

# Liquid-Crystalline Solvents as Mechanistic Probes. 26. Norrish II Photolyses and Deuterium Magnetic Resonance Studies on the Solubilization and Mobilities of 2- and *sym*-Alkanones in Interdigitated and Bilayer Gel Phases of Aqueous Surfactants<sup>1</sup>

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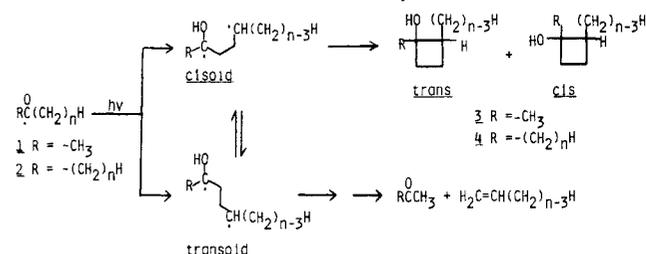
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**Abstract:** The Norrish II photolyses of 2- and *sym*-alkanones have been conducted in the aqueous gel phases of potassium stearate (KS), potassium palmitate (KP), and a 1/1 molar ratio of potassium stearate/1-octadecanol (KSO). From the elimination/cyclization and *trans/cis* cyclobutanol product ratios and deuterium magnetic resonance studies, we have been able to identify the initial ketone solubilization sites and the influence exerted by the ordered solvents on the intermediate 1,4-biradicals. Both the polarity and order of the local environment of the biradicals within the gels determine the product ratios. When the solutes are less than or about equal in length to the solvent amphiphile, they reside in extended conformations within a lipophilic layer; when the solutes are much longer than the amphiphile, they adopt a U-shape in order to remain within a single layer. Surprisingly, the long solutes remain U-shaped even in bilayers that could accommodate their extended conformations. In the gels, the product ratios are controlled by the lipophilic ordering imposed on the *sym*-alkanones and by the polarity of the layer interface experienced by the 2-alkanones. The *trans/cis* cyclobutanol ratios from the Norrish II reaction of the *sym*-alkanones, especially, display a very strong dependence upon the length matching between the ketones and the surfactants. The results suggest that small differences in solute order can lead to large differences in reaction selectivities.

Very ordered lyotropic phases, yet ones that have received almost no attention as reaction media, are the aqueous gels of surfactant molecules (Figure 1) like potassium stearate and potassium palmitate (KS and KP, respectively; each a completely interdigitated, layered assembly) and a 1/1 molar mixture of KS and 1-octadecanol (KSO, a noninterdigitated bilayer assembly).<sup>2</sup> By contrast, micelles, inverted micelles, microemulsions, Langmuir-Blodgett mono- and multilayers, lamellae, and vesicles have all been employed as reaction media.<sup>3</sup> X-ray diffractive characterization of the gels of KS, KP, and KSO<sup>2</sup> has shown their lipophilic parts to be organized in layers in a fashion similar to the thermotropic liquid-crystalline smectic B phase formed by *n*-butyl stearate (BS).<sup>4</sup>

Recently, we<sup>1b,5</sup> and others<sup>6,7</sup> demonstrated the utility of the Norrish II reactions of alkanones (Scheme I) and alkylphenones as probes of dynamic solvent control by ordered solvents. The different dynamic aspects of the ordering influences exerted by nearby solvent molecules on the solutes include the quantum

Scheme I. Norrish II Reaction of 2- and *sym*-Alkanones



efficiencies for ketone conversion, the elimination/cyclization product ratios (*E/C*), and the diastereomeric *trans/cis* cyclobutanol ratios (*t/c*). Potentially, each of these responds to different solute-solvent interactions. For instance, we found that the length of normal alkanones and the position of their carbonyl groups (specifically 1 and 2, Scheme I) are principal factors in determining the degree to which the order of smectic B and solid phases of BS controls the *E/C* and *t/c* ratios.<sup>5a</sup> Whitten et al.<sup>6c</sup> found that the quantum efficiency of the Norrish II reaction of the surfactant keto acid 16-oxo-16-(*p*-tolyl)hexadecanoic acid can vary from 1 in methanol to near 0 in monolayer assemblies due to the steric constraints imposed by the solvent. Turro et al.<sup>7b</sup> concluded from the *t/c* ratios of cyclobutanols from alkylphenone irradiations in micelles that the ketone reactive environment is similar in polarity to that of short-chain alcohols.

To compare the order imposed by a thermotropic smectic B phase<sup>5a</sup> with a lyotropic smectic-B-like gel phase,<sup>2</sup> we have extended our studies of the Norrish II reactions of 1 and 2 to KS, KP, and KSO gels as the solvents.<sup>1b</sup> The dynamic results are complemented by deuterium magnetic resonance (<sup>2</sup>H NMR) measurements of 1 and 2 (deuteriated at the carbons  $\alpha$  to the carbonyl groups) in the gels. By combining the static and dynamic data provided by both <sup>2</sup>H NMR spectra and Norrish II reactivities, we have constructed a rather comprehensive picture of solute photoreactions from solute excitation to the moment preceding the collapse of the 1,4-biradicals to products. The results, in toto, demonstrate the extreme sensitivity of cybotactic order (and, therefore, control of photoreactivity) to solute length and carbonyl location. They have allowed us to identify the variables in solute size and shape and in solvent order, which are key factors in

(1) (a) For part 25, see: Naciri, J.; Spada, G. P.; Gottarelli, G.; Weiss, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4352. (b) For a preliminary account of this work, see: Treanor, R. L.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 3137.

(2) Vincent, J. M.; Skoulios, A. *Acta Crystallogr.* **1966**, *20*, 432, 441, 447.

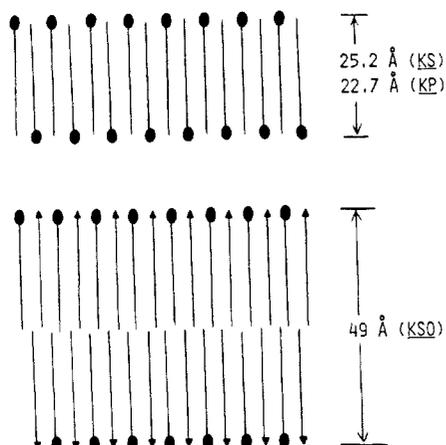
(3) (a) Thomas, J. K. *The Chemistry of Excitation at Interfaces*; American Chemical Society: Washington, DC, 1984. (b) Fox, M. A., Ed. *Organic Phototransformations in Nonhomogeneous Media*; American Chemical Society: Washington, DC, 1984. (c) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic: New York, 1975.

(4) Krishnamurti, D.; Krishnamurthy, K. S.; Shashidar, R. *Mol. Cryst. Liq. Cryst.* **1969**, *8*, 339. (b) Krishnamurti, D. *Mol. Cryst. Liq. Cryst.* **1970**, *6*, 407. (c) Sullivan, P. K. *J. Res. Natl. Bur. Stand., Sect. A* **1974**, *78A*, 129. (d) Krishnamurthy, K. S. *Mol. Cryst. Liq. Cryst.* **1986**, *132*, 255.

(5) (a) Treanor, R. L.; Weiss, R. G. *Tetrahedron* **1987**, *43*, 1371. (b) Zimmermann, R. G.; Liu, J. H.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5264. (c) Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7033.

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(7) (a) Leigh, W. J.; Jakobs, S. *Tetrahedron* **1987**, *43*, 1393. (b) Turro, N. J.; Liu, K. C.; Chow, M. F. *Photochem. Photobiol.* **1977**, *26*, 413. (c) Sharat, S.; Usha, G.; Tung, C. H.; Turro, N. J.; Ramamurthy, V. *J. Org. Chem.* **1986**, *51*, 3085.



**Figure 1.** Stylized representation of the molecular order in the aqueous gels. The dark circles and the straight lines represent the carboxylate head groups and the methylene chains of the amphiphiles, respectively. The dark triangles represent hydroxyl groups.

determining the degree to which a solute's reactivity will be affected by its environment.

### Experimental Section

**Materials.** Dry potassium stearate was prepared by the method of Skoulios<sup>2</sup> from an equimolar mixture of stearic acid (Aldrich 99+) and potassium hydroxide (Baker reagent 87%) dissolved in excess absolute methanol (Baker reagent). The purity of KS was checked by its melting point ( $>250$  °C); no melting was observed at 67–69 °C (stearic acid) or 153 °C (potassium hydrodistearate). KP was prepared in a similar manner from palmitic acid (Emery 95%, recrystallized from acetone) and then checked for purity as before. 1-Octadecanol (Aldrich 99%) was recrystallized 5 times from hexane or purified by preparative GC on a Varian Aerograph Model 920 chromatograph with a  $1/4$  in.  $\times$  5 ft column of 15% SE-30 on Chromosorb W. Perdeuterated stearic acid was purchased from Cambridge Isotope Laboratories and was 99% pure according to the manufacturer. 13-Pentacosanone was purchased from Lancaster Synthesis and recrystallized from hexane to give mp 73.5–74 °C. 12-Tricosanone was prepared from dodecanoyl chloride and triethylamine<sup>8</sup> and gave mp 68 °C. The origin and purity of the remaining starting materials, the elimination products, and the reduction products have been described.<sup>5a</sup> Elimination products and Norrish I alkanes were identified by coinjection with authentic materials on two different analytical GLPC columns. The identification of the *cis*- and *trans*-cyclobutanol products has been described.<sup>1b,5a</sup> *tert*-Butyl alcohol (Baker reagent) was distilled prior to use. Water was distilled once from potassium permanganate and then redistilled prior to use.

**Sample Preparation and Photolysis.** A 1.0–1.5 wt % mixture of ketone and dry amphiphile was ground to a fine powder. A portion of the mixture and the desired amount of nitrogen-bubbled water were sealed in a glass vial under  $N_2$ . The vial was suspended in refluxing water overnight and cooled to room temperature. Its contents were transferred under  $N_2$  to 1.5–1.8 mm o.d. Kimax capillary tubes, which were then flame sealed.

Prior to photolysis, the capillary tubes were heated to  $\geq 80$  °C (i.e., above the gel–middle phase transition temperatures) for 15 min, quenched at the desired temperature in a preequilibrated temperature bath ( $\pm 0.5$  °C), and kept there 1 h before photolysis. This procedure ensures homogeneous phase formation.<sup>2</sup>

Photolysis was accomplished with a 450-W medium-pressure Hanovia mercury lamp with a quartz cooling jacket immersed directly into the temperature bath. Irradiation times were varied empirically to attain ketone conversions of  $<15\%$ . Large *t/c* cyclobutanol ratios were determined at higher (ca. 60%) conversions. Relative quantum yields were determined by irradiating the sample of interest side-by-side with one of 8-pentadecanone in KS. Percent conversion ratios (at absolute conversions of  $<10\%$ ) were assumed equal to the ratios of the quantum efficiencies.

**Product Analysis.** After irradiation, the tubes were crushed in a round-bottomed flask containing 50 mL of ether and 1 drop of 0.1 N KOH. This mixture was stirred and refluxed for 30 min and stored at 0 °C for 10 min. The liquid was filtered through diatomaceous earth, and the earth was washed with 20 mL of cold ether. The combined

liquids were distilled carefully to remove almost all of the ether. The residue was analyzed with a Perkin-Elmer Model 3920 B or a Hewlett-Packard 5890A gas chromatograph, each equipped with flame ionization detectors. An Alltech RSL-300 or a Chrompack CP-Sil-19 CB wide-bore (0.53 mm  $\times$  10 m) fused-silica open tubular column was used to attain base-line separation of all photoproducts. A Perkin-Elmer M2 calculating integrator or a Hewlett-Packard 3393A integrator was used for peak area calculations. No correction was made for differential product responses; data were consistent between columns and chromatographs.

The relative areas of products and ketone extracted from the gels were compared with the same data from isotropic solution data calibrated with an internal standard. These data and the fact that no secondary photolysis products were seen under our irradiation conditions (although they were sought) allowed percent conversions to be calculated. Several checks of the extraction procedure were made. Photolysis products obtained from isotropic solution in known ratios and known percent conversions were doped into the amphiphile, which was then prepared and equilibrated as a normal photolysis sample. This procedure was repeated for several ketones (long and short; 2- and symmetrical) and included experiments with the addition of modified (spiked) product ratios. All trials gave results equal, within experimental error, to their preextraction values.

**<sup>2</sup>H NMR Studies.** The 2- and *sym*-alkanones were deuterated by exchange in monoglyme/ $D_2O/Na_2CO_3$  mixtures.<sup>9</sup> Four deuteration cycles afforded ketones with  $>70\%$  deuteration at the carbons  $\alpha$  to the carbonyl groups as determined by <sup>1</sup>H NMR. Isotropic solution ( $CHCl_3$ ) <sup>2</sup>H NMR spectra gave two peaks in the expected 3/2 ratio for the two nonequivalent exchangeable groups of the 2-alkanones; the *sym*-alkanones showed a single resonance. After exchange, the ketones were either recrystallized or chromatographed on silica (hexanes/ether) and were  $\geq 98\%$  structurally pure by gas chromatographic analyses.

The <sup>2</sup>H NMR samples with deuterated ketones were prepared in the same manner as that used for photolysis. The gels were placed into 5-mm NMR tubes and sealed. They were then heated to  $\geq 80$  °C and thermostated in the NMR probe ( $\pm 1$  °C as determined by the clearing points of various mesophases). A Bruker AM-300 WB spectrometer with an Aspect 3000 computer was employed for the deuterium spectra (obtained at 46.07 MHz, irradiated on resonance). The quadrupolar echo sequence<sup>10</sup> consisted of two 12.5- $\mu$ s 90° pulses, a 20- $\mu$ s delay between the 90° pulses, and a 0.2-s delay between cycles. With 50  $\mu$ s necessary for 360° rotation, our sweep width of effective power was limited to  $\pm 20$  kHz = 40 kHz.<sup>11</sup> As a result, information obtained beyond  $\pm 20$  kHz is precise with respect to position but is attenuated with respect to intensity. The free induction decay was collected (8K data points) in quadrature with an effective duty cycle of 0.27 s. Typically, 6000–10 000 accumulations gave sufficient signal-to-noise ratios for analysis. For determinations of precision, different samples on different days were analyzed for two ketones and gave a standard deviation in  $\Delta\nu_{90}$  (vide infra) of 0.5%.

### Results and Discussion

#### A Molecular Description of the Order of KS, KP, and KSO Gels.

KS-, KP-, and KSO-water mixtures have been studied extensively throughout their phase diagrams.<sup>2</sup> In addition to the more common middle (columnar nematic) and lamellar (neat soap) phases, they possess a range of compositions and temperatures in which gel phases form. Unless specified otherwise, the compositions of the gels used in our study are 50% water and 50% amphiphile (by weight).

The extensive data on KP, KS, and KSO gel phases demonstrate the closeness between their structures and order and those of the smectic B phase of BS.<sup>2,4</sup> In the gel phases, individual molecules are extended (all *trans* on average) and arranged in layers with their long axes normal to the layer plane that they define. Although KSO gels form normal noninterdigitated bilayers, the “bilayers” of KS and KP gels are almost completely interdigitated (Figure 1). Within each layer, the molecules rotate about their long axes and are hexagonally packed; additional water (beyond that required for phase formation) serves only to separate the layers of amphiphile from one another without disturbing the packing arrangement.<sup>2</sup> <sup>2</sup>H NMR studies of perdeuterated KS<sup>12</sup>

(9) Trost, B. M.; House, H. O. *J. Org. Chem.* **1965**, *30*, 1341.

(10) Davis, J. H.; Jeffery, K. P.; Bloom, M.; Valic, M. I.; Higgs, T. P. *Chem. Phys. Lett.* **1976**, *42*, 390.

(11) Bloom, M.; Davis, J. H.; Valic, M. I. *Can. J. Phys.* **1980**, *58*, 1510.

(12) (a) Mely, B.; Charvolin, J. *Chem. Phys. Lipids* **1977**, *19*, 43.

(8) Sauer, J. C. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. IV, p 560.

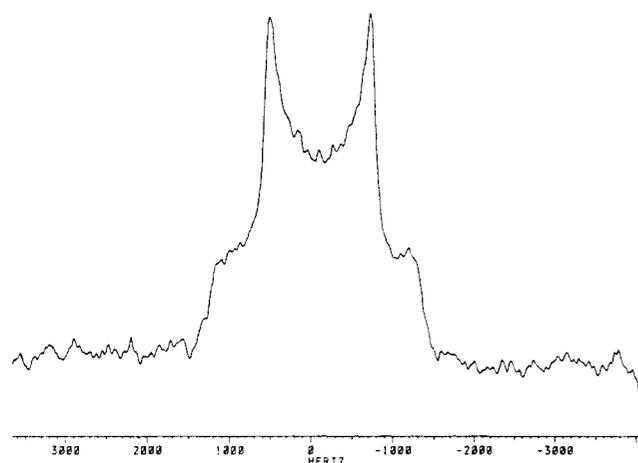


Figure 2.  $^2\text{H}$  NMR spectrum of  $\alpha$ -deuterated 10-nonadecanone in KS gel (50/50 (w/w)  $\text{H}_2\text{O}/\text{KS}$ ) at  $38^\circ\text{C}$ .

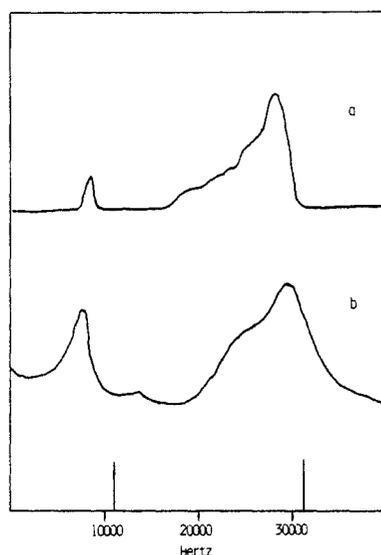


Figure 3. (a)  $^2\text{H}$  NMR spectrum of oriented, perdeuterated KS in KS gel (adapted from ref 12 with permission). (b)  $^2\text{H}$  NMR spectrum of unoriented perdeuterated KS in KSO gel (50/50 (w/w)  $\text{H}_2\text{O}/\text{KSO}$ ) at  $38^\circ\text{C}$ . See text for an explanation of the two vertical lines.

and  $\text{KP}^{13}$  in the gel phase have confirmed and extended these results.

The basic theory of  $^2\text{H}$  NMR for nonisotropic samples has been published in several reviews.<sup>14</sup> For nonaligned solvent systems with restricted motion, all angles of orientation ( $\theta$ ) of the solvent director with respect to the magnetic field are possible, and the deuterium quadrupolar coupling (the dominant interaction in samples of this nature) provides a spectrum containing several doublets (a Pake pattern,<sup>15</sup> Figure 2). For a deuterium attached to a rigid, rotating, all-trans methylene chain (the condition of highest order in liquid crystals and typical membrane models<sup>14</sup>) the doublet frequency difference ( $\Delta\nu_{90}$ , where  $\theta = 90^\circ$ ) is 63.75 kHz. As the motion of the C–D bond increases,  $\Delta\nu_{90}$  decreases (to 0 Hz in the case of isotropic motion or orientation at the magic angle,  $54^\circ 44'$ ).

Changes in composition and temperature within the neat gel phases of KS and KP affect their  $^2\text{H}$  NMR spectra only slightly. Figure 3a contains half of the oriented  $^2\text{H}$  NMR spectrum of a KS gel. The singlet at ca. 8 kHz represents the end methyl group,

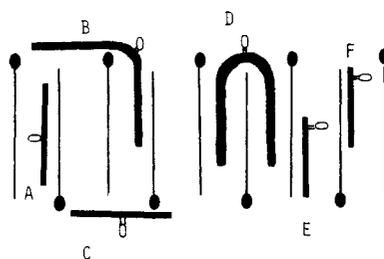
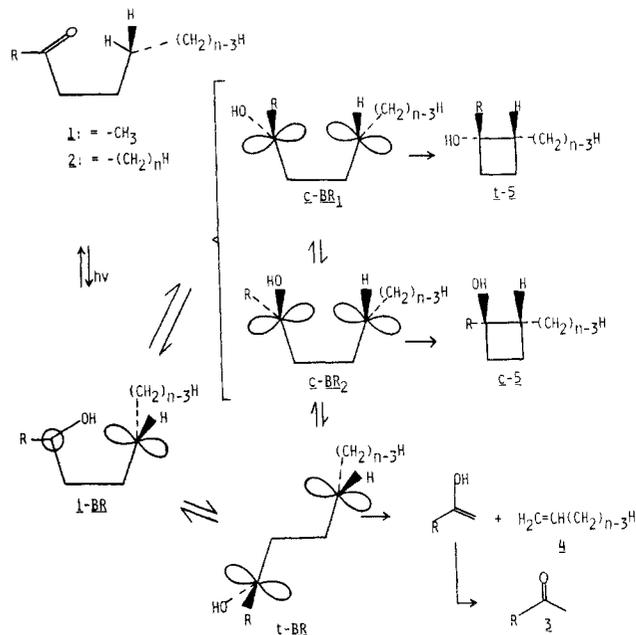


Figure 4. Stylized representation of the possible solubilization sites for 1 and 2 in KS and KP gels.

Scheme II. Representation of the Norrish II Pathways Leading to Elimination and Cyclization Products



and the remaining resonances represent the methylene units of the surfactant chain. The spikes are the  $\text{CD}_3$  and  $\text{CD}_2$  transitions calculated for a rigid, rotating, all-trans chain. Several families of order are apparent in the gel phase of KS, with the bulk of the resonances approaching the all-trans splitting frequency limit.

We have obtained a  $^2\text{H}$  NMR spectrum of perdeuterated KS in an unoriented KSO gel (Figure 3b) to complement the published X-ray data.<sup>2</sup> It is qualitatively similar to the KS spectrum, exhibiting fewer but more-ordered methylene types. "Stiffening" of lipophilic chains upon addition of 1-octadecanol is consistent with what is known about the addition of alcohols to bilayer (lamellar) phases.<sup>16</sup>

**Solvent–Solute Shapes and Their Influence on Solute Order and Mobility.** Thermodynamic studies of isomeric guest molecules in thermotropic mesophases demonstrate that the smallest disturbance to solvent order is introduced by a solute that mimics best the solvent in shape, size, and polarity.<sup>17</sup> As a corollary, we have adopted a working hypothesis that shape changes along the reaction coordinate of these solutes will be influenced most by local solvent order.<sup>1,5</sup> If the solute's reaction pathway includes large shape changes, the solvent order should sense them acutely: reaction rates and selectivities should be affected. Experimental evidence for both effects has come from prior studies on the photoreactions of 1 and 2 in BS.<sup>5a</sup>

Since only the group polarities of a carbonyl and a carbon–hydrogen bond (group dipoles are 2.40 and 0.30 D, respectively<sup>18</sup>)

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(14) Griffin, R. G. *Methods Enzymol., Lipids* **1981**, *72*, 109. (b) Jeffery, K. B.; Wong, T. C.; Tulloch, A. P. *Mol. Phys.* **1984**, *52*, 289. (c) Smith, I. C. P. In *NMR of Newly Accessible Nuclei*; Lazlo, P., Ed.; Academic: New York, 1983; Vol. 2, Chapter 1. (d) Charvolin, J.; Hendriks, Y. In *Nuclear Magnetic Resonance of Liquid Crystals*; Emsley, J. W., Ed.; D. Reidel: Dordrecht, 1985; Chapter 20.

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(17) (a) Schnur, J. M.; Martire, D. E. *Mol. Cryst. Liq. Cryst.* **1974**, *26*, 213. (b) Oweimreen, G. A.; Lin, G. C.; Martire, D. E. *J. Phys. Chem.* **1979**, *83*, 2111. (c) Martire, D. E. In *The Molecular Physics of Liquid Crystals*; Gray, G. W., Luckhurst, G. R., Eds.; Academic: New York, 1979; Chapter 11.

differentiate an alkanone and an alkane of the same length,<sup>19</sup> **1** and **2** are expected to be incorporated into the lipophilic layers of a gel<sup>20</sup> along side the amphiphile chains. The restrictions to their conformational changes (as exerted by the layers) should be a sensitive function of solute and amphiphile chain lengths.<sup>2a</sup> We will present experimental data that support this hypothesis and reject the other alkanone solubilization modes illustrated in Figure 4.

**Norrish II Reactions of Alkanones in Gel Phases.** The intramolecular photoreactions of linear alkanones have been investigated in detail in isotropic solutions.<sup>21</sup> Norrish II reactions (Scheme I) constitute the major pathway of alkanones like **1** and **2**.<sup>22</sup> Scheme II shows the minimal conformational changes necessary for the production of both cyclization (*trans*- and *cis*-cyclobutanols, *t*-**5** and *c*-**5**) and elimination (truncated alkanone **3** and alkene **4**) products from the initial hydroxy 1,4-biradical (*i*-BR) formed via  $\gamma$ -hydrogen abstraction. Each of the BRs in Scheme II represents a family of conformers that are structurally and chemically related.

In nonviscous isotropic solvents at room temperature, the fraction of singlet and triplet Norrish II components for linear alkanones is nearly equal and independent of chain length.<sup>23</sup> However, the triplet pathway is favored at lower temperatures.<sup>23</sup> Apparently, the higher viscosity of a solvent allows intersystem crossing to compete more efficiently with *i*-BR formation (via bending into a high-energy conformation like that shown in Scheme II) in the short-lived alkanone singlet state ( $\tau_s < 5$  ns<sup>24</sup>). Thus, hydrogen abstraction occurs primarily from the triplet states of **1** and **2** in the gel phases. The singlet component may be phase and solute-length dependent but should remain a minor process throughout. The longer lived <sup>3</sup>(*n*, $\pi^*$ ) states ( $\tau_1$  ca. 1  $\mu$ s in solution<sup>25</sup>) have much more opportunity to attain the abstraction geometry and form triplet biradicals (<sup>3</sup>BRs).

In order that the product ratios reflect the distribution of <sup>3</sup>BR conformers at the moment of intersystem crossing (eq 1 and 2),

$$\frac{E}{C} \approx \frac{{}^3(t\text{-BR})}{{}^3(c\text{-BR})} \quad (1)$$

$$\frac{t}{c} \approx \frac{{}^3(c\text{-BR}_1)}{{}^3(c\text{-BR}_2)} \quad (2)$$

(18) Smyth, C. P. *J. Chem. Phys.* **1937**, *4*, 209.

(19) The volume of a carbonyl is only ca. 15% greater than that of a methylene;<sup>19a-d</sup> the CCC bond angles of propane and acetone differ by only 4°.<sup>19a-d</sup> (a) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, 1967. (b) Sutton, L. E., Ed. *Tables of Interatomic Distances and Configurations in Molecules and Ions*; The Chemical Society: London, 1965. (c) Sutton, L. E., Ed. *Tables of Interatomic Distances, Special Publication No. 11*, The Chemical Society: London, 1958. (d) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*, Academic: New York, 1973; p 21.

(20) The alkanones employed in this study are virtually insoluble in the highly ionic aqueous regions which separate lipophilic layers.<sup>20a</sup> Thus, solubilization of **1** or **2** in sites like B or C of Figure 4 (vide infra) are unlikely. (a) Tewari, Y. B.; Miller, M. M.; Wasik, S. P.; Martire, D. E. *J. Chem. Eng. Data* **1982**, *27*, 451.

(21) (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92. (c) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(22) A minor photoreactive pathway available to **1** and **2** is the Norrish I process,<sup>21</sup> which involves  $\alpha$ -cleavage and eventual formation of alkanes, alkenes, aldehydes, and regenerated ketone. Norrish I products from **1** in KS gels amounted to approximately 10% of the Norrish II products and showed no perceptible alkanone length dependency. No Norrish I photoproducts from **2** were found in any of the gels. Cleavage of **2** probably does occur in the gels but the restricted volume in which the radical pair is produced favors regeneration of the starting ketone.<sup>22a,b</sup> (a) McBride, J. M.; Segmuller, B. E.; Hollingsworth, M. D.; Mills, D. E.; Weber, B. A. *Science (Washington, D.C.)* **1986**, *234*, 830. (b) Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 5291.

(23) (a) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1969**, *1*, 63. (b) Hartley, G. H.; Guillet, J. E. *Macromolecules* **1968**, *1*, 413.

(24) The singlet lifetimes of *n*-alkanones that cannot undergo the Norrish II reaction are reported to be <4.5 ns.<sup>24a,b</sup> These represent upper limits to singlet lifetimes of alkanones with  $\gamma$ -hydrogens. (a) Wilkinson, F. *Adv. Photochem.* **1964**, *3*, 255. (b) Dalton, J. C.; Sternfels, R. *J. Mol. Photochem.* **1974**, *6*, 307.

(25) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 903.

**Table I.** Photoproducts and <sup>2</sup>H NMR Splitting Frequencies from 9-Heptadecanone in Various Phases of KS and Water

H <sub>2</sub> O, wt %	temp, °C	E/C <sup>a</sup>	t/c <sup>a</sup>	$\Delta\nu_{90}$ , Hz ( $\pm 0.5\%$ )	phase
65	38			685	gel
55	38	2.1 $\pm$ 0.4	6.8 $\pm$ 0.5	961	gel
50	38	1.5 $\pm$ 0.6	5.6 $\pm$ 0.8	1373	gel
55	65	2.4 $\pm$ 0.5	1.4 $\pm$ 0.1		middle
55	48			0 <sup>b</sup>	gel-middle
55	24	2.9 $\pm$ 0.6	9.5 $\pm$ 1.3	1066 <sup>c</sup>	gel
55 <sup>d</sup>	24	3.5 $\pm$ 0.5	6.5 $\pm$ 0.5		cogel
25	71	1.4 $\pm$ 0.3	1.5 $\pm$ 0.1	0 <sup>e</sup>	lamellar

<sup>a</sup> E/C and t/c ratios reported are the average of two samples, with at least three injections per sample. Errors are one standard deviation from the average. <sup>b</sup> Broad Singlet (half-width = 900 Hz). <sup>c</sup> T = 22 °C. <sup>d</sup> The cogel phase was produced via a different thermal equilibration protocol. <sup>e</sup> T = 70 °C; singlet (half-width = 20 Hz).

several conditions must be met:<sup>26</sup> (1) the <sup>1</sup>BR lifetimes must be too short to allow structural changes, (2) all the preproduct <sup>3</sup>BR conformers must undergo intersystem crossing at about the same rate, and (3) the BR conformers must give rise to the products indicated in Scheme II. Available evidence indicates that the conditions are met (at least approximately) in the gels.

The first point is most clearly established: in the very viscous lipophilic portion of a gel, the very short-lived <sup>1</sup>BRs ( $\tau_s < 1$  ns<sup>27</sup>) should have very little opportunity to alter significantly their atomic positions before collapsing to product. Both comparisons of lifetimes of conformationally constrained and freely equilibrating <sup>3</sup>BRs<sup>5c,28</sup> and theoretical calculations<sup>29</sup> indicate that intersystem crossing can occur with about equal probability at many points on the triplet energy surface (point 2).

What remains to be demonstrated is the link between <sup>3</sup>BR conformers and products. For geometric reasons, only **4** and the enol of **3** can arise from *t*-BR: cyclization or return to the ketone cannot occur intramolecularly without conformational changes. The fate of *c*-BR is more complex.<sup>30</sup> When odd-electron overlap is possible and the *c*-BRs are not strained, cyclization dominates;<sup>28,30a,d</sup> when the *c*-BRs are strained or overlap between their singly-occupied orbitals is blocked by intramolecular constraints, elimination occurs in competition with or to the exclusion of cyclization.<sup>30</sup> The *c*-BRs from **1** and **2** are unencumbered intramolecularly and, therefore, should have no difficulty in cyclizing.

Since the two *c*-BRs from **1** are very similar in size and shape (i.e., the van der Waals volume of a methyl is close to that of a hydroxyl), their distribution should not be influenced by the order of the lyotropic portion of a gel phase. However, the shapes of the two diastereomeric *c*-BRs from **2** are very different and their formation should be influenced by the gel phase. *c*-BR<sub>1</sub> (trans alkyl groups) and its *trans*-cyclobutanol product are less bulky and, therefore, more like the solvent molecules in shape than *c*-BR<sub>2</sub> and its *cis*-cyclobutanol product.

(26) We have no substantive information concerning whether the preproduct biradicals reach their anisotropic equilibria in the gels prior to product formation. From the estimated rates of C-C bond rotations<sup>26b,26a-d</sup> and the lifetime of the <sup>3</sup>BR from 2-hexanone ( $\lambda = 25$  ns<sup>26e</sup>), the <sup>3</sup>BRs from **1** and **2** may reach a near-equilibrium state even in the gels. If they do, then each of the product ratios in eq 1 and 2 is also an equilibrium constant for the <sup>3</sup>BR precursors. (a) Golden, D. M.; Furuyama, S.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 57. (b) Pitzer, K. S. *Discuss. Faraday Soc.* **1951**, *10*, 66. (c) Lide, D. R., Jr. *J. Chem. Phys.* **1958**, *29*, 1426. (d) Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1958**, *29*, 914. (e) Naito, I. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2851.

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**Table II.** Photoproduct Ratios and  $^2\text{H}$  NMR Splitting Frequencies from **1** and **2** in Isotropic Solvents and KS Gels (50/50 (w/w)  $\text{H}_2\text{O}/\text{KS}$ ) at  $38^\circ\text{C}$ <sup>a</sup>

ketone	isotropic solvent		KS gel			
	<i>E/C</i>	<i>t/c</i>	<i>E/C</i>	<i>t/c</i>	rel quantum eff <sup>b</sup>	$\Delta\nu_{90}$ , Hz ( $\pm 0.5\%$ )
<b>1</b> ( $n + 2 =$ )						
13	$2.8 \pm 0.1^c$	$1.5 \pm 0.1^c$	$2.4 \pm 0.2$	$0.43 \pm 0.01$	1	1279
15	$2.9 \pm 0.1^c$	$1.2 \pm 0.1^c$	$2.6 \pm 0.3$	$0.42 \pm 0.04$	1	
	$3.3 \pm 0.2^d$	$2.8 \pm 0.1^d$				
17	$2.7 \pm 0.3^c$	$1.3 \pm 0.1^c$	$2.0 \pm 0.2$	$0.48 \pm 0.05$	1	1290
	$3.9 \pm 0.5^d$	$3.1 \pm 0.2^d$				
19	$2.9 \pm 0.2^c$	$1.3 \pm 0.1^c$	$2.2 \pm 0.2$	$0.59 \pm 0.03$	1	1247
21						1217
<b>2</b> ( $2n + 1 =$ )						
13	$2.0 \pm 0.1^c$	$2.2 \pm 0.1^c$	$1.3 \pm 0.4$	$2.1 \pm 0.2$	1	1270 <sup>e</sup>
15	$1.4 \pm 0.1^c$	$1.2 \pm 0.1^c$	$1.5 \pm 0.4$	$2.9 \pm 0.4$	1	1257 <sup>e</sup>
17	$1.8 \pm 0.1^c$	$1.3 \pm 0.1^c$	$1.5 \pm 0.6$	$5.6 \pm 0.8$	1	1373
	$2.4 \pm 0.1^d$	$2.7 \pm 0.2^e$				
19	$1.8 \pm 0.1^c$	$1.3 \pm 0.1^c$	$1.8 \pm 0.2$	$2.0 \pm 0.4$	1	1234
21	$1.8 \pm 0.1^c$	$1.2 \pm 0.1^c$	$2.2 \pm 0.3$	$2.2 \pm 0.3$	1	1269
	$2.3 \pm 0.1^d$	$3.2 \pm 0.2^d$				
23			$1.6 \pm 0.3$	$2.0 \pm 0.4$	0.1	1261
25			$0.6 \pm 0.2$	$0.22 \pm 0.04$	0.1	1220
27	$2.0 \pm 0.1^c$	$1.3 \pm 0.1^c$	$0.4 \pm 0.1$	$0.40 \pm 0.03$	0.1	1291
29			$0.6 \pm 0.2$	$0.20 \pm 0.04$	0.1	
31	$2.8 \pm 0.2^d$	$3.6 \pm 0.3^d$	$1.3 \pm 0.5$	$0.20 \pm 0.04$	1	1333
35			$1.6 \pm 0.3$	$0.27 \pm 0.04$	1	1335

<sup>a</sup> All the *E/C* and *t/c* ratios reported are the average of two samples, with at least three injections per sample. Errors are one standard deviation from the average. <sup>b</sup> Relative quantum efficiencies for disappearance of ketones. The absolute error limits are large and the numbers should be considered as no more than a crude measure of reactivity. <sup>c</sup> *tert*-Butyl alcohol,  $39^\circ\text{C}$ . <sup>d</sup> Hexane,  $39^\circ\text{C}$ . <sup>e</sup> Ca. 50% and 20%, respectively, of the integrated area appeared as a singlet at  $\nu = 0$  Hz for  $2n + 1 = 13$  and 15.

**Comparison of Norrish II Photoselectivity and  $^2\text{H}$  NMR Splittings of 9-Heptadecanone in Aqueous KS Phases.** Table I contains *t/c* and *E/C* ratios from 9-heptadecanone in the cogel, gel, middle, and lamellar phases of KS. The relative quantum efficiencies for reaction were approximately equal in all the phases. However, even within the gel phase, a temperature dependence upon the product ratios is observed; a similar effect obtains in KP gels (vide infra). Since X-ray and  $^2\text{H}$  NMR data<sup>2,12</sup> indicate that chain packing of the undoped gel is invariant with respect to its composition, we were surprised to find that the *t/c* ratios and  $\Delta\nu_{90}$  of 9-heptadecanone are composition dependent. For instance, at  $38^\circ\text{C}$ ,  $\Delta\nu_{90}$  increases dramatically as the aqueous content of the gel decreases from 65% to 50% (Table I).

In other systems, we have observed that solute reaction selectivity can be lower in a solid than in a less-ordered mesophase.<sup>5a,b,22b</sup> The cogel (a solid, hydrated soap) and gel phases of KS provide another example of this phenomenon. The Norrish II reaction of 9-heptadecanone in the cogel is less selective than in the more "fluid" gel phase. A possible explanation is that the gel possesses a greater ability to respond to shape changes along the alkanone's reaction coordinate. The ketone in the cogel may exist in a rigid, large cavity that provides sufficient space for solute motions but is inflexible. A somewhat analogous case may have been observed for the Norrish II reactions of alkylphenones in Dianin's complex.<sup>31</sup>

As expected from the  $\Delta\nu_{90}$  values, the relatively disordered middle and lamellar phases of KS provide no detectable Norrish II selectivity for 9-heptadecanone. The *t/c* ratios are consistent with the cybotactic region being somewhat polar and are reminiscent of results obtained for Norrish II photolyses of alkylphenones in micelles.<sup>7b</sup>

**Determination of 1 Solubilization Sites and Mobility in Gel Phases from  $^2\text{H}$  NMR Spectral Data and Norrish II Product Ratios.** The Norrish II photoproduct ratios and the (approximate) relative quantum efficiencies for **1** in KS and KP gels are shown in Tables II and III. The similarity in shape between *c*-BR<sub>1</sub> and *c*-BR<sub>2</sub> derived from **1** makes it reasonable to assume that polarity effects are the primary factor in determining the *t/c* ratios in both the ordered and disordered environments.<sup>21</sup> Since the shorter **1** ( $n + 2 = 13$ –19) in the gels provide *t/c* ratios that are  $< 1$  (i.e.,

**Table III.** Photoproduct Ratios from **1** and **2** in KP Gels (50/50 (w/w)  $\text{H}_2\text{O}/\text{KP}$ ) at 15 and  $25^\circ\text{C}$ <sup>a</sup>

ketone	<i>E/C</i> $25^\circ\text{C}$	<i>t/c</i>	
		$25^\circ\text{C}$	$15^\circ\text{C}$
<b>1</b> ( $n + 2 =$ )			
13	$2.8 \pm 0.4$	$0.37 \pm 0.03$	
15	$1.8 \pm 0.2$	$0.40 \pm 0.03$	
17	$1.7 \pm 0.2$	$0.56 \pm 0.05$	
18	$0.9 \pm 0.1$	$0.71 \pm 0.04$	
<b>2</b> ( $2n + 1 =$ )			
13	$0.7 \pm 0.2$	$2.2 \pm 0.1$	$2.0 \pm 0.1$
15	$1.2 \pm 0.2$	$3.0 \pm 0.2$	$6.6 \pm 0.6$
17	$1.1 \pm 0.4$	$1.7 \pm 0.1$	$1.4 \pm 0.2$
19	$0.8 \pm 0.3$	$2.1 \pm 0.1$	$1.9 \pm 0.1$

<sup>a</sup> All the *E/C* and *t/c* ratios reported are the average of two samples, with at least three injections per sample. Errors are one standard deviation from the average.

ratios expected of a very polar environment<sup>21</sup>), the carbonyl group must reside near the aqueous interface of the interdigitated gel layers (site F as opposed to site E in Figure 4). Furthermore, the observation of only one Pake pattern for the two nonequivalent exchangeable groups of **1** indicates that both are in a similar environment.

From the  $\Delta\nu_{90}$  values (Table II) the locus of reactivity in **1** does experience some selective ordering by the KS gel layers. For the ketones studied, the maximum  $\Delta\nu_{90}$  occurs for  $n + 2 = 17$  (the same number of saturated carbons as in a KS molecule) and decrease slightly for longer ketones. In spite of this ordering, no chain-length-dependent selectivities in *t/c* or *E/C* ratios or in relative quantum yields are observed for **1** in KS and KP gels. We reason that the order experienced by **1** at the KS or KP gel interface is insufficient to alter the biradical equilibria. Thus, the data indicate that **1** effectively replaces a solvent molecule in a KS or KP gel, with its carbonyl located at the water-amphiphile interface. In this environment, the alkanone simultaneously experiences both the most- and least-ordered portions of its solvent neighbors (the carboxyl head group and the end methyl of the chain, respectively<sup>12</sup>). In summary, the data indicate that *i*-BR is formed in a somewhat ordered reactive environment that is quite porous to the intrusion of water molecules.

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**Table IV.** Photoproduct Ratios at 38 °C and  $^2\text{H}$  NMR Splitting Frequencies at 70 °C from **1** and **2** in KSO Gels (50/50 (w/w)  $\text{H}_2\text{O}/\text{KSO}$ )<sup>a</sup>

ketone	<i>E/C</i>	<i>t/c</i>	rel quantum eff <sup>b</sup>	$\Delta\nu_{90}$ , Hz ( $\pm 0.5\%$ )
<b>1</b> ( $n + 2 =$ )				
13	$5.0 \pm 0.9$	$0.9 \pm 0.3$	1	
15	$5.1 \pm 0.3$	$1.1 \pm 0.3$	1	
17	$6.9 \pm 0.3$	$1.1 \pm 0.2$	1	
<b>2</b> ( $2n + 1 =$ )				
13	$1.2 \pm 0.2$	$4.6 \pm 0.6$	1	3264
15	$1.0 \pm 0.3$	$8.5 \pm 0.5$	1	4513
17	$1.5 \pm 0.5$	$12.7 \pm 1.5$	1	4847
19	$2.1 \pm 0.3$	$3.5 \pm 0.5$	1	3621
21				2937
25	$1.6 \pm 0.3$	$2.6 \pm 0.3$	0.1	884
27	$0.2 \pm 0.2$	$1.0 \pm 0.1$	0.1	732
31	$0.0 \pm 0.2$	$0.4 \pm 0.05$	0.1	2196
35	$2.0 \pm 0.4$	$0.4 \pm 0.04$	1	3051

<sup>a</sup> All the *E/C* and *t/c* ratios reported are the average of two samples, with at least three injections per sample. Errors are one standard deviation from the average. <sup>b</sup> Relative quantum efficiencies for disappearance of ketones. See Table II.

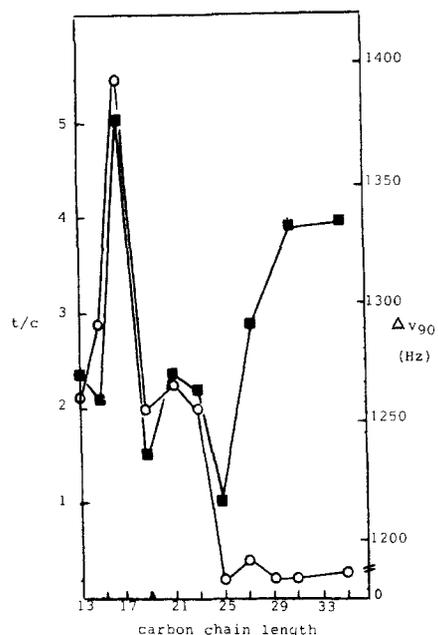
The Norrish II data for **1** in KSO gels (Table IV) indicate that the cybotactic region experienced by the BRs in this solvent is less polar than that in KS gels: the *t/c* ratios compare favorably with those obtained in *tert*-butyl alcohol. They are consistent with **1** in KSO gels being solubilized much like they are in KS gels (with their carbonyls near the water-amphiphile interface), but the interstitial hydroxyl groups from 1-octadecanol making the spaces between carboxyls more ordered and less permeable to water molecules.

As expected from the similarity in shape and size of *c*-BR<sub>1</sub> and *c*-BR<sub>2</sub> from **1**, no length-dependent changes in the *t/c* ratios could be detected from irradiations conducted in KSO gels or smectic BS.<sup>5a</sup> In smectic BS, for which layer boundaries are characterized by slightly increased disorder (but no change in polarity), the *E/C* ratios from **1** are length dependent and maximize near the length of a stearyl group. The *E/C* ratios from **1** in KSO gels differ from values obtained in KS gels, KP gels, or *tert*-butyl alcohol due to the greater order of the bilayer. However, the data do not permit a more detailed assessment of the ketone length dependency.

**Determination of 2 Solubilization Sites and Mobility in Gel Phases from  $^2\text{H}$  NMR Spectral Data and Norrish II Product Ratios.** The Norrish II results for **2** are presented in Tables II–IV. Within the family of **2** in KS and KSO gels, the *t/c* ratios indicate that the shorter members ( $13 \leq (2n + 1) \leq 23$ ) and the longer members ( $23 < (2n + 1) \leq 35$ ) are solubilized in very different fashions in KS gels. In KSO gels, the operational limit of a shorter **2** is  $2n + 1 = 25$ .

The *t/c* ratios of the shorter and longer groups are  $>1$  and  $\leq 1$ , respectively, in the gels of KS and KSO. Thus, without regard for intermolecularly imposed constraints on the two *c*-BRs, the *t/c* ratios for the longer **2** indicate that the carbonyl undergoes reaction in a very polar (water-like) environment; the *t/c* ratios for the shorter **2** are compatible with carbonyls being in a much less polar environment, like the center of a gel layer (site A of Figure 4).

In addition, the *t/c* ratios from KS and KSO gels are largest for 9-heptadecanone, the **2** whose methylene chain length matches that of a KS molecule. The selectivity is very specific: the KS and KSO gels influence much less the *c*-BRs from **2**, which are two carbons longer or shorter than 9-heptadecanone. The *t/c* ratios from **2** in KP gels at 15 °C (Table III) are highest for 8-pentadecanone, the **2** whose methylene chain length matches that of a palmitate molecule. The *t/c* ratios obtained at 25 °C show the same trend, but their differences are much smaller due to the KP gel being near its phase transition temperature (28 °C). In all three gels, the greatest *t/c* selectivity occurs when the chain length of **2** matches the lipophilic length of the gelling molecule. This length dependence is somewhat similar to, but more dramatic



**Figure 5.** *t/c* cyclobutanol ratios (O) and  $^2\text{H}$  NMR  $\Delta\nu_{90}$ 's (■) versus chain length for **2** in KS gels (50/50 (w/w)  $\text{H}_2\text{O}/\text{KS}$ ) at 38 °C.

than, that observed for **2** in the smectic phase of BS.<sup>5a</sup>

For **2**, the biradical precursor to *c*-5, *c*-BR<sub>2</sub>, is clearly a bulkier-shaped species than *c*-BR<sub>1</sub>. The local order of the solvent matrix in the middle of a gel layer apparently retains sufficient flexibility to tolerate the kinking necessary to form *c*-BR<sub>1</sub> (a locally felt disturbance that makes, in this phase, a small contribution to the total solvent disorder). On the other hand, kinking to form *c*-BR<sub>2</sub> emanates locally, from the middle of a gel layer, but forces the intermediate into a more globular shape that is resisted throughout the thickness of the solvent layer.

All of the shorter **2** yield *E/C* ratios in the gels that mimic isotropic solution values and appear independent of chain length. In BS<sup>5a</sup> and some other ordered solvents<sup>32</sup> for which a layer middle is more ordered than layer ends, the *E/C* product yields are very dependent upon the length of **2**. We suggest that the results, again, are due to the middle of a gel layer being amenable to some forms of BR chain kinking. Interchange between *t*-BR and *c*-BR<sub>1</sub> causes a local change in guest shape that is not felt acutely in the relatively disordered layer middle: overall, both conformers are reasonably extended and bear some resemblance to the neighboring solvent chains. Thus, there is little or no *E/C* discrimination. As the region around the locus of reactivity becomes more ordered, the shape differences between *t*-BR and *c*-BR<sub>1</sub> become more important. Evidence for this hypothesis is found in our results for **2** with BS as solvent.<sup>5a</sup> In the smectic B phase at 20 °C, the *E/C* ratio from **2** with 21 carbons is 5.5; in the solid phase at 0 °C the ratio is  $>15$ .

Gross changes in ground-state conformations between shorter and longer **2** are expressed in the *E/C* and *t/c* ratios and in the relative quantum efficiencies. The shorter **2** in KS and KSO gels give *E/C* and *t/c* ratios  $>1$ . The first members of the longer **2** group give *E/C* and *t/c* ratios  $\leq 1$ . The *E/C* ratio increases to the shorter group values when the total solute length approaches twice that of KS. The longest member of the shorter group and the shorter members of the longer group suffer a corresponding ca. one order of magnitude decrease in relative quantum efficiency.

These data, in conjunction with the  $^2\text{H}$  NMR spectra of **2** in KS and KSO gels (Tables II and IV), confirm the existence of two very different, solute-length-dependent solubilization sites and give insight into their nature. Unfortunately, the  $^2\text{H}$  NMR spectra for **2** in KSO gels at 38 °C were not axially symmetric. The greater KSO gel order makes motions of the C–D bonds too slow to be averaged on the NMR time scale at this temperature. Thus,

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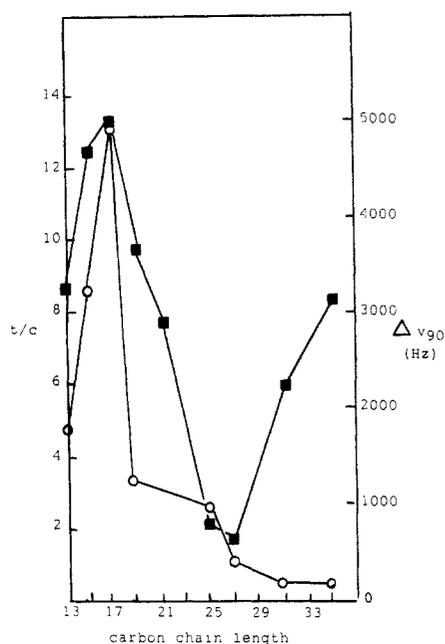


Figure 6.  $t/c$  cyclobutanol ratios (O, 38 °C) and  $^2\text{H}$  NMR  $\Delta v_{90}$ 's (■, 70 °C) versus chain length for **2** in KSO gels (50/50 (w/w)  $\text{H}_2\text{O}/\text{KSO}$ ).

$^2\text{H}$  NMR spectra of **2** in KSO gels were recorded at 70 °C, very near the gel-middle transition temperature.<sup>2</sup>

As seen in Figures 5 and 6, there is a remarkable similarity between the changes in  $t/c$  and  $\Delta v_{90}$  for the shorter **2** in KS and KSO gels. The  $^2\text{H}$  NMR spectra for 7-tridecanone and 8-pentadecanone show a singlet component in addition to the expected Pake pattern in the KS gel. The singlets indicate isotropic-like motion available to a measurable fraction of these ketones within the gel. This must influence their Norrish II ratios, contributing to the apparent lack of selectivity. The transition to longer **2** is marked by a decrease in both  $\Delta v_{90}$  and  $t/c$  ratios. However, whereas the  $t/c$  ratios remain small and nearly constant throughout the long series, the  $\Delta v_{90}$  values (like the  $E/C$  ratios) slowly rise toward the value obtained for 9-heptadecanone as **2** approaches twice the length of a KS molecule.

The solubilization sites already proposed for the shorter **2** in the KS, KP, and KSO gels (site A, Figure 4) require that gauche conformations along neighboring solvent chains be introduced to maintain van der Waals contact among the molecules when **2** is shorter than the lipophilic portion of KS. When **2** is longer than the lipophilic portion of KS, the ketone must either adopt gauche kinks, protrude into the aqueous portion of the gel (for KS gels), or cross a bilayer boundary (for KSO gels). In this way, **2** both slightly shorter than and slightly longer than KS will experience somewhat disordered, nonpolar environments at the locus of photoreaction. The diminished relative quantum efficiencies experienced by the longest members of the short **2** family in KS and KSO gels are due to the extreme conformational changes that **2** undergo to remain within the thickness of a KS gel layer. As a consequence, either hydrogen abstraction is difficult or return to **2** from *i*-BR is easy.

Both the Norrish II and  $^2\text{H}$  NMR data in KS and KSO gels favor a U-conformation for the longer **2**, which allows the carbonyl groups to be near a layer interface and the alkyl chains to reside within the lipophilic portion of a layer (site D, Figure 4). The decreased relative quantum efficiencies and the low  $E/C$  and  $t/c$  ratios reflect the difficulty these ketones encounter in adopting a conformation in which intramolecular  $\gamma$ -hydrogen abstraction and *t*-BR and *c*-BR<sub>1</sub> conformations are attained. Molecular models clearly show that a U-shaped BR can lead preferentially to *cis*-cyclobutanol.

The increases in relative quantum yields and in the  $E/C$  product ratios that occur as **2** approaches twice the length of the lipophilic portion of a KS molecule indicate that the alkyl chains of the longest 1,4-biradicals are held less rigidly than the other U-shaped

biradicals. The BRs from the more exposed ketones have much greater conformational freedom than those that are contained within a lipophilic layer. Thus, the 25–29 carbon length **2** are more deeply imbedded within a layer since, when U-shaped, they do not occupy the full length of the stearyl chain; the **2** with 31 and 35 carbons are nearer to twice the length of a stearyl chain and can move their BRs more easily into the disordered part of the aqueous region (or reach cavities in a gel layer where water penetration has occurred). In essence, the shorter members of the longer **2** family bury their carbonyl deeper into a lipophilic layer and the longer members allow their carbonyl to be more exposed to the aqueous portion.

Remarkably, even though the longer **2** have seemingly preferable solubilization sites available to them in KSO gels (N.B., extension of their chains within or across the lipophilic portion of the bilayer), they choose to bend into a U-shape and to occupy no more than half of the bilayer.

In a separate study, Gulik et al.<sup>33</sup> conjectured that bipolar isopranyl ether lipids (bolaamphiphiles<sup>34</sup>) may form lamellar phases in which individual molecules may be U-shaped. The polarity of their head groups draws them to positions at or near an interface with water. Similarly, the hydrophobic nature of the end groups of **2** makes them prefer an environment removed from an aqueous interface. Thus, although both molecules may adopt U-shapes, they are inverted with respect to one another. The same factors responsible for lipids with two long chains and a polar head group (e.g., phospholipids and spingolipids) being bent rather than linear in membranes and vesicles must apply here.<sup>35</sup> Apparently, very long **2** bend to avoid contact of their more-ordered methylenes with the highly disordered middle of a bilayer and to take advantage of the attractive interactions between a carbonyl group and the polar bilayer interface. The length at which **2** changes from a (distorted) linear conformation to a U-shaped one in KSO gel is a complex function of several forces whose contributions are known only qualitatively.<sup>35</sup>

**Conclusions.** We have demonstrated the extreme sensitivity of solute length to the influence of solvent order on the Norrish II reactions of alkanones in three aqueous gel phases. The product ratios, when combined with  $^2\text{H}$  NMR splitting parameters, provide a qualitative picture of the shape changes that occur from excitation of the reactants to formation of the immediate precursors of products.

From the results, we have identified two very different solubilization sites for the ketones in the gels. One aligns the shorter alkanones along the lipophilic chains of the gel molecules; the other bends the longer ketones into a U-shape so that their carbonyls are near an aqueous interface and their chains are imbedded in the lipophilic portion of a layer.

The 2-alkanones find their carbonyl groups near the aqueous interface of a lipophilic layer, also. Their polar hydroxy 1,4-biradicals become highly hydrated and react in a less lipophilically ordered environment than the BRs from the shorter *sym*-alkanones. The relative length of the ketones (as compared to the gel amphiphile) determines the proximity of the biradicals to the aqueous interface.

The longer **2** prefer to adopt a U-shape rather than a fully extended conformation even in the KSO gel whose bilayer width could accommodate an extended conformation. The reasons the ketones bend are the same as those that explain the structure of lipid bilayers.

The combination of static and dynamic techniques used here to investigate solute order and mobility in organized media should be of general applicability. To the best of our knowledge, the only other example of this approach is the separate studies of Lahav et al.<sup>36</sup> and Meirovitch<sup>37</sup> on the channel inclusion complexes of

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acetone in deoxycholic acid. We are presently using these techniques to elucidate the influence of solvent order on Norrish II photoreactions of ketones in the solid and rotator phases of alkanes<sup>32</sup> and in the ordered phases of *trans,trans*-4-butylbicyclohexyl-4'-carbonitrile.<sup>38</sup>

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## Chiral Discotic Columnar Mesophases from the $\alpha$ and $\beta$ Anomers of Penta-*O*-*n*-alkanoylglucopyranoses<sup>1</sup>

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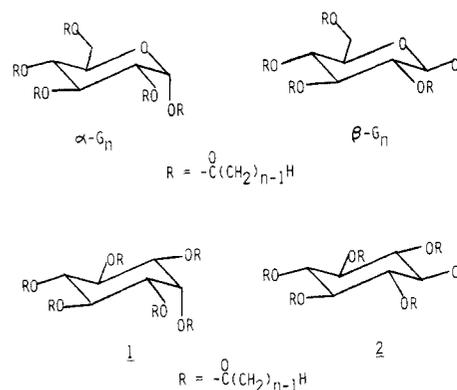
**Abstract:** The detailed phase behavior of the  $\alpha$  and  $\beta$  anomers of penta-*O*-*n*-alkanoylglucopyranoses ( $\alpha$ - and  $\beta$ - $G_n$ , where *n*, the number of carbons in each alkanoyl chain, is 10–16 or 18) has been investigated by differential scanning calorimetry, X-ray diffraction, optical microscopy, and circular dichroism. All members of both anomeric series form at least one columnar discotic mesophase. The shorter chained  $\alpha$  anomers, especially, give rise to a reentrant solid phase upon slow heating of their mesophases. The same molecules pack helically in columns with 6 molecules completing a full twist. No evidence was obtained for rotational ordering of molecules within columns of the longer chained  $\alpha$ - $G_n$  or  $\beta$ - $G_n$ . However, shorter homologues of both series appear to form columns whose total shapes may become twisted. The thermal histories of samples, in terms of both their duration at one temperature and their rates of heating or cooling, determine the packing arrangements and (to a lesser extent) the heats of transition. A detailed discussion of the phases and the factors responsible for their formation is presented.

The unifying feature of all columnar mesophases is the shape of the individual constituent molecules.<sup>2</sup> Whereas most nematic, smectic, and cholesteric molecules are somewhat cylindrical, discotic molecules (as their name implies) are relatively flat and coin-shaped.<sup>3,4</sup> Most known mesomorphic discotic molecules consist of a rigid, aromatic core symmetrically surrounded by 6–8 substituent chains.<sup>5</sup> Recently, we discovered a new class of mesomorphic discotic molecules which are peralkanoylated cyclic mono- and disaccharides. Their cores are nonaromatic, unsymmetrical, and chiral. In a preliminary communication, we reported on the mesomorphic properties of two examples, the  $\alpha$  and  $\beta$  anomers of penta-*O*-*n*-decanoylglucopyranose ( $\alpha$ - and  $\beta$ - $G_{10}$ ).<sup>6</sup> Here, we describe in detail the homologous series of anomeric peralkanoylated glucopyranoses ( $\alpha$ - and  $\beta$ - $G_n$ , where *n* = 10–16, 18) for which each molecule contains only 5 chains. Since the  $G_n$  are prepared in one step from commercially available, inexpensive reagents, they can be obtained easily in large quantities.

Smectic mesophases of cyclic saccharides that are monosubstituted at the anomeric carbon are well documented.<sup>7</sup> The report nearly 50 years ago that tetraacetyl alkylglucopyranosides do not exhibit a mesophase<sup>8</sup> may have dissuaded others from seeking liquid crystallinity in longer pentaacylated glucopyranosides. In fact, several  $\alpha$ - and  $\beta$ - $G_n$  have been synthesized in the interim.<sup>9</sup> A careful reading of the original literature<sup>9a</sup> does allow one, in retrospect, to suspect that they are mesomorphic. In spite of this, the prevalent view is that compounds like  $\alpha$ - and  $\beta$ - $G_n$  are not.<sup>10</sup>

The closest relatives of the  $G_n$  are the peralkanoylated inositols prepared by Kohne and Praefcke.<sup>11</sup> Like the peralkanoylated *myo*-inositols (1), the  $\alpha$ - $G_n$  have one axial substituent (at the anomeric carbon). Like the *scyllo*-inositols (2), the  $\beta$ - $G_n$  have

only equatorial substituents when the glucopyranose ring is in a chair-like conformation.



(1) Part 29 in our series "Liquid-Crystalline Solvents as Mechanistic Probes". For part 28, see: Treanor, R. L.; Weiss, R. G. *J. Phys. Chem.* **1987**, *91*, 5552.

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