

Norrish II reactions of rod-like ketones in ordered media comprised of rod-like layered solvent molecules¹

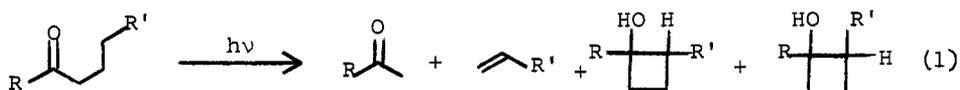
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Abstract - Product ratios from the Norrish II photoreactions of homologous series of 2- and *sym*-alkanones have been measured in the ordered phases of heneicosane, *n*-butyl stearate, and aqueous gels containing potassium palmitate, potassium stearate, and 1/1 potassium stearate/1-octadecanol. These results have been combined with other data (depressions of phase transition temperatures and quadrupolar splittings from deuterium magnetic resonance spectra) to elucidate the modes of ketone solubilization, the dependence of solute length on local solvent order, and the influence of that order on solute photoreactivity. Several distinct solubilization modes of the ketones have been identified and the extreme sensitivity between solute/solvent shape matching and Norrish II product selectivity is demonstrated.

INTRODUCTION

Previously, we have developed models which relate the degree to which an ordered solvent influences the reactions of a solute to three principal factors (ref. 2): (1) the similarity in size, shape, and polarity between a solute and the solvent molecules; (2) the magnitude of the shape changes which the solute experiences along its reaction coordinate; and (3) the flexibility of the ordered matrix. In essence, solutes which most resemble the solvent disturb its order least. Solute shape changes occurring from molecules which initially fit very well into a stiff solvent matrix are most easily detected.



$$\underline{1}: \text{R} = -\text{CH}_3; \text{R}' = -(\text{CH}_2)_{n+1}\text{H} \\
 n+5 = \quad \quad \quad n+5 =$$

a) 11	f) 19
b) 13	g) 20
c) 15	h) 21
d) 17	i) 22
e) 18	j) 23

$$\underline{2}: \text{R} = -(\text{CH}_2)_n\text{H}; \text{R}' = -(\text{CH}_2)_{n-2}\text{H} \\
 2n+1 = \quad \quad \quad 2n+1 =$$

a) 11	g) 23
b) 13	h) 25
c) 15	i) 27
d) 17	j) 29
e) 19	k) 31
f) 21	l) 35

Others (ref. 3) and we (ref. 4) have tested these simple hypotheses by examining the Norrish II photoreactions (ref. 5) (equation 1) of a wide variety of ketones in several different liquid-crystalline environments. Here, we present results from irradiation of two homologous series of *n*-alkanones (1 and 2) (ref. 6) whose rod-like structures are similar to the ordered molecules in which they are dissolved. In fact, the major difference between an *n*-alkanone and the corresponding *n*-alkane is electronic: the group dipoles of methylene and a carbonyl are 0.35 and 2.4 D, respectively (ref. 7); but a carbonyl occupies only ~15% more volume than a methylene (ref. 8) and their bond angles to neighboring carbons differ by only ~4° (ref. 8).

The ordered media chosen for this study include the solid phases of an *n*-alkane (heneicosane; C21), the smectic B and solid phases of *n*-butyl stearate (BS), and aqueous gel phases of potassium palmitate (KP), potassium stearate (KS), and 1/1 (mol/mol) mixtures of KS/1-octadecanol (KSO). Experiments with 1 and 2 have been conducted also in disordered media (hexane, *t*-butyl alcohol, and the isotropic phases of the ordered

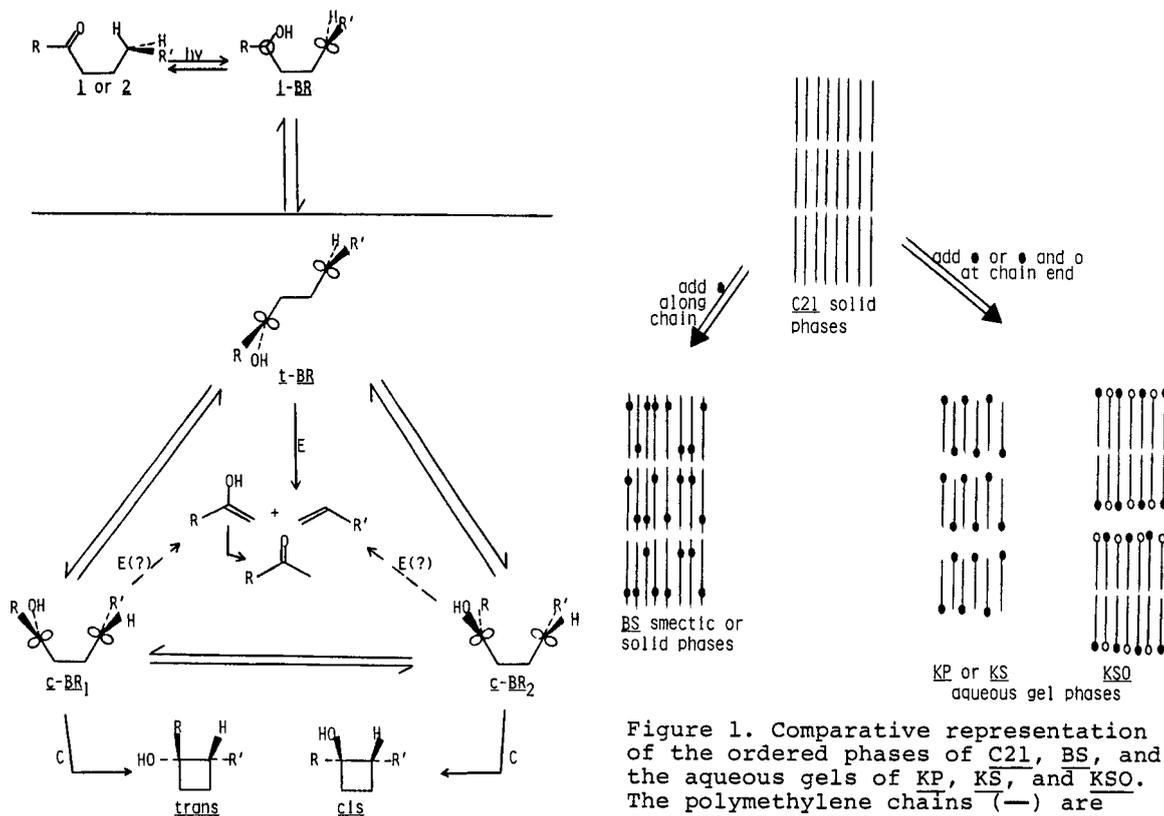
solvents) to calibrate the influence of solvent order on the photorearrangements. These experiments allow subtle differences in phase organization and unexpected changes in ketone solubilization sites to be detected. They also demonstrate the extreme sensitivity of Norrish II product selectivity to solute-solvent interactions and size and shape matching.

NORRISH II PROCESSES IN ANISOTROPIC ENVIRONMENTS

Since its discovery, the Norrish II reaction has been investigated both to understand the subtleties of its mechanism and for its synthetic utility (ref. 9). The ratios of elimination to cyclization products (E/C) and of diastereomeric cyclobutanols (t/c) respond to different properties of a solvent matrix.

A detailed mechanism of the Norrish II reaction which emphasizes the shape differences of its intermediates is presented in Scheme 1. In non-viscous isotropic solvents, initial γ -hydrogen abstraction occurs from both short-lived singlet ($\tau < 4.5$ ns (ref. 10)) and longer-lived triplet n, π^* states (refs. 6a, 11). Lower temperatures and higher solvent viscosities can make the conformational changes necessary for hydrogen abstraction in 1 or 2 too slow to compete effectively with intersystem crossing. Since the ordered solvents employed here are extremely viscous, we believe that the reaction from 1 and 2 emanates predominantly from their triplet manifolds. Available evidence indicates that the triplet-singlet intersystem crossing rates of the two families of pre-product hydroxy-1,4-biradicals, c-BR and t-BR, are similar (refs. 4e, 13, 14). Once formed, the singlet BRs collapse to products before significant structural changes can occur (refs. 5c,d, 15). Thus, the E/C and t/c product ratios reflect the populations of the ³BR conformations at the moment of intersystem crossing.

The t-BR can give rise only to elimination products. The extent to which c-BR yields elimination products also is not known. When structurally-locked ketones which must yield c-BR conformations have been irradiated, product mixtures have varied from almost exclusively the elimination type to the cyclization type (refs. 13, 16). In the absence of excessive ring strain (ref. 16c), the major product determining factor from c-BR appears to be the angles of the singly occupied p-orbitals at the 1 and 4 carbons: good



Scheme 1. Mechanism of Norrish II rearrangements of 1 and 2.

Figure 1. Comparative representation of the ordered phases of C21, BS, and the aqueous gels of KP, KS, and KSO. The polymethylene chains (—) are drawn as extended conformations with carboxy (●) and hydroxy (○) groups included where appropriate.

overlap enhances cyclization (ref. 16a). Although 1 and 2 are nearly free of internal constraints to adopting c-BR conformations which lead to cyclization, external impositions of the ordered matrices may influence the course of their reactions (ref. 2). Regardless, changes in product ratios from members of a homologous series of conformationally labile ketones like 1 or 2 must be attributed to extrinsic factors (such as solvent order, viscosity, or polarity).

The influence of polarity on Norrish II product ratios has been documented (ref. 17). With 1 and 2, we find little difference between E/C ratios both among homologs of one series of ketones and when solvent is changed from hexane to t-butyl alcohol. However, the t/c ratios in t-butyl alcohol are consistently lower than those measured in hexane. Again, the ratios vary little when homologs of 1 or 2 are compared in the same solvent.

THE MEDIA: ROD-LIKE MOLECULES PACKED HEXAGONALLY OR ORTHORHOMBICALLY INTO LAYERS

Ordered, layered phases of rod-shaped molecules offer an interesting variety of environments in which to conduct solute reactions. The organizations of the solvents employed in this work are shown in Figure 1.

Infrared spectroscopic and X-ray diffraction evidence, especially, has shown that C21 forms a soft solid (Phase II) in which the constituent molecules are arranged in extended conformations with their long axes normal to and hexagonally packed in the layers (ref. 18). The molecules rotate about their long axes and adopt gauche (defect) conformations more frequently near a layer end than in a layer middle (refs. 18c, 19). In the more ordered, lower temperature solid (Phase I), rotation is damped, very few defects occur, and layer packing collapses to orthorhombic (ref. 18).

n-Butyl stearate (BS) may be considered C21 into which a carboxy group has been inserted. The perturbation caused by the carboxy allows a smectic B mesophase (whose organization is like that of Phase II) to form prior to crystallization (ref. 20) the first solid phase is very similar to phase I (refs. 20, 21). A lower temperature solid phase has not been characterized completely, but it is layered like the higher temperature solid (ref. 21).

Attachment of a carboxy (or hydroxy) group at the chain terminus of an n-alkane results in a surfactant molecule capable of forming lyotropic mesophases. At 50% surfactant by weight and in the temperature ranges shown, KP, KS, and KSO form layered gels in which the intralayer organization is smectic B-like (refs. 22, 23). The KP and KS gels are almost completely interdigitated bilayers (ref. 22); the KSO bilayers are not interdigitated (ref. 22).

Evidence presented here and arguments developed previously (ref. 2) indicate that 1 and 2 are solubilized within (rather than between) layers of C21, BS, and the gels, and with their long molecular axes parallel to the solvent directors. The differing locations of the carbonyl groups of 1 and 2 (and, therefore, their loci of reaction) permit regions near both the end and middle of the ordered solvent layers to be probed.

NORRISH II REACTIONS OF 1 AND 2 IN ORDERED SOLVENTS

In C21: homogeneous well-ordered layers of non-polar molecules (ref. 24)

The absence of hetero groups along the backbone of C21 permits the influence of "undisturbed" layers of extended rod-like molecules on the Norrish II reactions of 1 and 2 to be probed. The product ratios from irradiations of 1% ketone solutions in the isotropic phase (45°C), solid phase II (35°C), and solid phase I (25°C) of C21 are given in Table 1.

Except in phase I, the t/c ratios from 1 vary only slightly with solute chain length or solvent phase. The greatest selectivity of the E/C ratios from 1 obtains with 1g in phase I, but high ratios are observed from 2-alkanones which are between five carbons shorter and two carbons longer than 1g. In phase II, only 1g demonstrates considerable E/C selectivity. Interestingly, 1g is one carbon shorter than C21.

The lack of t/c selectivity in all but the optimal cases (i.e., 1g and, to a lesser extent, 1h and 1i in phase I) is consistent with our model (ref. 2) describing the interactions between solutes and ordered solvents. Figure 2a is a cartoon representation of the t-BR and c-BR shapes, with otherwise extended alkyl chains, from 1 which fit well into a C21 (or other polymethylene) layer. Since methyl and hydroxyl groups occupy comparable volumes, c-BR₁ and c-BR₂ appear very similar in shape. Also, the motions required to form them from i-BR or t-BR involve similar shape changes and should occur with comparable difficulty. Thus, the gauche twists near the layer ends and the intrinsically lower order of phase II are sufficient to mask the shape differences between t-BR₁ and c-BR₂ except in the case of the most ordered 2-alkanones.

Table 1. Norrish II product ratios from 1 and 2 in C21.

T(°C)		<u>1</u>			<u>2</u>	
		E/C	t/c		E/C	t/c
45	b	3.1+0.1	1.7+0.1	c	1.5+0.1	2.1+0.1
35		2.9+0.1	1.3+0.1		1.8+0.4	1.8+0.1
25		3.0+0.1	1.1+0.1		2.6+0.1	1.5+0.1
45	c	3.3+0.1	1.8+0.1	d	1.4+0.1	2.4+0.1
35		3.7+0.3	1.6+0.1		2.4+0.1	5.9+0.1
25		16.2+0.4	1.6+0.1		5.0+0.9	1.5+0.7
45	d	3.3+0.2	1.7+0.4	f	1.8+0.1	2.5+0.1
35		4.6+0.7	3.4+0.2		3.5+0.1	24.9+3.0
25		15.0+4.0	2.4+0.4		>69+7	0.9+0.4
45	e	4.0+0.3	1.5+0.2	g	2.0+0.1	2.0+0.2
35		3.9+0.2	4.6+0.2		2.1+0.1	10.8+0.5
25		26.4+18.3	3.6+0.1		8.1+0.3	9.0+0.8
45	g	4.9+1.0	1.6+0.1	h	2.3+0.4	2.9+0.3
35		18.1+3.5	4.7+0.9		2.9+0.5	18.0+1.0
25		167+12	17.6+7.9		4.3+0.6	15.0+0.7
45	h	2.4+0.6	1.0+0.1	k	2.4+0.2	2.1+0.1
35		5.7+1.3	2.5+0.2		2.9+0.4	5.1+0.7
25		46+16	3.6+0.9		2.8+0.1	8.1+1.3
45	i	4.0+0.2	1.7+0.2			
35		8.5+0.9	2.8+0.1			
25		28.9+2.8	3.7+1.6			
45	j	3.1+0.7	1.9+0.2			
35		1.6+0.3	2.4+0.2			
25		3.6+0.1	3.0+0.1			

We suspect that the lack in phase I of E/C selectivity from 1j, a solute only 2 carbons longer than C21, is due to the *gauche* twists that the alkanone must adopt in order to remain within one solvent layer. Conformations which place a *gauche* twist near the carbonyl group of 1 and, thereby, force the carbonyl and its neighboring methyl to lie at a layer interface (Figure 3) should be especially disruptive to local solvent order.

Somewhat surprisingly, selectivity in the E/C ratios from 2 is observed only in phase I while phase II creates the greater selectivity in t/c ratios. As expected, the magnitudes of the effects on 2 photoproduct ratios from the very ordered phases of C21 are larger than in the less ordered phases of BS (*vide infra*). Figure 2b provides an adequate basis for explaining most of the observations in Table 1.

The resemblance between the shapes of *t*-BR and *c*-BR₁ from 2 makes them difficult to distinguish in phase II. In phase I, *t*-BR and *c*-BR₁ whose lengths lie within ±4 carbons of C21 are influenced by its solvent order. Shorter and longer 2 and their BRs must disturb solvent order to such an extent that the shape differences become unimportant.

Corroboration of the relative disturbing influences of 1 and 2 on C21 order is found in the melting point (phase II-isotropic) ranges of C21 solutions containing 10% (w/w) ketone. Alkanones much shorter than C21 depress its melting point more than the longer ketones, but both are more disruptive than 1 and 2 of lengths near C21. At 1% (w/w) concentrations, all of the ketones appeared to form well-dispersed solid solutions for which the melting point ranges are small.

The origin of the t/c ratio changes in Phase I is less clear. For 2 shorter than or equal in length to C21, the ratios indicate that the *c*-BR product precursors experience minimal solvent influence. However, this assessment may be incorrect since it is doubtful that the stiff matrix of phase I would allow significant interconversion of *c*-BR₁ and *c*-BR₂. Also, as temperature is lowered within phase I, the t/c ratios from 2f indicate that it produces progressively more *c*-BR₂, the bulkiest of the pre-product intermediates. For irradiation of 2 longer than C21 in phase I, an excess of *trans*-cyclobutanol, comparable to the amounts formed in phase II, is observed. In fact, all of the t/c ratios (and perhaps even the E/C ratios) in phase I may be predetermined by the distribution of sites into which the solvent matrix places 2. If the ketones are nearly immobilized, the t/c ratios are proportional to the mole fraction of 2 which is locked initially in conformations similar to *c*-BR₁ or *c*-BR₂, the quantum efficiency of the Norrish II reaction from each conformation, and, perhaps, the proportion of reaction which proceeds directly from the ketone singlet and triplet states. Further experimentation is required to clarify this aspect of the influence of phase I order on the photoreactions of 2. Experiments with 1 and 2 in other *n*-alkane solid phases are currently in progress.

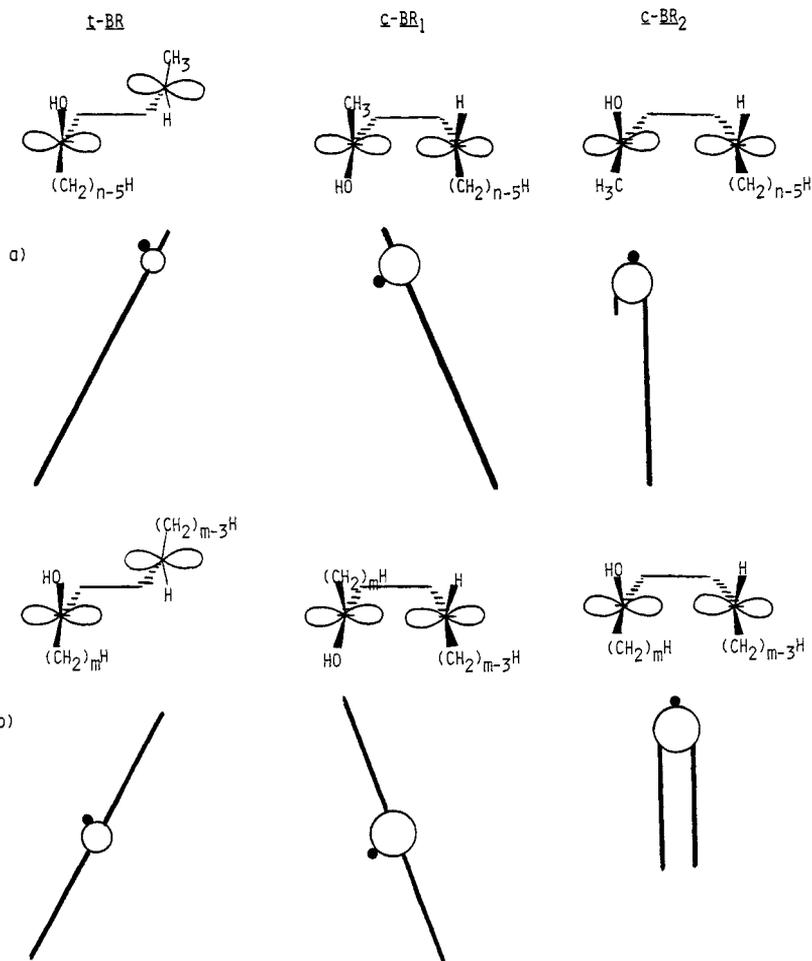


Figure 2. Pre-product hydroxy-1,4-biradicals from 1 (a) and 2 (b) in cartoon representations with extended methylene chains (—) and the relative sizes of the biradical centers (O) and hydroxy groups (●) shown.

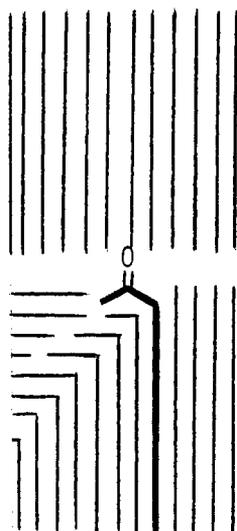


Figure 3. Cartoon diagram showing a possible location of the carbonyl of long 1 in solid C21.

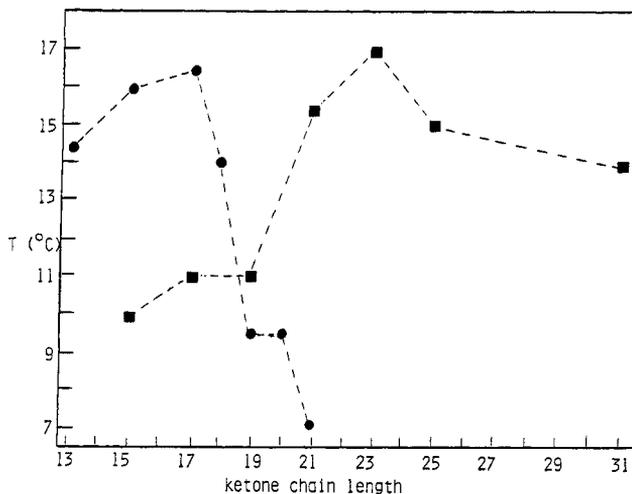


Figure 4. Smectic-biphasic transition temperatures of 50% (by wgt) of 1 (●) or 2 (■) and BS versus ketone chain length.

The t/c ratios from 2 in phase II can be rationalized more easily since the greater flexibility of the solvent molecules should allow for continued close solute-solvent contact along the reaction coordinate of 2 and should permit at least some interconversion among the BR conformations. Thus, the very large excess of trans-cyclobutanols from 2 near in length to and somewhat longer than C21 arises from the energetic preference of the solvent matrix for the less bulky c-BR₁ conformation. The fluxionality of phase II makes unnecessary and unlikely special sites like those invoked to explain the very low t/c ratios in phase I. Extremely rigid environments, like those offered by undisturbed phase I, can only accept solutes whose size and shape match closely a solvent molecule (e.g., 2f).

In BS: slightly disturbed layers of non-polar molecules containing one polar group (ref. 25)

The disturbing influences of the ketones on the anisotropic phases of BS were assessed from the depression in the optically observed phase transition temperatures caused by each homolog (Figure 4). Under the photolysis conditions (<1.4% by weight of 1 or 2 in BS), none of the ketones caused a measurable change in the smectic-isotropic temperature. At 50% by weight of ketone, the smallest depression of the smectic-biphasic (solid ketone plus isotropic liquid) transition, indicative of the smallest disturbance to order, occurred with 1d (17 carbon chain length) and 2g (23 carbon chain length). Solute-solvent length comparisons are sufficient to explain the latter result. We believe that the former result arises from attractive dipolar interactions between the carbonyl groups of 1 and the carboxyls of neighboring BS molecules in a smectic layer. The 2-alkanones longer than 1d must either displace the carbonyl from the carboxyl or permit one of two energetically unfavorable circumstances (the introduction of gauche twists along the solute chains or penetration of a solute chain into a neighboring solvent layer) to arise. In support of this explanation, the smallest depression of the solid-isotropic phase transition temperature of C21 occurs with sym- and anti 2-alkanones whose lengths are nearly the same as the solvent molecules (ref. 20).

The Norrish II results from 1 and 2 in BS are summarized in Table 2. The maximum E/C product selectivity from the 2-alkanones was obtained with 1d and 1e (i.e., the ketone which disturbs solvent order least and its immediate homolog). No influence of solvent order or solute chain length on t/c ratios can be discerned. Unfortunately, the photoproducts from 2g (which fits best into BS layers) and 2h could not be separated analytically from the solvent. However, two major conclusions can be derived from the available data: 1) both the E/C and t/c ratios from 2 are phase and solute length dependent; 2) maximum selectivities obtain for 2 which are near the length of BS.

Table 2. Norrish II product ratios from 1 and 2 in isotropic (30°C), smectic (20°C), and crystalline (10°C) BS.

T(°C)	<u>1</u>		<u>2</u>	
	E/C	t/c	E/C	t/c
	a		a	
30	2.9±0.3	1.3±0.1	2.0±0.4	1.8±0.5
20	3.1±0.3	1.2±0.1	1.8±0.4	1.5±0.5
10	2.6±0.3	1.2±0.1	2.0±0.3	1.6±0.3
	b		c	
30	3.5±0.4	1.5±0.1	1.9±0.5	2.4±0.6
20	4.0±0.3	1.4±0.1	2.3±0.3	2.8±0.5
10	4.2±0.4	1.3±0.1	3.2±0.6	3.5±0.4
	c		d	
30	3.6±0.2	1.3±0.1	2.2±0.6	2.2±0.6
20	11.7±1.7	1.3±0.3	3.2±0.8	10.8±1.6
10	19.8±1.7	1.8±0.1	7.0±1.0	11.5±2.3
	d		e	
30	3.7±0.4	1.5±0.1	2.0±0.3	1.8±0.2
20	15.1±2.7	1.9±0.3	6.2±0.9	13.3±0.3
10	27.4±3.2	1.9±0.3	10.0±2.3	11.3±0.9
	e		f	
30	3.7±0.4	1.1±0.1	2.0±0.2	2.5±0.6
20	14.8±2.3	1.6±0.2	5.5±1.0	14.1±0.1
10	31.3±3.3	1.3±0.2	15.0±5.0	12.0±3.0
	f		i	
30	4.1±0.2	1.3±0.2	2.8±0.5	2.2±0.3
20	16.5±1.6	2.4±0.1	3.2±0.5	7.2±0.5
10	22.8±3.8	2.5±0.1	6.3±1.3	6.1±0.7
	g		j	
30	3.9±0.5	1.0±0.1	2.7±0.7	2.2±0.3
20	10.4±1.7	1.5±0.1	3.6±0.5	5.9±0.1
10	18.5±3.0	1.5±0.2	2.9±1.1	7.0±0.3

Size and shape comparisons among the BRs and the location of the biradicaloid centers near the more disorganized layer ends can explain the invariance of the t/c ratios from 1 in the BS phases: as mentioned previously, c-BR₁ and c-BR₂ from 1 have very similar shapes (Figure 2a).

The t-BR from 1 resembles an extended BS molecule, but differs from either c-BR conformation. The E/C product ratios show that these shape differences are sufficient to be discerned at a BS layer end when the precursor ketone is near in length to 1d. Since the selectivity experienced upon irradiation of 1 is greater than that of 2 (which suffers BR shape changes near the more ordered middle of a BS layer), the differences between the BRs from 1 are probably exacerbated by interactions of their biradicaloid centers with solvent carboxyl groups. Specifically, the hydroxy of a BR may be hydrogen-bonded to a nearby carboxyl: the aforementioned dipolar interactions between the carbonyl of 1 and a carboxyl group of BS ensure that the biradicaloid centers will be near a carboxyl at the moment of their formation.

The cartoon representations of the BRs from 2 (Figure 2b) show that c-BR₁ resembles somewhat t-BR, but both differ drastically in shape from c-BR₂. Thus, the E/C ratios become more selective as the length of 2 approaches that of BS and the temperature is decreased (i.e., as the order near the middle of a BS layer increases and becomes less yielding to deviations from rod-like solute shapes). Similar arguments do not explain the selectivity changes in the t/c ratios which decrease when BS passes from its smectic to solid phases. However, the yield of the bulkier cis-cyclobutanols from 2 which respond to solvent order represents only <1% of the total in the smectic and solid phase reactions. We suspect that, as in the C21 solid phases, much of the cis-cyclobutanol in these cases derives from a small fraction of 2 which resides at defect sites of (especially) the solid matrices. Gauche twists of 2 near the carbonyl groups and/or placement of 2 between BS layers can enhance c-BR₂ formation.

In aqueous gels: slightly disturbed layers of surfactant molecules (ref. 26)

The similarity in order between layers of BS phases and surfactant layers of aqueous gels does not require that they influence the Norrish II reactivity of alkanones similarly. The layer boundary of BS is non-polar while that of the gels is discontinuous and very polar. Thus, differences are expected in the photoreactivity of 1, especially, in the two solvent types.

To obtain a more quantitative picture of the order experienced by the ketones in the gels, we have recorded deuterium magnetic resonance (ref. 27) Pake (or powder) patterns (ref. 28) of 1 and 2 which are deuterated at the positions alpha to the carbonyl. The 90° quadrupolar magnetic resonance splittings, $\Delta\nu_{90}$, provide a measure of the degree to which motion about the C-D bonds is restricted by their local environment. The most ordered environment of a rod-like molecule which rotates about its long axis in a surfactant layer is calculated to provide $\Delta\nu_{90} = 63.75$ kHz while isotropic motions give $\Delta\nu_{90} = 0$ Hz (ref. 27). It should be remembered that $\Delta\nu_{90}$ values and product ratios provide complementary mechanistic information: the former (like depressions in phase transition temperatures) probe the order of the ketones prior to their reaction; the latter offer insights into the influence of solvent order on the shape changes suffered by the BR intermediates.

The most striking observation from the E/C and t/c product ratios from 1% (w/w) of 1 is that they do not vary appreciably in the gel phases as a function of chain length. The t/c ratios are low and suggest that the carbonyl groups experience a polar environment as they react. The limited $\Delta\nu_{90}$ values for 1b-1f are also nearly constant (~1200-1300 Hz). Cyclobutanol (t/c) ratios and $\Delta\nu_{90}$ values are plotted versus the chain length of 2, the ketone series for which the most extensive data was collected, in the interdigitated bilayer gel of KS (Figure 5) and the normal bilayer gel of KSO (Figure 6). The t/c product ratios and $\Delta\nu_{90}$ values follow very similar changes up to chain lengths slightly longer than the surfactant molecules and exhibit maxima for 2d, the ketone expected to fit best into the layers. Thereafter, the t/c ratios remain very low (symptomatic of BRs reacting in a very polar environment), while $\Delta\nu_{90}$ rises (to values near to those of 2d) for 2 which approach twice the surfactant length (2k and 2l). The maximum selectivity in the t/c ratios in each of the gels, including KP, is observed with the 2 whose extended length is nearest that of the polymethylene portion of a surfactant molecule.

The E/C ratios from 2 further demonstrate the dependence of product selectivity on ketone chain length. In both gel types, the E/C ratios are low and almost constant for 2 of lengths up to slightly longer than the surfactant molecules. Thereafter, the E/C ratios decrease further to <1 (indicating preferred cyclization) and then rise at still longer ketone lengths to values near those found with the short 2.

Since the product ratios and $\Delta\nu_{90}$ exhibit similar patterns of change with ketone length in the normal and interdigitated bilayer gels, we conclude that these solvents enforce similar constraints to solute motions.

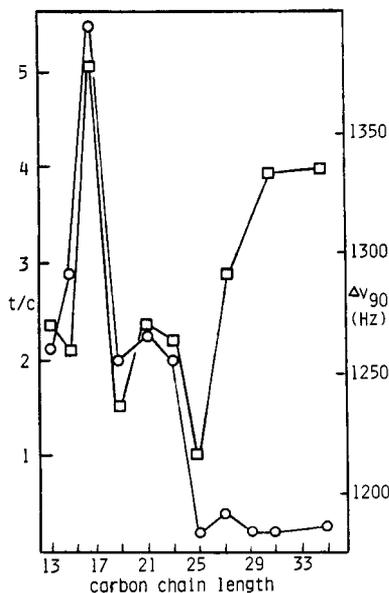


Figure 5. Deuterium quadrupolar splittings and t/c ratios at 38° C from 2 versus ketone chain length in the KS gel phase.

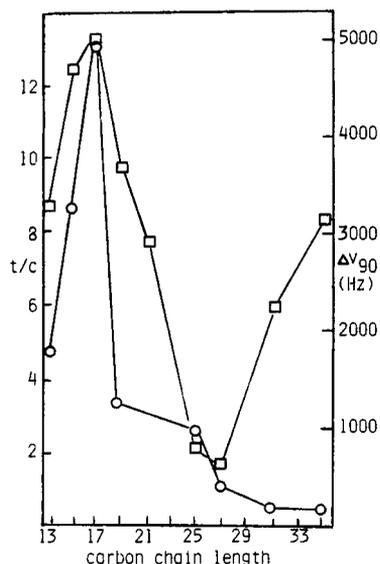


Figure 6. Deuterium quadrupolar splittings at 70° C and t/c ratios at 38° C from 2 versus ketone chain length in the KSO gel phase.

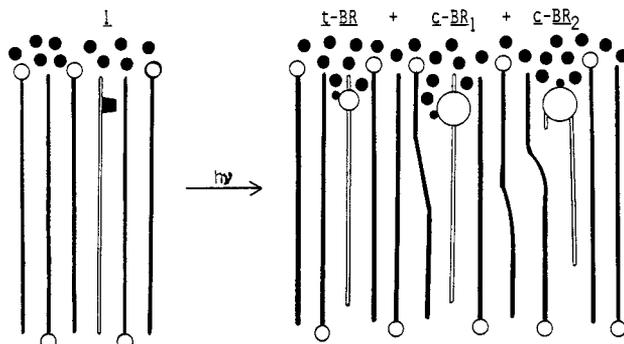


Figure 7. Shape representations of 1 and its BRs in an aqueous gel layer. Water molecules (●) are included to show how they may solvate the biradical centers.

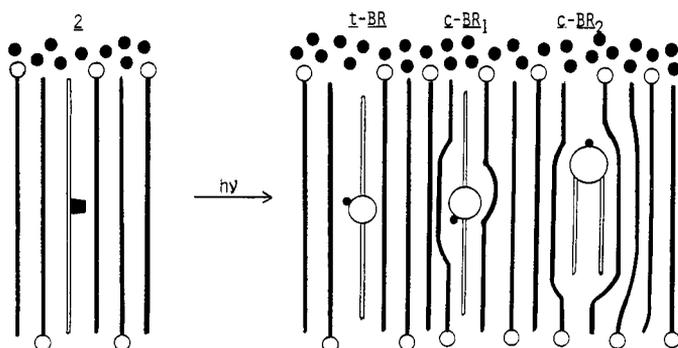
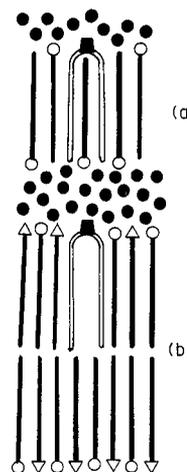


Figure 8. Shape representations of 2 and its BRs in an aqueous gel layer. Water molecules (●) are included to show that they do not have an easy access to the biradicaloid centers.

Figure 9. Representation of solubilization sites of very long 2 in hairpin conformations in KS (a) and KSO (b) gels. The exposure of the carbonyl groups of 2 (■) to water (●) is shown.



The results from 1 can be understood with the aid of representations of the BRs in the gels (Figure 7). The $\Delta\nu_{90}$ values indicate that all of the carbonyl groups experience a similar environment. The very low t/c ratios further define the location of 1 and the biradicaloid centers of the BRs to be near a polar interface of a gel layer. Thus, water molecules can access the loci of reactivity in 1, making differences among the BR shapes indistinguishable to nearby surfactant molecules.

As shown in Figure 8, the carbonyl groups of 2 (which are shorter than or comparable to the length of the surfactants) and the BRs derived from them reside near the middle of a gel layer. Unlike in 1, they are shielded from the aqueous portions of the phase and experience an ordered polymethylene part of a surfactant layer (ref. 24). However, the

shape differences between t -BR and c -BR₁ from the shorter 2 are apparently too small to be detected by even the layer middle. The projections of the two alkyl chains in c -BR₂ make it much more disruptive to the surfactant layers than either t -BR or c -BR₁.

The longer 2 (i.e., those longer than an extended surfactant molecule) must either adopt more gauche twists to stay within an interdigitated bilayer (of KP or KS gels) or traverse a gel layer boundary. For KSO gels, the latter option requires only that a molecule of 2 cross the bilayer mid-plane, without encountering a polar region hostile to its alkyl chains. For KP and KS gels, traversing a gel layer boundary places part of 2 in an unfavorable aqueous environment. Alternatively, the longer 2 may adopt a hairpin conformation which exposes the carbonyl groups to a polar layer interface, but protects all but the neighboring methylenes within the hydrophobic layer interior (Figure 9).

Of these, only the hairpin conformation is consistent with the product ratios and the Δv_{90} values. The very low t/c ratios from longer 2 require that their BRs be exposed to a very polar environment. At the same time, the increase in Δv_{90} as 2 approaches twice the length of a surfactant molecule in both KS and KSO gels indicates that the methylenes alpha to the carbonyl groups become increasingly ordered (as they do when the length of shorter 2 approach that of a surfactant molecule). The 2 of intermediate length are most disordered (yielding the smallest Δv_{90} values and the lowest product selectivities) since they either contain several gauche twists or are hairpin shaped, but are too short to occupy the equivalent space of two surfactant molecules.

Long 2 adopt hairpin conformations in KSO gels, rather than traversing the bilayer midplane, for reasons which are probably related to why phospholipids bend to form bilayers (ref. 29): both 2 and phospholipids consist of a polar head group flanked by two alkyl chains. Also, the region near a KSO midplane is somewhat disordered. A molecule of 2 traversing the midplane would increase solvent order (i.e., decrease total entropy) and, thereby, increase the free energy of the system.

Thus, the combination of product ratios and Δv_{90} values allow at least two very different solvation sites to be identified for alkanones in aqueous surfactant gels. The same approach should prove useful in determining the modes of solubilization and solvent control over solute reactivity in other surfactant organizes.

CONCLUSIONS

We have demonstrated the utility of product ratios from Norrish II photoreactions, especially when coupled with independent experimental techniques, to define the specificity of interactions between alkanone solutes and their ordered environments. The data have also allowed subtle changes in the modes of ketone solubilization to be detected. Comparisons of the influence of the layered phases on product selectivity show that although the gross manifestations of one type of solvent order on the ketone reactions, as expressed by several related solvents, may be similar, they include important and sometimes unexpected differences.

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REFERENCES

- Part 32 in our series, "Liquid-Crystalline Solvents as Mechanistic Probes." For Part 31, see: M.F. Sonnenschein and R.G. Weiss, J. Phys. Chem. submitted.
- R.G. Weiss, Tetrahedron accepted.
- W.J. Leigh and S. Jakobs, Tetrahedron **43**, 1393-1408 (1987).
- a) J.M. Nerbonne and R.G. Weiss, Isr. J. Chem. **18**, 266-271 (1979). b) R.G. Zimmermann, J.H. Liu and R.G. Weiss, J. Am. Chem. Soc. **108**, 5264-5271 (1986). c) R.L. Treanor and R.G. Weiss, J. Phys. Chem. **91**, 5552-5554 (1987). d) R.L. Treanor, unpublished results. e) D.A. Hrovat, J.H. Liu, N.J. Turro and R.G. Weiss, J. Am. Chem. Soc. **106**, 7033-7037 (1984). f) Z. He, unpublished results.
- a) P.J. Wagner, Acc. Chem. Res. **4**, 168-177 (1971). b) N.J. Turro, J.C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk and N. Schore, Acc. Chem. Res. **5**, 92-101 (1972). c) N.C. Yang and S.P. Elliot, J. Am. Chem. Soc. **91**, 7550-7551 (1969). d) L.M. Stephenson, P.R. Cavigli and J.L. Parlett, J. Am. Chem. Soc. **93**, 1984-1988 (1971).
- Ketones 1 and 2 have been irradiated under conditions for which Norrish I cleavage reactions, a competing process involving α -cleavage, are important. a) M.V. Encina and E.A. Lissi, J. Photochem. **6**, 173-181 (1976/77). b) G.H. Hartley and J.E. Guillet, Macromolecules **1**, 413-417 (1968). c) F.J. Golemba and J.E. Guillet, Macromolecules **5**, 63-68 (1972).

7. C.P. Smyth, J. Chem. Phys. **4**, 209-219 (1937).
8. a) G. Herzberg, Electronic Spectra of Polyatomic Molecules, Van Nostrand, Princeton, NJ (1967). b) L.E. Sutton, Ed., Tables of Interatomic Distances and Configurations in Molecules and Ions, The Chemical Society, London (1965). c) E. Sutton, Ed., Tables of Interatomic Distances, Special Publication No. 11, The Chemical Society, London (1958). d) A.I. Kitiagorodsky, Molecular Crystals and Molecules, p. 21, Academic Press, New York (1973).
9. P.J. Wagner, In Rearrangements in the Ground and Excited States, Vol. 3, pp.381-444, P. de Mayo, Ed., Academic Press, New York (1980).
10. a) F. Wilkinson, In Advances in Photochemistry, Vol. 3, p. 255, W.A. Noyes, Jr., G.S. Hammond, and J.N. Pitts, Jr., Eds., Interscience, New York (1964). b) J.C. Dalton and R.J. Sternfels, Mol. Photochem. **6**, 307-314 (1974).
11. M.V. Encina and M.V. Lissi, J. Photochem. **4**, 321-328 (1975).
12. J.R. Scheffer, M. Garcia-Garibay and O. Nalamasu, In Organic Photochemistry, Vol. 8, chap. 4, A. Padwa, Ed., Marcel Dekker, New York (1987).
13. R.A. Caldwell, T. Majima and C. Pac, J. Am. Chem. Soc. **104**, 629-630 (1982).
14. But see: a) L. Salem and C. Rowland, Angew. Chem. Int. Ed. Engl. **11**, 92-111 (1972). b) W. Adam, S. Grabowski, R.M. Wilson, K. Hannemann, and J. Wirz, J. Am. Chem. Soc. **109**, 7572-7573 (1987).
15. C. Doubleday, J. McIver and M. Page, J. Am. Chem. Soc. **107**, 7904-7909 (1985).
16. a) H.R. Sonawane, B.S. Nanjundiah, S.I. Rajput and M. U. Kumar, Tetrahedron Lett. **27**, 6125-6128 (1986). b) J. Moron and G. Roussi, J. Org. Chem. **43**, 4215-4220 (1978). c) L.J. Johnston, J.C. Scaiano, J.W. Sheppard, and J.P. Bays, Chem. Phys. Lett. **124**, 493-498 (1986).
17. a) N.J. Turro, K.-C. Liu and M.-F. Chow, Photochem. Photobiol. **26**, 413-415 (1977). b) M.V. Encina and E.A. Lissi, J. Photochem. **5**, 287-296 (1976).
18. a) M.G. Broadhurst, J. Research (NBS) **66A**, 241-249 (1962). b) M. Maroncelli, S.P. Qi, H.L. Strauss and R.G. Snyder, J. Am. Chem. Soc. **104**, 6237-6247 (1982). c) M. Maroncelli, H.L. Strauss and R.G. Snyder, J. Chem. Phys. **82**, 2811-2824 (1985). d) A.A. Schaefer, C.J. Busso, A.E. Smith and L.B. Skinner, J. Am. Chem. Soc. **77**, 2017-2018 (1955).
19. M.S. Brown, D.M. Grant, W.J. Horton, C.L. Mayne and G.T. Evans, J. Am. Chem. Soc. **107**, 6698-6707 (1985).
20. a) J.S. Dryden, J. Chem. Phys. **26**, 604-607 (1957). b) D. Krishnamurti, K.S. Krishnamurthy and R. Shashidhar, Mol. Cryst. Liq. Cryst. **8**, 339-366 (1969). c) K.S. Krishnamurthy and D. Krishnamurti, Mol. Cryst. Liq. Cryst. **6**, 407-413 (1970).
21. P.K. Sullivan, J. Research (NBS) **78A**, 129-141 (1974).
22. J.M. Vincent and A. Skoulios, Acta Crystallogr. **20**, 432-440, 441-447, 447-451 (1966).
23. a) B. Mely and J. Charvolin, Chem. Phys. Lipids **19**, 43-55 (1977). b) J.H. Davis Biochim. Biophys. Acta **737**, 117-171 (1983).
24. a) A. Nuñez and R.G. Weiss, J. Am. Chem. Soc. **109**, 6215-6216 (1987). b) A. Nuñez, unpublished results.
25. R.L. Treanor and R.G. Weiss, Tetrahedron **43**, 1371-1391 (1987).
26. a) R.L. Treanor and R.G. Weiss, J. Am. Chem. Soc. **108**, 3137-3139 (1986). b) R.L. Treanor and R.G. Weiss, J. Am. Chem. Soc. in press.
27. a) R.G. Griffin, Meth. Enzymol, Lipids **72D**, 108-174 (1981). b) K.R. Jeffery, T.C. Wong and A.P. Tulloch, Mol. Phys. **52**, 289-306 (1984). c) I.C.P. Smith, In NMR of Newly Accessible Nuclei, Vol. 2, Chap. 1., P. Lazlo, Ed., Academic Press, New York (1983). J. Charvolin and Y. Hendrikx, In Nuclear Magnetic Resonance of Liquid Crystals, Chap. 20, J.W. Emsley, Ed., D. Reidel, Boston (1985).
28. G.E. Pake, J. Chem. Phys. **16**, 327-336 (1948).
29. D.J. Mitchell and B.W. Ninham, J. Chem. Soc., Faraday Trans 2 **77**, 601-629 (1981).