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HIGHLY STEREOSELECTIVE PHOTODIMERIZATION OF 1,3-DIMETHYLTHYMINE IN LIQUID CRYSTALLINE MEDIA

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Abstract: Ordered media such as cholesteric and smectic solvents greatly enhance the stereoselectivity and the rate in photodimerization of 1,3-dimethylthymine, in contrast to the isotropic phase reactions leading to a poor product-selectivity.

There has been considerable current interest in the chemical effects produced by organized molecular assemblies such as miscelles, monolayers and liquid crystals.[1-3] This is primarily because of their analogies to some biological systems such as membranes and related structures.

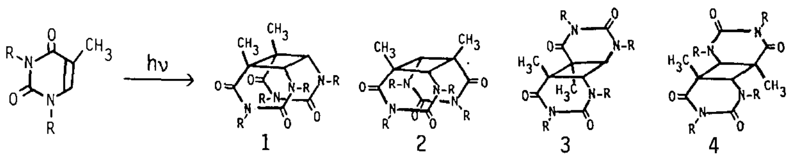
In spite of a number of cumulative data to demonstrate synthetic utility of liquid crystalline media, only few examples are really encouraging in controlling stereochemical courses of photochemical[2] and thermal reactions.[3] A well-documented photodimerization of thymine base[4] seems to be a good subject of reaction to be conducted in liquid crystals, which would provide information regarding highly preferred orientations of collisions. This paper describes the stereochemical effects of such anisotropic media on photodimerization of 1,3-dimethylthymine which has a greater solubility in organic solvents than thymine itself.

Anisotropic solvents used in this study include cholesteryl oleyl carbonate (mesomorphic range: $-10^\circ \overset{\text{s}}{-} 19^\circ \overset{\text{ch}}{-} 37^\circ\text{C}$),[5] cholesteryl linoleate ($20^\circ \overset{\text{s}}{-} 36^\circ \overset{\text{ch}}{-} 39^\circ\text{C}$)[5] and butyl stearate ($15^\circ \overset{\text{s}}{-} 26^\circ\text{C}$),[6] which exhibit cholesteric (ch) or smectic (s) mesophase at a reasonable temperature range. Smectic structure is of particular interest, since it is much more tightly ordered than cholesteric and nematic phases which are quite similar to isotropic media with regard to "microscopic matrix effect" determined by the short-range orientational order.[3]

Low concentrations (1 to 10 w/w%) of dimethylthymine were irradiated by low pressure Hg-lamp in isotropic and anisotropic media including the frozen solutions, and conversion yields and isomer ratios were determined as a function of temperature and solvent phase (Table 1).

As previously reported,[4] all of four possible cis-fused cyclobutane-type dimers (1-4) were formed on irradiation of dimethylthymine in the isotropic solvents including water, dioxane and dimethylsulfoxide. And even their frozen solutions resulted still in non-selective formation of cis-syn (1) and cis-anti (2) dimers (in nearly equal amounts). In contrast, highly preferential dimerization was occurred on irradiation in the liquid crystalline solutions at temperatures such as to preserve mesomorphic states. Thus, cis-syn dimer was nearly exclusively formed, when the medium was maitained anisotropic, regardless to smectic or cholesteric phases. Such a high ratio sharply decreased in the control experiments conducted in the isotropic phases over phase-transfer temperature. Low selectivity also resulted from disturbance of the mesophase structure by addition of dioxane and dimethylsulfoxide.

Photodimerization in the presence of the triplet quencher, cis-piperylene, resulted in a large decrease of dimer formation with no appreciable effects on the ratio, indicative of the contributions of the triplet state dimerization which was more likely in highly viscous and



1 2 3 4

Table 1. Effects of Ordered Media on Photodimerization of Dimethylthymine[a]

solvent media	temperature	phase	conversion	1 : 2
cholesteryl oleyl carbonate	-30 (°C)	solid	43 (%)	86 : 14
	10	smectic	49	93 : 7[b]
	15	smectic	46	96 : 4
	23	cholesteric	34	93 : 7[b,c]
	30	cholesteric	27	92 : 8
	43	isotropic	11	71 : 29
	50	isotropic	11	65 : 35
+ DMSO (1:2)	23	isotropic	12	72 : 28
+ dioxane (1:1)	23	isotropic	10	79 : 21
+ cholesteryl linoleate (1:1)	23	cholesteric	28	91 : 9
cholesteryl linoleate	10	solid	32	91 : 9
	30	smectic	17	94 : 6
	43	isotropic	7	77 : 23
butyl stearate	21	smectic	28	94 : 6
	32	isotropic	7	51 : 49
butyl oleate	32	isotropic	3	62 : 38
water	-70	solid	65	42 : 58
DMSO	-70	solid	28	40 : 49[d]
dioxane	2	solid	3	32 : 68

a) The 1 w/w% solutions thermostated at the specified temperatures were irradiated in a layer 0.5 mm thick with a low pressure Hg-lamp (160 w) without filter for 4 hr. Analyses of conversion and product distribution were performed by HPLC (LiChrosorb RP-18, CH_3CN/H_2O (1:6), UV-236 nm). b) The same ratio was obtained at lower stages of conversion up to 10%. c) In the presence of 2% piperylene, 10%-conversion was observed in a ratio of 93:7. d) In addition, 3 and 4 were formed in a ratio of 5:6.

dilute media such as liquid crystalline solvents.[2]

Higher degree of conversion was smoothly attained in mesomorphic and solid media than in isotropic solvents. Dimers (1 and 2) undergo an apparent photolysis to monomer ten times faster in the isotropic solvents and this photo-equilibrium may be responsible partly for such a conversion rate.

The long and short-range order of liquid crystalline phases should influence solute molecules to align themselves in the defined packing arrangement, and hence the preferred orientations of solute-solute collisions may result in a high stereoselectivity and an increased rate of reaction as presented herein.

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