

chromatography (benzene as eluent) followed by recrystallization from 2-butanone/95% ethanol to yield the following transition temperatures:

$$k \ 78.5-80.0^\circ\text{C} \ c \ 92.5^\circ\text{C} \ i \ [\text{lit.}^{41} \ k \ 77.5^\circ\text{C} \ c \ 92^\circ\text{C} \ i]$$

***N,N'*-Diacylindigos. General Synthetic Considerations.** Indigos were synthesized initially in their *trans* configurations. Preparatory procedures and intermediate purifications were performed in very diffuse white or red light. The purified materials were stored under nitrogen in the dark at or below 0 °C. HPLC analyses showed all of the indigos thus prepared to be >99% pure.

***N,N'*-Diacetylindigo (1)** was synthesized in 63% yield by the method of Blanc and Ross.<sup>28c</sup> After being recrystallized 5 times from benzene and being dried in the dark at room temperature and ca. 30 torr for 6 days, material of mp 268–269 °C dec [lit. mp 256–257 °C<sup>14</sup>; 263–264 °C<sup>28c</sup>] was obtained.

***N,N'*-Dibenzoylindigo (2)** was synthesized by the method of Posner.<sup>42</sup> After 3 recrystallizations from xylene, a 22% yield of mp 260–262 °C dec [lit.<sup>14</sup> mp 256–257 °C] was obtained.

***N*-Acetylindigo.<sup>43</sup>** A 2.8 g-portion of 1 was heated at 80–100 °C in 30 mL of a 20/80 (v/v) water/pyridine mixture for 2 h. After evaporation of the solvent under aspirator vacuum, the crude product was purified by column chromatography (1% acetone in CH<sub>2</sub>Cl<sub>2</sub> as eluent) to yield 1.3 g (55%) of mp 187–189 °C dec [lit. mp<sup>43</sup> 185–186 °C].

***N*-Acetyl-*N'*-stearoylindigo (3).** A solution of 340 mg of *N*-acetylindigo, 775 mg of freshly distilled stearoyl chloride (bp 165 °C (0.8 torr)), 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and 3 mL of pyridine were refluxed overnight under nitrogen. The solvent was removed under reduced pressure, the residue was chromatographed (1% acetone in CH<sub>2</sub>Cl<sub>2</sub> as eluent), and the main fraction was recrystallized from hot hexane to yield 430 mg (68%) of 3. After repeated recrystallizations from hexane or hexane/ethyl acetate under nitrogen, material of mp 98–101 °C dec was obtained: NMR (CDCl<sub>3</sub>; 60 MHz) 0.9–2.0 ppm (m, 33 H), 2.60 (s, 3 H, CH<sub>3</sub>O), 2.85 (t, *J* = 6 Hz, 2 H, –CH<sub>2</sub>O–), 7.1–8.6 (m, 8 H, Ar); IR (KBr pellet) 2920, 2900, 2800, 1700, 1680, 1598 cm<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>: C, 75.76; H, 8.12. Found: C, 76.01; H, 8.25.

***N,N'*-Distearoylindigo (4).** A mixture of 2 g of indigo, 20 mL of dry pyridine (distilled from P<sub>2</sub>O<sub>5</sub>), and 15 g of freshly distilled stearoyl chloride was refluxed under a dry atmosphere for 25 min. It was poured with stirring into 10% aqueous HCl

and filtered while warm. The dark precipitate was boiled in 200 mL of absolute ethanol for 20 min and filtered. The residue was recrystallized from petroleum ether to give 1.5 g (32%) of crude 4. After being chromatographed (benzene) twice and recrystallized twice from petroleum ether, material of mp 111–112 °C [lit. mp<sup>14</sup> 101–102 °C] was obtained.

**Preparation of Kinetic Samples.** Due to the sensitivity of the indigos to visible light, their solutions were prepared and handled in very diffuse white or red light. Cells and all glassware in contact with the solutions were cleaned thoroughly by washing with soapy water, water, ethanol, acetone, and finally distilled water. The glassware was dried at 120 °C and stored in a desiccator until being used.

Solutions of (1–2) × 10<sup>-4</sup> M *trans-N,N'*-diacylindigos in benzene or toluene were deoxygenated in 1.0-cm quartz cuvettes by bubbling dry N<sub>2</sub> through for several minutes. The cuvettes were closed tightly with Teflon stoppers and were thermostated in the cell compartment of the spectrophotometer.

Solutions in CE were prepared by placing measured aliquots of the indigos dissolved in CH<sub>2</sub>Cl<sub>2</sub> (passed through a silica column and distilled immediately prior to use) into ampules containing preweighted amounts of homogeneous CE. The CH<sub>2</sub>Cl<sub>2</sub> was removed slowly under vacuum to avoid bumping. A heat-swirl-cool sequence was repeated. The samples were brought to 1 atm under nitrogen and sandwiched between two quartz plates separated by a 0.2-mm Teflon spacer which was thermostated in the cell compartment of the spectrophotometer.

Solutions in BS were prepared directly under nitrogen by heating the indigo and solvent to an isotropic temperature (>30 °C) and swirling. For isotropic and some smectic B phase experiments, the nitrogen saturated solutions were placed in capped 1-mm quartz cells and thermostated. In other smectic B phase experiments, the solutions were degassed at 0.1 torr in the isotropic phase, cooled, and flame-sealed in 0.4-mm cells made from Kimax flattened capillaries (Vitro Dynamics).

**Kinetic Procedures.** The samples were temperature equilibrated for 1–2 h and then irradiated to obtain 20–80% of the *cis* isomer. Temperatures were measured several times during each run with a calibrated thermister.

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**Registry No.** *trans*-1, 2533-03-1; *trans*-2, 72738-57-9; *trans*-3, 102396-59-8; *trans*-4, 72751-95-2; *trans-N*-acetylindigo, 102396-60-1; indigo, 482-89-3.

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## Liquid-Crystalline Solvents as Mechanistic Probes. 20. Crystalline and Smectic B Solvent Control over the Selectivity of Photodimerization of *n*-Alkyl Cinnamates<sup>1</sup>

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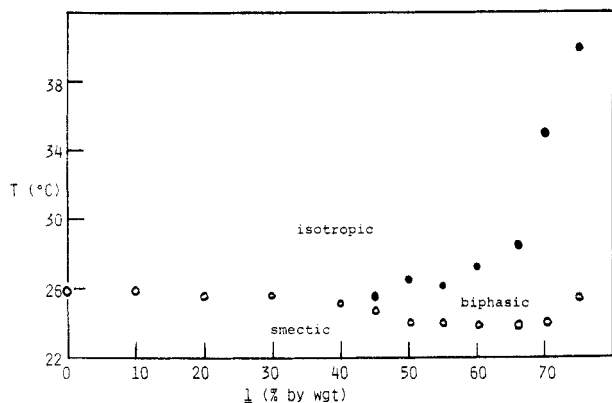
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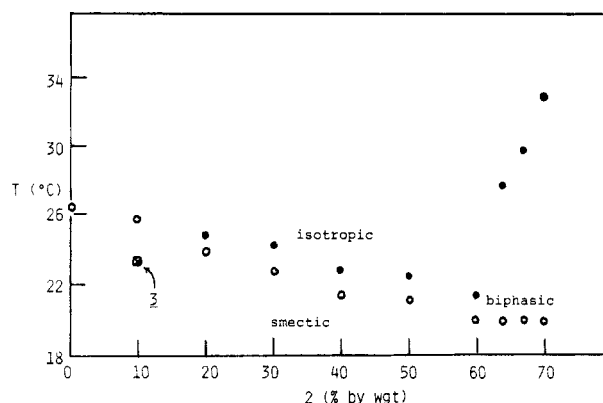
The photodimerizations of *n*-octadecyl, *n*-hexadecyl, and *n*-tetradecyl esters of *trans*-cinnamic acid have been investigated in the crystalline, smectic B, and isotropic phases of *n*-butyl stearate. A strong preference for head-to-tail dimerization is found in the ordered solvent phases. Dipole-dipole-induced interactions between cinnamates and solvent-mediated solute alignments are the factors that combine to control the regioselectivity of photodimerization. The ability of cinnamate esters to be incorporated into the ordered solvent phases is extremely dependent upon the length of the *n*-alkyl solute chains. However, ease of incorporation has little influence upon regioselectivity.

Photodimerization of crystalline cinnamic acid,<sup>2</sup> substituted cinnamic acids,<sup>3</sup> and *n*-octadecyl *trans*-cinnamate,<sup>4</sup>

of glassy ethyl cinnamate,<sup>5</sup> and of solid poly(vinyl cinnamate)<sup>6</sup> have been investigated as empirical methods to



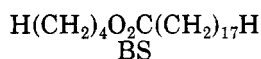
**Figure 1.** Phase-transition temperatures vs. weight percent of 1 in BS.



**Figure 2.** Phase-transition temperatures vs. weight percent of 2 in BS. One point for 3 is shown.

probe molecular organization and to direct reaction stereochemistry. Recently, we<sup>7</sup> demonstrated that photodimerization of neat 5 $\alpha$ -cholestan-3 $\beta$ -yl *trans*-cinnamate in its cholesteric phase provides strong evidence for preferred pairwise antiparallel arrangements of cinnamates.

In the present study, we have investigated the consequences of photodimerizing *n*-octadecyl *trans*-cinnamate (1), *n*-hexadecyl *trans*-cinnamate (2), and *n*-tetradecyl *trans*-cinnamate (3) in *n*-butyl stearate (BS).



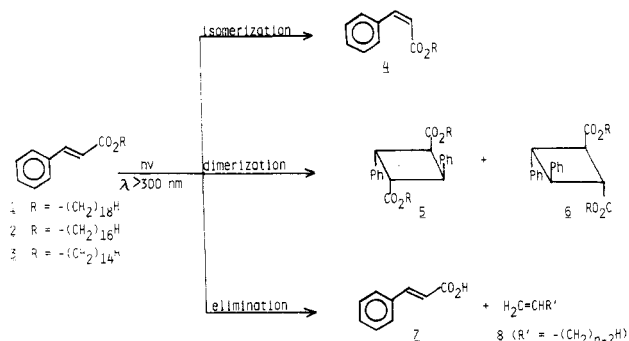
BS exhibits an enantiotropic smectic B phase between 13 and 26 °C: the long axes of the fully extended constituent molecules are hexagonally packed and approximately perpendicular to the plane of the molecular layers.<sup>8a</sup> A somewhat similar orthorhombic layered arrangement of molecules is found in the crystalline phase of BS.<sup>8b</sup> The selection of 1–3 was based upon the similarity of their shape and length to that of BS. As such, they are predicted to be incorporated efficiently into the BS crystalline and smectic B phases.

In theory, 1–3 can produce two families of photodimers which are classified as head-to-head (H–H) and head-to-tail (H–T) (vide infra). BS phase-induced changes in the distribution of products (H–T/H–H) can be interpreted as a measure of the degree to which solvent order controls solute orientations and reactivity. Using this criterion, we find that the smectic B and solid phases of BS behave quite similarly. Both exert very strong control over photodimer formation. The evidence for head-to-tail ordering of cinnamate solutes in smectic B and crystalline BS is even stronger than that found in neat cholesteric phases of 5 $\alpha$ -cholestan-3 $\beta$ -yl *trans*-cinnamate<sup>7</sup> and demonstrates the potential for solvent-induced alignment in controlling the regioselectivity of solute reactions.

## Results and Discussion

**Solubilization of 1–3 in BS.** Plots of transition temperatures (heating cycles) versus weight percents of cinnamate are shown in Figures 1 and 2. The solid to smectic

### Scheme I



B phase transitions are not reported since they were difficult to detect by optical microscopy. The open circles represent the smectic B to isotropic phase transitions at low percentages and the smectic B to biphasic (isotropic liquid plus solid) transition at higher percentages. The closed circles show transition temperatures from the biphasic region to the isotropic phase. Upon cooling the isotropic melt, the biphasic region was not observed; transitions occurred directly from the isotropic to liquid-crystalline phases at the temperatures detected upon heating.

Remarkably, at least 70% of 1 and 2 but no more than 10% of 3 could be solubilized in smectic BS. In spite of the similarity of the solutes, 3 depresses the smectic to isotropic transition temperature to a much greater extent (on a weight or molar ratio basis) than either 1 or 2. This and the observation that the onset of the biphasic region with 2 occurs at a much smaller weight percentage than with 1 demonstrate the extreme sensitivity of the solutes' lengths to their acceptance by the BS smectic and crystalline matrices.

The extended molecular length of 2 equals approximately that of BS, 1 exceeds the length of BS by ca. two carbon-carbon bonds, and 3 is shorter than BS by ca. two carbon-carbon bond lengths. Thus, the solute which is slightly longer than the solvent disturbs the ordered phases least! The slightly shorter solute is clearly recognized as an impurity by the surrounding matrix.

The sensitivity of smectic BS to the shape and extended length of a solute has been recognized in Norrish I<sup>9a</sup> and Norrish II<sup>9b</sup> reactions of ketones and in the thermal isomerizations of an indigo dye.<sup>9c</sup> The solubility behavior of 1–3 affords an extreme example of the effects observed

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Table I. Irradiations of 1-3 in BS

cinnamate	% cinnamate (by wt)	phase (T, $\pm 0.5$ °C)	% conversion <sup>a</sup> ( $\pm 5\%$ )	trans/cis <sup>b</sup> ( $\pm 0.1$ )	H-T/H-H <sup>c</sup>	% dimers <sup>d</sup> ( $\pm 10\%$ )	$\Phi_{rel}$
1	10	isotropic (32)	50	0.9		0 <sup>e</sup>	
		smectic (18)	37	2.3	10.2 ( $\pm 0.9$ )		
	20	isotropic (32)	41	4.3	2.5 ( $\pm 0.9$ )	67	
		smectic (18)	12	9.1	8.0 ( $\pm 0.6$ )	19	
		solid (8)	9	15.7	8.0 ( $\pm 0.6$ )	36	
	40	isotropic (32)	42	3.6	2.6 ( $\pm 0.5$ )	62	
			17	7.8	2.3 ( $\pm 0.1$ )	39	1.00
		smectic (18)	11	11.5	9.4 ( $\pm 0.4$ )	30	
			14	11.0	9.8 ( $\pm 0.9$ )	41	0.22
		solid (8)	10	11.5	10.5 ( $\pm 0.2$ )	22	
	75	isotropic (32)	56	2.7	3.3 ( $\pm 0.1$ )	71	
		smectic (18)	14	15.6	14.2 ( $\pm 0.3$ )	61	
solid (8)		12	15.6	15.1 ( $\pm 0.3$ )	53		
		37	2.4	12.5 ( $\pm 0.3$ )	29		
		40	40	2.4	3.3 ( $\pm 0.7$ )	38	
2	10	isotropic (32)	40	2.4			
		smectic (18)	12	10.6	>20 <sup>f</sup>	31	
	20	isotropic (32)	40	2.4			
		smectic (18)	12	10.6	>20 <sup>f</sup>	33	
		solid (8)	12	11.0	>20 <sup>f</sup>	38	
	40	isotropic (32)	40	2.4	2.2 ( $\pm 0.1$ )	38	
			19	8.5	2.7 ( $\pm 0.1$ )	50	1.1
		smectic (18)	14	10.8	>20 <sup>f</sup>	43	
			17	11.0	>20 <sup>f</sup>	64	0.27
		solid (8)	12	11.2	>20 <sup>f</sup>	39	
	70	isotropic (46)	49	2.4	2.4 ( $\pm 0.6$ )	56	
		smectic (18)	14	11.2	16.4 ( $\pm 0.3$ )	45	
3	10	isotropic (32)	53	0.9	e		
		smectic (18)	37	1.9	9.4 ( $\pm 0.2$ )	11	

<sup>a</sup> % conversions are for disappearance of the *trans* isomer and use  $\omega$ -undecylenyl benzophenone-4-carboxylate as standard. <sup>b</sup> *trans/cis* isomer ratios corrected for detector response assuming  $\epsilon_{trans} = 2.25\epsilon_{cis}$  at 254 nm. Each point is an average of at least two independent trials and two HPLC injections per trial. <sup>c</sup> (H-T)/(H-H) dimer ratios reported assuming  $\epsilon_{H-T} = \epsilon_{H-H}$  at 254 nm. Each data point is an average of at least two independent trials and three HPLC injections per trial. <sup>d</sup> % of product which is dimers calculated from % conversion and *trans/cis* isomer ratio without correcting for differing HPLC responses of monomers and dimers. <sup>e</sup> None detected. <sup>f</sup> Estimated limit of HPLC detection.

previously. Additionally, it demonstrates that favorable solute-solute interactions can lead to induction of liquid-crystallinity in cinnamates which are not mesomorphic themselves. Mesomorphism persists in mixtures of 1 and 2 which contain a minority of BS molecules.

**Photochemistry of 1-3 in BS.** Cinnamate esters are known to undergo *trans-cis* isomerization,<sup>10</sup> dimerization,<sup>4-6</sup> and ester cleavage<sup>7</sup> upon irradiation (Scheme I). All of these processes were observed to some extent when 1-3 were irradiated in the isotropic, liquid-crystalline, and solid phases of BS. The data are summarized in Table I.

The conversions of the cinnamates (>20% initial weight percentages) in the smectic B and crystalline phases of BS were kept below 15% since higher percent conversions altered the morphology of the phases. At 10% initial concentrations of cinnamates, the sensitivity of our analytical methods required >15% conversions. Fortunately, higher percent conversion (up to 37%) of the lower initial loadings resulted in no discernible changes in the phases, as detected by optical microscopy.

*Trans-cis* isomerization of the cinnamate double bond is a competing process in all the phases of BS and acts as an internal clock for dimerization.<sup>7</sup> As expected, the competition between isomerization and dimerization is favored by the latter as the initial solute concentrations increase. Since isomerization involves a relatively small perturbation of the surrounding solvent molecules, it occurs with almost equal facility in the isotropic, smectic, and solid phases of BS. Ester cleavage (another unimolecular photochemical process first observed with 5 $\alpha$ -cholestan-3 $\beta$ -yl *trans*-cinnamate<sup>7</sup>) represented less than 5% of the total reactive pathways.

**Selectivity and Efficiency of Photodimerization in BS.** The relative quantum efficiencies ( $\Phi_{rel}$ ) for the sum of isomerization and dimerization of 40% mixtures of 1 or 2 were determined in the isotropic and smectic B phases

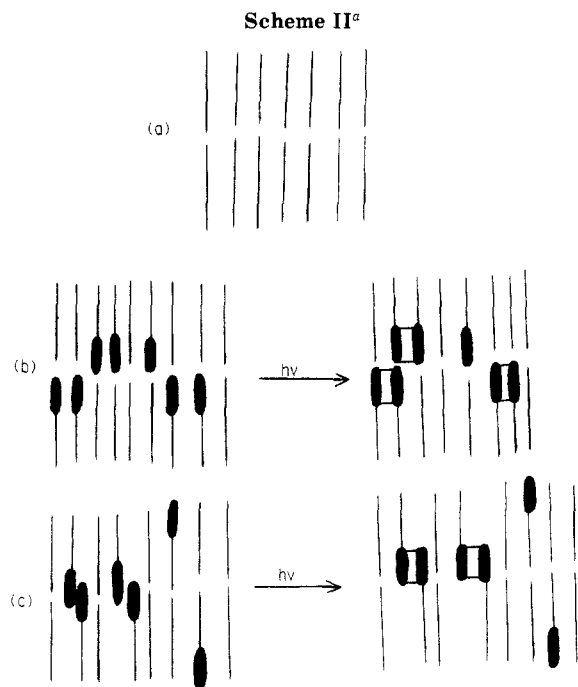
of BS. Normally, such measurements in mesophases lead to erroneous results due to birefringence and reflectance.<sup>11</sup> However, when the sample optical density at the irradiation wavelength is very high (>10), as in the case here, absorption dominates the extraneous effects.<sup>11</sup> From the results in Table I, reaction in the smectic phase is 4-5 times less efficient than in the isotropic phase. However, the H-T/H-H ratios show that the smectic phase is much more selective than the isotropic phase. These observations are a direct consequence of the restricted mobility and specific ordering experienced by cinnamates in the smectic phase.

It is noteworthy that the greater selectivity of smectic-phase irradiation continues for *all* solute concentrations. Bolt, Quina, and Whitten<sup>4</sup> were able to demonstrate complete topochemical control of photodimerization by two crystalline forms of 1. We suggest that many of the factors controlling crystalline packing are important in our BS-cinnamate mixtures, also.

**Possible Alignments of 1-3 in the Ordered Phases of BS and Their Reactive Consequences.** Two probable arrangements of long-chain cinnamates in the ordered phases of BS are shown in Scheme II. Assuming an extended conformation for the alkyl chains, dimerization between molecules *within a layer* can result only in head-to-head dimers and dimerization of molecules *between adjacent layers* can lead only to H-T dimers. Of the possible dimers,<sup>5</sup> only the (H-T)  $\alpha$ -truxillate (5) and (H-H)  $\delta$ -truxinate (6) were detected in the irradiated samples. Other dimers, if formed, are beyond the limit of

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<sup>a</sup> (a) Representation of smectic B solvent organization of BS (—). (b) Representation of orientations of cinnamates (—●) within smectic or crystalline BS assuming the solutes are constrained within one layer. Without diffusion, cinnamate pairs must yield H-H dimers upon irradiation. (c) Representation of cinnamate orientations within smectic or crystalline BS assuming the solutes are antiparallel aligned and partially overlapping. The pairs must yield H-T dimers without diffusion.

our detection (estimated at 5% of 5 or 6).

Since a very small fraction of the dimers formed in the ordered phases is H-T, interlayer dimerizations must be strongly favored, regardless of the size discrepancy between extended BS and the cinnamates. Interdigitation among neighboring cinnamates (a static effect) or facile diffusion between layers of cinnamates whose equilibrium position is restricted within one layer (a dynamic effect) can explain the selectivities. Given the high viscosities of smectic<sup>12</sup> and crystalline phases, the low rates of diffusion,<sup>13</sup> and the relatively short lifetimes of the excited states of cinnamates,<sup>14</sup> it is unlikely that large movements of molecules between layers can occur with sufficient velocity to compete with unimolecular excited state deactivation processes (including *trans* → *cis* isomerization). However, short movements, which would bring cinnamates in neighboring layers into overlap for head-to-tail dimerization, are possible. Given the relatively large amounts of H-H dimers obtained from isotropic phase irradiations, there is every reason to believe that pairs of neighboring cinnamates *within a layer, were they available*, would dimerize H-H upon excitation. Their absence and the preponderance of H-T dimers argues strongly for initial, interlayer pairing of cinnamates prior to irradiation as the preferred mode of association. Such orientations can be rationalized easily on the basis of dipole-dipole interactions<sup>15</sup> and the ob-

servation that cinnamate 1, which is longer than BS, is incorporated into the smectic phase most efficiently: partial head-to-tail cinnamate-cinnamate overlap makes an associated pair of 1 closer to twice the length of BS (and, thus, better able to fit within a smectic double layer).

X-ray diffraction studies on several liquid-crystalline molecules with large dipole moments (homologues of mesogenic *trans,trans*-4-alkylbicyclohexane-4-carbonitriles,<sup>16</sup> 4-(*n*-alkoxyphenyl)-4-cyanobenzoates and 4-(cyano-phenyl)-4-*n*-alkoxybenzoates<sup>17</sup>) strongly suggest that alignment in the mesophases includes pairwise, antiparallel interactions which result in interdigitation. The dominance of  $\alpha$ -truxillate dimer coupled with the results cited above argues strongly for the cinnamates in ordered phases of BS being preferentially antiparallel and partially interdigitated (c in Scheme II).

**Conclusions.** The smectic B and crystalline phases of BS have been demonstrated to effect the regioselective dimerization of three long-chain cinnamates by allowing them to align with partially interdigitated antiparallel associations. The apparent dipole-dipole-induced drive for this alignment is stronger than the tendency of the solute molecules to respect the layer boundaries of smectic BS. Although photoselectivity appears to be influenced only slightly by small changes in the total solute length, the solubilities of the cinnamates are influenced drastically. The fact that matrix morphology translates to product regiochemistry represents a new potential route, employing thermotropic mesophases, to steer intermolecular synthetic processes. These results complement our previous observations that reactive channels of molecular processes can be opened and closed selectively by solvent order.<sup>9</sup>

### Experimental Section

<sup>1</sup>H NMR spectra were obtained with a 300-MHz Bruker AM300 spectrometer interfaced to an Aspect 3000 computer or a 90-MHz Fourier transform Bruker Model Hfx-10 spectrometer. Infrared and ultraviolet spectra were recorded respectively on Perkin-Elmer Model 457 and Perkin-Elmer 552 absorption spectrophotometers. Melting points and transition temperatures were measured on a Kofler micro-hot stage microscope with polarizing lenses or a Gallenkamp melting point apparatus and are corrected. Analytical HPLC was conducted on a Water Model 6000A HPLC connected to a Waters 440 UV detector (254 nm) and a Varian CDS 111 integrator. A Waters Rad-Pak B silica column was employed with 95/5 (v/v) chloroform/*n*-hexane as eluent for the separation of 4-6 from the starting *trans* isomers. For determination of percent conversions,  $\omega$ -undecylenyl benzophenone-4-carboxylate<sup>18</sup> was used as a standard and added to the samples after irradiation. A Rad-Pak C<sub>18</sub> column with methanol as eluent was used to separate and detect *trans*-cinnamic acid,  $\alpha$ -truxillic acid, and  $\delta$ -truxinic acid (obtained from the basic hydrolysis of the irradiated samples).

**Materials.** *trans*-Cinnamic acid (Aldrich, 97%), mp 133-134 °C, was recrystallized from 1,2-dichloroethane. 1-Octadecanol, 1-hexadecanol, and 1-tetradecanol (all from Aldrich) were used as received. Chloroform, hexane, and methanol were HPLC grade. *n*-Butyl stearate (Eastman Kodak) was purified as described previously.<sup>11</sup> It exhibits an enantiotropic smectic phase between 13.5 and 26.0 °C [lit.<sup>8</sup> 15-26.1 °C].  $\alpha$ -Truxillic acid (mp 290-293 °C [lit.<sup>19</sup> mp 274-278 °C (uncorrected)]) and  $\delta$ -truxinic acid (mp 185-191 °C [lit.<sup>20</sup> mp 175 °C (uncorrected)]) were synthesized by known procedures.<sup>19,20</sup>  $\omega$ -Undecylenyl benzophenone-4-carboxylate was synthesized by the procedure of Bichan and

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Winnik.<sup>18</sup> 1-Hexadecene (Aldrich, 94%) and 1-tetradecene (Aldrich, 92%) were used as received for detection of cleavage products.

*n*-Octadecyl *trans*-cinnamate (1), mp 47–49 °C (lit.<sup>3</sup> mp 48–50 °C), *n*-hexadecyl *trans*-cinnamate (2), mp 39.6–40.6 °C, and *n*-tetradecyl *trans*-cinnamate, mp 29.5–31.5 °C, were synthesized and purified following reported procedures.<sup>4,7</sup> The *cis* isomers of 1–3 were formed by irradiating nitrogen saturated solutions ( $5 \times 10^{-4}$  M) of 1–3 in *n*-hexane.<sup>10</sup> Aliquots were withdrawn periodically and analyzed by HPLC until a constant *trans*/*cis* ratio was obtained. The presence of the *cis* isomer in the irradiated samples was confirmed by <sup>1</sup>H NMR of the residues, obtained after removal of solvent.

The <sup>1</sup>H NMR (CDCl<sub>3</sub>) of *trans*-1 is reported below along with that of *cis*-1. The *cis*-1 spectrum was obtained by difference, removing the peaks (at appropriate intensities) from the spectrum of the mixture. *trans*-1: <sup>1</sup>H NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si)  $\delta$  0.89 (t, 3 H, *J* = 6 Hz), 1.2–1.8 (m, 32 H), 4.2 (t, 2 H, *J* = 6.7 Hz), 6.43 (d, 1 H, *J* = 16.0 Hz), 7.35 (m, 5 H), 7.68 (d, 1 H, *J* = 16.0 Hz). *cis*-1: <sup>1</sup>H NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si),  $\delta$  0.89 (t, 3 H) 1.2–1.8 (m, 32 H), 4.09 (t, 2 H, *J* = 6.7 Hz), 5.94 (d, 1 H, *J* = 12.7 Hz), 6.96 (d, 1 H, *J* = 12.7 Hz), 7.5 (m, 5 H).

**Characterization of the  $\alpha$ -Truxillate (5) and  $\delta$ -Truxinate (6) Dimers of 1–3.** The procedure for the dimers of 1 is described. The  $\alpha$ -truxillate and  $\delta$ -truxinate dimers were synthesized by solid-state photodimerization of the  $\alpha$  and  $\delta$  crystal forms of 1 as reported.<sup>4</sup> The  $\alpha$ -truxillate and  $\delta$ -truxinate dimers obtained from the irradiation of 1 in BS had the same retention volumes as those of the correspondingly synthesized dimers.

Further confirmation of the  $\alpha$ -truxillate and  $\delta$ -truxinate dimers of 1 was obtained by hydrolyzing the dimer diesters<sup>5</sup> and detecting the diacids by HPLC. Samples irradiated in BS were first subjected to preparative TLC (silica gel, 50:50 chloroform-*n*-hexane) to remove BS. The resulting material, a mixture of the starting cinnamate and the dimers, was dissolved in hot 95% ethanol and added to an equimolar amount of sodium hydroxide dissolved in 95% ethanol. The solution was stirred at 70 °C for 15 min, and then the excess ethanol was removed by distillation. Water was added to the resulting solid to dissolve the sodium salts of cinnamic acid,  $\alpha$ -truxillic acid, and  $\delta$ -truxinic acid. The long-chain alcohol precipitated from the aqueous solution upon cooling and was filtered. The filtrate was carefully acidified (10% aqueous

HCl) to precipitate the mixture of organic acids. The solid was filtered, dissolved in methanol, and identified by comparison of HPLC retention volumes during separate injections and coinjections with authentic dimers. The  $\alpha$ -truxillate and  $\delta$ -truxinate natures of the dimers from 2 and 3 were confirmed similarly.

**Detection of Cleavage Products.** Products arising from ester cleavage of 1–3 (*trans*-cinnamic acid, 1-octadecene, 1-hexadecene, and 1-tetradecene) were detected on C<sub>18</sub> and silica HPLC columns, and their identities were confirmed by coinjection with known samples.

**Irradiations.** Solutions of 1, 2, and 3 in BS were prepared by vigorously stirring the components at ca. 30 °C. The viscous liquids were viewed under a microscope with polarizing lenses to ascertain homogeneity: samples with microcrystallites display a distinct pattern. Phase-transition temperatures were measured for each concentration of cinnamate in BS. Solutions of cinnamates in BS were placed in 0.04-cm path length Kimax cells which were flame-sealed under vacuum ( $3 \times 10^{-4}$  torr). Samples were thermostated for at least 10 min prior to being irradiated with a Hanovia 450-W medium-pressure mercury lamp fitted with a Pyrex filter. After irradiation, the contents of the cells were dissolved in chloroform and products were analyzed by HPLC. No correction was made for the difference in detector response between dimers and monomers at 254 nm.

**Determination of Relative Quantum Efficiency for Photoreaction of 1 and 2 in the Liquid-Crystalline and Isotropic Phases.** Four 30-mg samples of 1 and 2 in BS (40% by wt) were prepared as described earlier and sealed in Kimax cells whose exposed surface area was matched. One pair of samples (one each of 1 and 2) was irradiated together at 18 °C for 15 min, and the other pair was irradiated at 32 °C (as soon as the bath temperature had been raised and equilibrated) for 4 min, under otherwise identical conditions. The samples were then analyzed as before by HPLC and the percent conversion per unit of irradiation time taken as the relative quantum efficiency normalized to the isotropic value of 1 (see Table I).

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## Spectra of Isomeric Enols

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The NMR and IR spectra of two isomeric nonequilibrating enols are investigated with regard to current theories of strongly hydrogen-bonded systems and to theories concerning possible ring current in hydrogen-bonded enol systems. No evidence is found for ring current. The results of the spectral studies are compared to MM2 calculations of structure. The latter predict little stabilization for the enolic hydrogen bond, in contrast to experimental results. The results of recent modifications of MM2 enabling a better approximation of the hydrogen bonds are reviewed.

Keto-enol tautomerism is an integral part of many reactions involving carbonyl compounds, although the enol forms, per se, rarely have been studied.<sup>1</sup> In the last

century, Claisen, Wislicenus, Knorr, Hantzsch, and Knoevenagel and their co-workers were able to isolate enols by crystallization.<sup>2-7</sup> The classic work of Meyer and co-

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