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# HIGHLY STEREOCONTROLLED PHOTODIMERIZATION OF TETRAMETHYLURACIL BY SMECTIC LIQUID CRYSTALLINE PHASE

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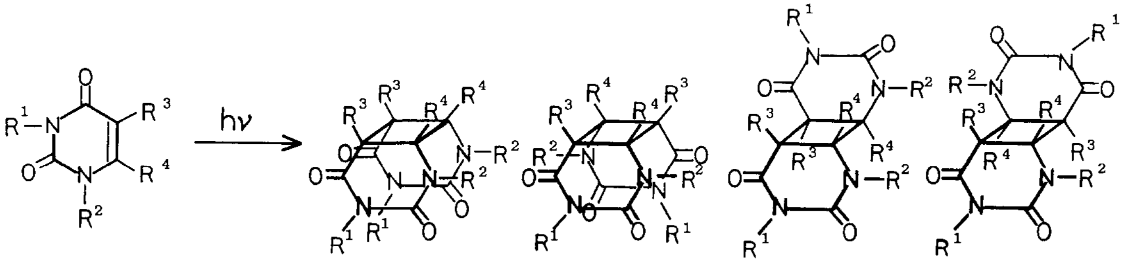
Summary: Smectic liquid crystalline media significantly enhance the stereoselectivity and the rate in the photodimerization of uracil derivatives, in strong contrast to the isotropic phase reactions, which give poor dimer-selectivity and yields.

There is considerable current interest in the molecular recognition by organized molecular assemblies such as micelles, monolayer, inclusion complexes and liquid crystals. This is primarily because of their analogies to some biological systems.

The reactivity of a molecule incorporated in a liquid crystal possessing properties intermediate to liquids and solids, is expected to be quite different from those in isotropic solvents and crystals. So, there have appeared various papers directed toward the use of liquid crystalline media to modify chemical reactivity, but only a few authors have obtained really encouraging results in controlling the stereochemical courses and the rates of photochemical$^{1)}$ and thermal reactions.$^{2)}$

This paper presents the promising feature of smectic liquid crystals which play a crucial role in highly stereoselective photoconversion of uracil derivatives. Smectic (s) structure is of particular interest, since it is much more tightly ordered than nematic (n) and cholesteric (ch) mesophases, which are quite similar to isotropic media with regard to microscopic matrix effect.$^{3)}$

n-Butyl stearate (mesomorphic range reported: $15° \xrightarrow{s} 26°C)^{4)}$ and cholesteryl oleyl carbonate ($-10° \xrightarrow{s} 19° \xrightarrow{ch} 37°C)^{5)}$ were used in this study as anisotropic solvents, which exhibit enantiotropic smectic phases in the adequate ranges. The former ester may be a solvent of choice owing to high photostability and availability. A well-documented photodimerization of 1,3,5,6-tetramethyluracil (TMU) seems to be a suitable reaction for the present study,$^{6)}$ and should provide information regarding highly preferred orientations of solutes in liquid crystalline media. Thus, low concentrations ($0.5 - 1.5\text{X}10^{-2}$M) of tetramethyluracil were irradiated with a high pressure Hg-lamp in isotropic and anisotropic media including frozen solutions. Concentrations were kept low enough to maintain highly ordered mesophase during the irradiation$^{7)}$ and to clear the solubility limits of the photoproducts. Photodimer distribution and conversion yields were determined as a function of



TMU **1** **2** **3** **4**

$R^1=R^2=R^3=R^4=Me$ cis-syn cis-anti trans-syn trans-anti

temperature and solvent phases (Table 1). As, among the cyclobutane type dimers, cis-anti isomer previously assigned6) had a configurational ambiguity, X-ray crystal analysis was performed to confirm the structure **2** unequivocally.8)

The photolysis of tetramethyluracil in isotropic solvents such as water, acetonitrile, dioxane, and ethyl acetate is known to result in non-selective formation of cis-anti **2** and trans-anti **4** dimers (in a rough ratio of 2 : 1) as major products and the dimer distribution to be independent of solvent polarity.6) And isotropic solution-phase dimerization was observed to occur very inefficiently, particularly in such low concentrations. In contrast, highly preferential and smooth dimerization of uracils occurred on irradiation of the butyl stearate solutions at temperatures such that the smectic and crystalline states were retained. Thus, trans-anti dimer **4** was formed over 94% selectivity in addition to cis-anti isomer **2** in smectic media, while frozen solutions gave the reverse selectivity with preferential formation of cis-anti dimer **2**. This is surprising since somewhat similar layered arrangements of constituent molecules are found in both the smectic and crystalline phases.9) Such a marked tendency was also observed when the photodimerization was conducted in isotropic and anisotropic cholesteryl oleyl carbonate. As seen in Table 1, the cholesteric solvent order has no perceptible effects on the photodimerization of uracil derivative, just as observed in isotropic phases. Non-selective and inefficient photodimerization occurred in the isotropic solutions of n-butyl palmitate, n-butyl oleate, and ethyl stearate, which were closely similar to n-butyl stearate, but exhibited no liquid crystalline forms clearly. The data are summarized in Table 1.

Figures 1 and 2 demonstrate dramatic changes in both selectivity and dimerization rate on the phase-transition of anisotropic into isotropic phases at nearly 25°C. These results provide a clean example for the previous observations that reactive channels of intermolecular processes can be opened and closed selectively by solvent order which is interconvertible.10)

1,3,5,6-Tetramethyluracil within smectic and crystalline media may be aligned preferentially in an anti-parallel head-to-tail arrangement compatible with facile anti-dimer formation, while 1,3,5-trimethyluracil (thymine derivative) should exist in head-to-head orientations in both liquid crystalline

Table 1. Photodimerization of 1,3,5,6-Tetramethyluracil in Anisotropic, Isotropic, and Solid Phases a)

| Solvent b) | Temperature(Phase) | Concentrn (W/W) | Time | Dimer Yield c) | Relative Ratio c) | | |
|---|---|---|---|---|---|---|---|
| | | | | | **2** | : | **4** |
| BS | 5°C(solid) | 0.1% | 5h d) | 98% | 67 | : | 33 |
| BS | 16° (smectic) | 0.1 | 5 d) | 91 | 11 | : | 89 |
| BS | 18° (smectic) | 0.3 | 8 e) | 72 | 12 | : | 88 |
| BS | 22° (smectic) | 0.3 | 8 f) | 7 | 6 | : | 94 |
| Bs | 23° (smectic) | 0.3 | 8 e) | 70 | 9 | : | 91 |
| BS | 24° (smectic) | 0.3 | 8 e) | 43 | 18 | : | 82 |
| BS | 25° (isotropic) | 0.3 | 8 e) | 14 | 58 | : | 42 |
| BS | 32° (isotropic) | 0.3 | 8 e) | 4 | 54 | : | 46 |
| BS + 10% $CH_3CN$ | 16° (isotropic) | 0.3 | 8 e) | 5 | 62 | : | 38 |
| BS + 10% DMF | 16° (isotropic) | 0.3 | 8 e) | 6 | 70 | : | 30 |
| COC | -40° (solid) | 0.3 | 8 f) | 9 | 95 | : | 5 |
| COC | 4° (smectic) | 0.3 | 8 f) | 11 | 10 | : | 90 |
| COC | 10° (smectic) | 0.3 | 8 f) | 7 | 12 | : | 88 |
| COC | 23° (cholesteric) | 0.3 | 8 f) | 0.8 | 63 | : | 37 |
| COC | 40° (isotropic) | 0.3 | 8 f) | 0.2 | 71 | : | 29 |
| n-Bu palmitate | 16° (isotropic) | 0.3 | 24 e) | 3 | 62 | : | 38 |
| n-Bu oleate | 16° (isotropic) | 0.3 | 24 e) | 2 | 57 | : | 43 |
| Et stearate | 16° (solid) | 0.3 | 3 d) | 80 | 87 | : | 13 |
| Et stearate | 38° (isotropic) | 0.3 | 5 d) | 2 | 65 | : | 35 |
| ice | -7° (solid) | 1 | 2 d) | 35 | 97 | : | 3 |
| $H_2O$ | 20° (isotropic) | 1 | 5 d) | 28 | 62 | : | 27 g) |

a) The solutions thermostated at the specified temperatures (± 0.5°C) were irradiated in a layer 0.5 mm thick with a high pressure Hg-lamp through a pyrex filter. b) BS: n-Butyl stearate purified by recrystallization from diethyl ether before use. COC: Cholesteryl oleyl carbonate purified by careful column chromatography on silica gel ($CH_2Cl_2$-n-hexane, 1:2, v/v). c) Product yields and distributions were analyzed by HPLC [Particil-5, ODS-3, $CH_3CN/H_2O$ (1:4), UV-235 nm]. Each data point is an average of at least two independent trials and two HPLC injections per trial. d) With a 400W Hg-lamp. e) With a 200W Hg-lamp. f) With a 100W Hg-lamp. g) In addition, cis-syn dimer **1** was formed in 11% relative yield.

including smectic mesophase and frozen phase dimerizations, as previously reported.5)

The present study clearly demonstrates the potential for solvent-induced alignment in highly controlling the regio- and stereoselectivity of solute reactions.

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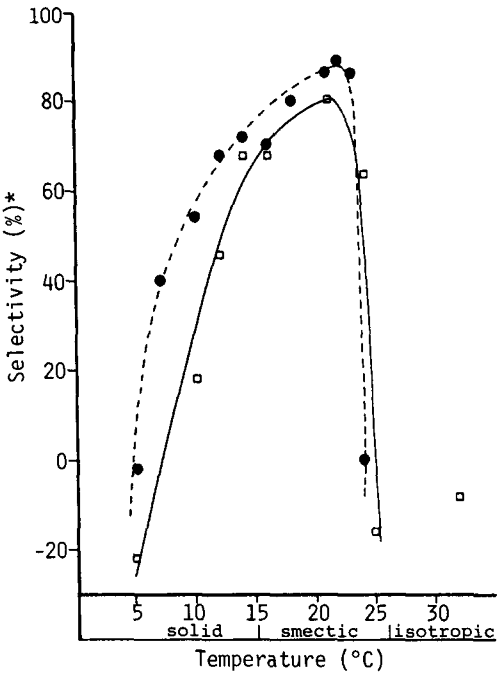

Fig. 1. Photodimerization of TMU in n-Butyl Stearate
□: 200W Hg-lamp, ●: 100W Hg-lamp

$$* \frac{(\text{Dimer } \mathbf{4} - \text{Dimer } \mathbf{2})}{(\text{Dimer } \mathbf{4} + \text{Dimer } \mathbf{2})} \times 100\ (\%)$$

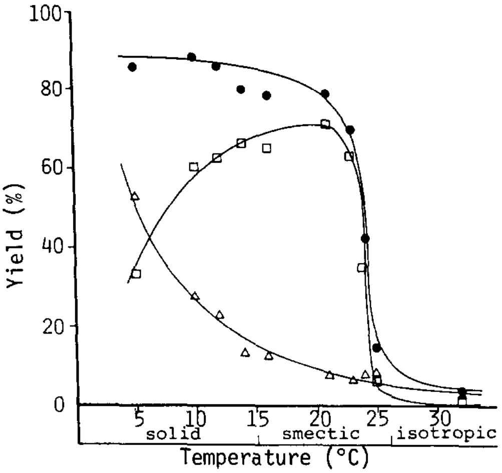

Fig. 2. Photodimerization of TMU (200W Hg-lamp) in n-Butyl Stearate
△: cis-anti dimer **2**, □: trans-anti dimer **4**,
●: cis-anti **2** and trans-anti **4** dimers

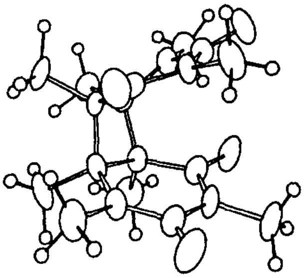

Fig. 3. X-Ray Crystal Structure of **2** as the cis-anti Photodimer[8]

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