deep within the alkyl portion of the monolayer it is likely that this environment is inherently much more rigid than the ester region of the smectic phase of *n*-butyl stearate.¹⁹

Behavior of 1,4-Biradicals in the Smectic Phase of *n*-Butyl Stearate. The increase in the ratio of elimination-to-cyclization products can be explained in terms of the conformations which are required for the two processes.^{2d,e} Type II γ H-abstraction produces radical centers whose orbitals are initially orthogonal; however, the transition state for cyclobutanol formation requires that the singly occupied orbitals point toward one another. This geometry requires a rotation of the phenyl-substituted radical center away from its equilibrium position placing the phenyl ring perpendicular to the long axis of the ketone and the surrounding *n*-butyl stearate molecules. The resulting conformation would cause a disruption of the smectic structure and as a consequence geometries leading to cyclobutanol formation are unfavorable.

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Alternatively, rotation of the unsubstituted radical center would cause intermolecular and intramolecular disturbance for several methylene units along the alkyl chain. The transition state for elimination does not require that these orbitals point at each other, but only that they overlap sufficiently with the C2–C3 σ bond which is cleaved in the process.^{2c} Since the methylene units which separate the radical centers are free to rotate, it is expected that such geometries can be reached without significantly displacing the phenyl-substituted radical center and the alkyl chain from their equilibrium positions. It is reasonable to expect that such motions would cause little, if any, disruption of the liquid crystalline structure. Hence, an enhancement in the formation of elimination products is easily rationalized. Similar influences should be operative in the solid phase with the larger increases being caused by the more restrictive environments as described above.

Since ketones **1a** and **1b** possess alkyl chains which are considerably shorter than *n*-butyl stearate, they are not as rigidly incorporated into the liquid crystalline lattice as ketones **1c–e**; therefore, they should disrupt their local smectic environment to a much greater extent. Consequent, disruption of solvent order should result in a less anisotropic environment and greater conformational lability experienced by ketones **1a** and **1b** and the corresponding 1,4-biradicals. Since the environment is considerably less rigid, motions of the phenyl ring which allow for formation of the cyclobutanol products are no longer hindered. Hence, conformations of the 1,4-biradical from **1a** and **1b** which lead to elimination products are not necessarily more favorable than those which lead to cyclization products in the liquid crystalline phase. Therefore, no change in the product ratio is expected and none is observed.

While similar arguments can be used to account for the increase in the elimination-to-cyclization ratio observed for the type II reaction of ketone **2**, further explanation is necessary to account for changes in the cyclobutanol stereochemistry. In general *trans*-/*cis*-cyclobutanol ratios are >1 due to the steric factors involved in forming a *cis*-cyclobutanol.^{2d,16a} Since cyclization of the 1,4-biradical from **2** is highly unfavorable in the smectic phase of *n*-butyl stearate, energy differences between pathways leading to the two stereoisomers will be increased. Hence, it is not surprising that the *trans*-/*cis*-cyclobutanol ratio increases in the smectic relative to the isotropic phase of *n*-butyl stearate. A similar change was observed for the cyclobutanols formed from photolysis of 5-nonanone in urea inclusion compounds.⁷ In both cases it appears that conformations of the biradical which lead to the *trans*-cyclobutanol (alkyl groups in the *trans*, pseudoequatorial position) are more compact and less disruptive of their environment than those which lead to the *cis* isomer. Again, the dependence on ketone structure is evidenced by the insensitivity of the cyclobutanol stereochemistry to changes in solvent phase for ketone **3**.

Although the steady-state product ratios provide evidence for conformational control of the biradical intermediate by the liquid crystal, they do not indicate where on the potential surface this control is occurring. For simple alkylphenones type II γ H-abstraction occurs from the excited triplet state of the ketone resulting in the formation of a triplet 1,4-biradical. In order for product formation to occur the triplet biradical must intersystem cross to form a singlet biradical. The resulting singlet biradical is considered to be a very short-lived species, and once formed it rapidly and irreversibly forms products. The elimination/cyclization ratios obtained are found to be larger in polar solvents than in nonpolar solvents. Similarly, biradical lifetimes are also found to increase in polar solvents. Both of these effects have been attributed to changes in the biradical conformation as a result of hydrogen bonding to the hydroxyl group of the biradical. It is known that both the separation and relative orientation of the singly occupied orbitals of the biradical strongly influence the rate of intersystem crossing.²⁰ Therefore, it has been proposed that the decay of triplet-derived biradicals is controlled by triplet–singlet intersystem crossing and that as a result of the short singlet

biradical lifetimes the product ratios reflect the conformation of the triplet biradical at the point of intersystem crossing.^{18,21}

The results presented here (i.e., a large change in the product ratio and no change, within experimental error, in the biradical lifetime²²) seem to indicate that the final product ratio is a consequence of conformational control on the singlet rather than the triplet biradical surface. However, it is highly unlikely that the conformational distribution of the longer-lived triplet biradical would not also be affected. Therefore, even though conformations of the triplet biradical which result in cyclobutanol formation are disfavored in the smectic phase of the liquid crystal, due to restrictions in the motion of the phenyl-substituted radical center, sufficient rotational mobility exists in the methylene units to allow for singlet–triplet degeneracies in the biradical. This is supported by recent *ab initio* MCSCF calculations on tetramethylene which indicate that numerous singlet–triplet degeneracies are accessible by rotations about any of the carbon–carbon bonds of the biradical.^{21c}

Conclusions

The results presented here indicate that solvent order can strongly influence the course of the type II photochemical reaction of *n*-alkylphenones and dialkyl ketones. This effect is evidenced by the substantial increases in both the elimination/cyclization product ratios and the ratio of the stereoisomeric cyclobutanols produced in the smectic relative to the isotropic phase of *n*-butyl stearate. While the liquid crystalline order is of primary importance in this effect, consideration must also be given to the structure of the ketone since reaction specificity depends upon the intimacy of specific solute–solvent interactions. Time-resolved experiments indicate that the triplet biradical lifetime is not affected by the conformational restrictions imposed upon it by the liquid crystal. It is apparent from these results that although intersystem crossing in biradicals may be conformation dependent there need not be any direct correlation between steady-state product ratios and measured biradical lifetimes. These results are of interest in terms of the effects of liquid crystalline order on chemical reactions as well as mechanistic studies on biradical species. Further studies on structurally interesting biradicals and liquid crystal are warranted.

Experimental Section

Hexane (Baker reagent), heptane (Mallinckrodt reagent), *n*-heptadecane (Aldrich 99%), and *n*-butyl acetate (Aldrich 99+%) were used as received. *tert*-Butyl alcohol (Baker reagent) was distilled (bp 81 °C). Both commercial (Sigma) and synthetically prepared¹⁰ *n*-butyl stearate were used. Valerophenone (**1a**), 10-nonadecanone (**2**), and 2-undecanone (**3**) were obtained from Aldrich and used as received. By GC analysis, **2** and **3** were >99% and 96% pure, respectively. Undecanophenone (**1b**) (Aldrich 98%) was purified by sublimation (mp 29–30 °C). NMR spectra were obtained on a 60-MHz Varian A-60 or an 80-MHz Bruker WP-80 spectrometer. IR spectra were recorded on either a Perkin-Elmer 457 grating spectrophotometer or a Perkin-Elmer 1420 ratio recording spectrophotometer. Mass spectra were obtained on an AEI MS-12 medium resolution mass spectrometer. Melting points were taken on a Thomas-Hoover capillary melting point apparatus or a Kofler hot-stage microscope equipped with polarizing lenses and are corrected.

Synthesis of Ketones 1c–e. Ketones **1c–e** were prepared via Friedel–Crafts acylation of benzene with the acid chloride prepared by reaction of thionyl chloride with the corresponding carboxylic acid. A typical preparation of eicosanophenone (**1d**) involved stirring 4.0 g (0.013 mol) of the eicosanoic acid (Aldrich 99%) with 20 mL of thionyl chloride at 85 °C until HCl evolution stopped. The excess thionyl chloride was removed under vacuum to yield a yellow oil. This oil was dissolved in 140 mL of benzene (freshly distilled from CaH₂) and cooled in an ice bath to 0 °C. Aluminum chloride (4.0 g, 0.03 mol) was added in small portions over 10 min. The mixture was allowed to warm to room tem-

(21) (a) Doubleday, C. *Chem. Phys. Lett.* **1979**, *64*, 67. (b) Doubleday, C. *Ibid.* **1982**, *85*, 65. (c) Doubleday C. E., unpublished results.

(22) Note Added in Proof: This explanation is based on the assumption that the biradical lifetime is determined by intersystem crossing^{17,20} and not the rates of the individual product-forming steps. However, it has been pointed out, based on the latter assumption, that since cyclization is the slower of the two competing reactions slowing it down further makes only a small change in the observed lifetime which could be lost in the experimental error. We thank Prof. P. J. Wagner for bringing this point to our attention.

(20) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

perature and then heated to reflux. After 3 h the solution was cooled to room temperature, poured into 150 mL of ice water, and extracted with ether. The ether extracts were combined and washed with 5% NaHCO₃, water, and saturated NaCl solution. The ether layer was dried over MgSO₄, filtered, and evaporated to yield 4.7 g of a yellow solid. This solid was recrystallized from ethanol to give 4.3 g (90%) of eicosanophenone (**1d**) as a white, flaky solid (mp 69–70.5 °C). The same procedure was used to prepare octadecanophenone (**1e**) (mp 64–65 °C) and docosanophenone (**1e**) (mp 73.5–75 °C). The purity of ketones **1c–e** was >99% as determined by GC analysis. The spectroscopic properties of all three ketones were found to be the same: UV (heptane) $\epsilon_{320} = 50 \text{ M}^{-1} \text{ cm}^{-1}$; IR (CCl₄) 2930, 2860, 1693, 1600, 1470, 1450 cm⁻¹; NMR (CDCl₃) δ 0.9 (3 H, t) 1.25 (**1c**, 32 H; **1d**, 34 H; **1e**, 36 H), 2.95 (2 H, t), 7.4–8.1 (5 H, m).

Photolysis of Ketones 1a–d in Standard Isotropic Solvents. Solutions of ~0.02 M ketone in *n*-heptane, *n*-butyl acetate, or *n*-heptadecane were argon purged for 15 min in 0.1-cm precision quartz UV cells after which the cells were stoppered and sealed with Parafilm. The degassed samples were placed in a constant-temperature water bath thermostated with a Neslab Endocal RTE 9DD refrigerated circulation bath. The sample was then irradiated with a 1000 W Hg–Xe Oriel arc lamp (Model 6141) filtered thru a 10 cm cooled water filter, a 0.25 m high intensity monochromator (Kratos, Model GM 252) set for $313 \pm 6 \text{ nm}$, and a 7-54 Corning filter to reduce sample heating. Irradiation times were 4 min for *n*-butyl acetate and 20 min for *n*-heptane or *n*-heptadecane solutions. After photolysis 50 μL of a $\sim 7 \times 10^{-3} \text{ M}$ solution of 1-undecanol in diethyl ether was added as a standard. A 1 μL sample was analyzed on a Varian 3700 gas chromatograph equipped with a 10% OV-17 on GasChrom Q Deactiglas column (Applied Science, 6 ft \times 2 mm). The GC conditions used were those necessary for the clean separation of *n*-butyl stearate from the ketone and products. This usually involved a temperature program from 100 °C to 250–270 °C at 4 °C or 5 °C per min depending on the ketone. These conditions were then used for both the standard solvents and *n*-butyl stearate to ensure that the product ratios for each ketone were internally consistent. The product peaks were quantitated by integration on a Hewlett-Packard 3390A reporting integrator. Conversions were determined by comparison with unphotolyzed solutions and were kept below 30%.

Acetophenone was identified by comparison of the GC retention time with authentic material. The cyclobutanols **6c** and **6d** were characterized after isolation (reverse-phase HPLC, 100% CH₃OH) from photolyzed solutions of the corresponding ketones in hexane. Both cyclobutanols showed strong hydroxyl absorptions at 3600 cm⁻¹ in CCl₄ and an exchangeable proton in the NMR. Both cyclobutanols showed only one peak under the GC conditions used in the analysis described above. While the reported product ratios are uncorrected for relative detector response, corrected runs were made for ketone **1c** and mass balances were found to be >95% in all the solvents used including *n*-butyl stearate.

Photolysis of Ketones 1a–e in *n*-Butyl Stearate. Samples were prepared by transferring a weighed quantity of a 1.0 mol% (~0.02 M) mixture of the ketone in *n*-butyl stearate to a 0.1-cm quartz UV cell. The samples were then argon purged in the isotropic phase at ~35 °C, sealed, and photolyzed as described above. After photolysis the entire sample was diluted with 50 μL of the 1-undecanol/ether solution and analyzed by GC, as described above. Samples photolyzed in the smectic and solid phases were cooled slowly thru the phase transition temperatures and allowed to equilibrate at the photolysis temperature for 5–10 min. Photolysis time was the same as that for *n*-butyl acetate (4 min) for ~30% conversion.

Photolysis of Ketones 2 and 3 in *n*-Hexane and *tert*-Butyl Alcohol. Nitrogen-purged solutions of 0.1 M ketone were irradiated in a Pyrex vessel at room temperature with a Hanovia 450-W medium-pressure Hg lamp (Model 679 A36) housed in a water-jacketed quartz well. Aliquots were analyzed on a Perkin-Elmer 2920 B Gas Chromatograph with a 10% OV-17/Chromosorb W column (7 ft \times 1/8 in.). Product peaks were quantitated by integration on a Perkin-Elmer M-2 calculating integrator. Conversions were kept below 5% for **2** to avoid further photolysis of ketone **3**.

Photolysis of Ketone 2 in *n*-Butyl Stearate. Samples of ketone **2** (1.0% by weight) in *n*-butyl stearate (a 0.5 °C depression of the transition temperature was observed) were irradiated in a Pyrex cell for 5 and 12 h at 20 or 31 °C. The samples were then diluted with acetone and analyzed by GC as described for the standard solvents. The percent conversions at both temperatures were 5% and 30% for 5 and 12 h of irradiation, respectively. Ratios of the two isomeric products, **8t** and **8c**, from the secondary photolysis of **3** were obtained at the higher conversions of **2**.

Cyclobutanols **7** and **8** were characterized by analyzing hexane solutions of **2** and **3** which had been photolyzed to >95% conversion. After removal of the solvent IR spectra showed strong hydroxyl stretches and NMR spectra (CDCl₃) indicated the presence of an exchangeable proton at δ 2.88 which disappeared upon addition of a drop of D₂O. Mass spectra of the photoproducts included a strong peak corresponding to the mass of the parent ion and others indicative of the splitting patterns of the starting ketones.

Laser Flash Photolysis. The biradical lifetime measurements were obtained by using a standard laser flash photolysis setup. The frequency quadrupled output (266 nm, fwhm 4 ns, 5–10 mJ/pulse) of a Quantel Nd-YAG laser was used to excite the sample. A pulsed 400 W Xe arc lamp (Photochemical Research Associates, Model 301 power supply; Model M-305 pulser) was used as the analyzing light source and was directed on-axis with the excitation source. The transmitted light was passed through an ISA H-10 monochromator ($\lambda_{\text{obsd}} 317 \text{ nm}$)¹⁷ and monitored with a RCA 4840 photomultiplier tube. The output from the photomultiplier tube was terminated by using a 50 Ω load resistor and analyzed by using a Tektronix 7912 AD programmable digitizer as part of a Tektronix WP2252 signal processing system. The samples were contained in 0.1-cm precision quartz cells and prepared in the manner described for the steady-state experiments. All experiments were carried out in a quartz cell holder which was thermostated with a continuous flow of nitrogen.

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Registry No. **1a**, 1009-14-9; **1b**, 4433-30-1; **1c**, 6786-36-3; **1d**, 4443-66-7; **1e**, 5667-66-3; **2**, 504-57-4; **3**, 112-12-9; **6a**, 82245-43-0; **6b**, 92346-28-6; **6c**, 92346-29-7; **6d**, 92346-30-0; **6e**, 92346-31-1; *trans*-**7**, 92346-34-4; *cis*-**7**, 92346-35-5; **8t**, 92346-32-2; **8c**, 92346-33-3; *n*-butyl stearate, 123-95-5; acetophenone, 98-86-2; eicosanoic acid chloride, 40140-09-8; eicosanoic acid, 506-30-9.