

**Diastereoselectivity in ($2\pi + 2\pi$) Photocycloaddition of Cholesteryl Cinnamate to Methyl 9-Phenanthrenecarboxylate:
Control of the Stereoselectivity in Liquid Crystalline Phase**

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Photocycloaddition of cholesteryl cinnamate with methyl 9-phenanthrenecarboxylate in benzene at ambient temperature gave a ($2\pi + 2\pi$) photocycloadduct in 8% diastereomeric excess (de). When the reaction was carried out in neat conditions at 150–170 °C, the major product was reversed to another diastereomer, in which de was given in 14%.

Molecular assemblies and chemoselectivities in organic reactions in liquid crystalline media have been attracted considerable interest.¹ As for the photoreaction in liquid crystalline media, photodimerization of acenaphthylene² and 1,3-dimethylthymine,³ photoasymmetric synthesis of helicenes,⁴ photocyclization of α -(*N*-methylanilino)styrene,⁵ photochemical interconversion of sulfoxide,⁵ photolysis of ketones,⁶ have been extensively studied. Although cholesteric liquid crystals, due to their macroscopic twist,⁷ are expected to induce specificity in chirality in photochemical reactions, optical yields of the photochemical reactions in cholesteric media were extremely low as exemplified by the photoasymmetric synthesis of helicenes in the maximum 1.1% ee.⁴ Here we report that diastereoselectivity in photocycloaddition and photodimerization of cholesteryl carboxylates depended on reaction phases, and that the best diastereomeric excess (de) of 14% was given at anisotropic environment.

Photoirradiation of a benzene solution containing methyl 9-phenanthrenecarboxylate (**1**) and cholesteryl cinnamate (**2**, mp 158.2–160 °C) by a high-pressure Hg lamp through Pyrex filter at ambient temperature gave a ($2\pi + 2\pi$) photocycloadduct **3** in a 74% isolated yield along with formation of a small amount of *cis*-adduct (9%) (Scheme 1, Table 1, run 1).^{8,9} De of **3** (8%) was determined by ¹H NMR of the diastereomeric mixture of **3**. When the photoreaction was carried out in toluene, both

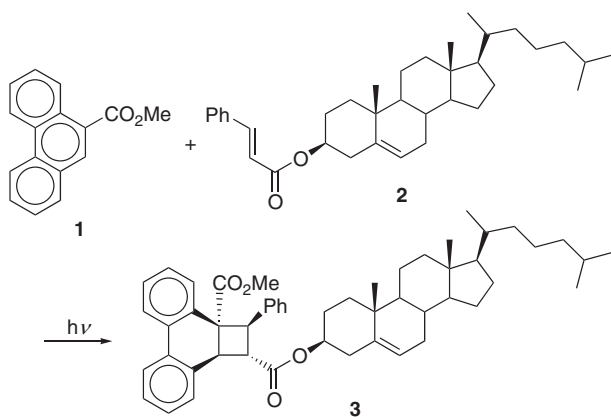


Table 1. ($2\pi + 2\pi$) Photocycloaddition of methyl 9-phenanthrene-carboxylate (**1**) with cholesteryl cinnamate (**2**)

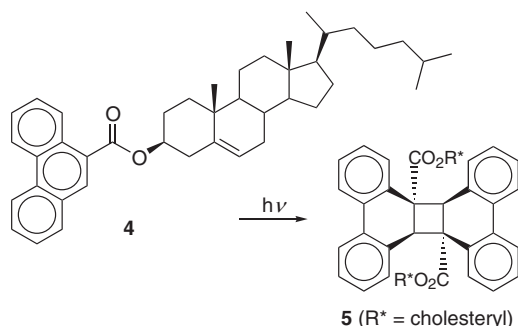
Run	Solvent	Temp / °C	Irradn Time / h	Yield of 3 ^a / %	de of 3 ^b / %
1	benzene ^c	20	5	74	8 (46:54)
2	toluene ^c	20	5	48	2 (49:51)
3	CH ₃ CN ^d	20	5	<1	—
4	CH ₃ CN : CH ₂ Cl ₂ = 1 : 1 ^d	20	5	37	0 (50:50)
5	CH ₃ CN : CH ₂ Cl ₂ = 1 : 2 ^d	20	5	72	0 (50:50)
6	neat ^e	150–170	6	36	14 (57:43)
7	neat ^e	20 (preheated at 150–170)	24	17	8 (54:46)
8	cholesterol ^f	150–170	5	68	6 (53:47)

^aIsolated yield based on **1**. ^bDetermined by ¹H NMR. Values in parenthesis are the product ratios of diastereomers of **3**. Left value and right value in parenthesis correspond to integrals at 5.37 and 5.30 ppm in ¹H NMR spectra (CDCl₃), respectively. ^c[**1**] = 0.05 M, [**2**] = 0.25 M. ^d[**1**] = 0.01 M, [**2**] = 0.05 M. ^e5 equiv. of **2** (based on **1**) was used. ^f5 equiv. of **2** (based on **1**) and 5 equiv. of cholesterol (based on **1**) were used.

chemical yield and de decreased (run 2). Although the reaction in acetonitrile did not give any adduct, addition of dichloromethane increased the yield of **3**, without any face-differentiation (runs 3–5). It is noteworthy that when the reaction was conducted in neat conditions at 150–170 °C (that is near the melting point of **2**) to obtain the cholesteric mesophase, 14% de was obtained (run 6).¹⁰ We also attempted the photoreaction at ambient temperature after the preheating the mixture of **1** and **2** at 150–170 °C to once melt the mixture, 8% de was obtained (run 7). Moreover, in the presence of cholesterol at 150–170 °C, the chemical yield of **3** increased to 68% but de decreased to 6% (run 8). It is interesting that the major product was reversed to another diastereomer when the reactions were done in cholesteric anisotropic environment compared with the reactions in isotropic media such as benzene and toluene.

Then we turned our attention to the photodimerization of cholesteryl 9-phenanthrenecarboxylate (**4**, mp 161–178 °C) (Scheme 2).¹¹ Photoreaction of **4** in benzene at room temperature gave only head-to-tail *syn*-dimer **5** in 55% yield, 8% de (Table 2, run 1).¹² Photoreaction at lower temperature in toluene did not improve the de (run 2). In a similar neat conditions at 150–170 °C, the photodimer **5** was not obtained at all, probably due to the restricted mobility of the molecules (runs 3, 4).

The fluorescence of **1** in benzene was efficiently quenched by **2** ($k_q = 9.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), and a weak exciplex emission was observed at ca. 460 nm.¹³ These photocycloaddition and photodimerization proceed regio- and stereospecific manner,

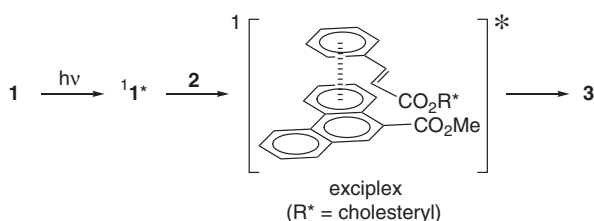


Scheme 2.

Table 2. Photodimerization of cholesteryl 9-phenanthrenecarboxylate (**4**)

Run	Solvent	Temp / °C	Irradn Time / h	Yield of 5 ^a / %	d.e. of 5 ^b / %
1	benzene ^c	20	72	55	8 (54:46)
2	toluene ^d	-70	20	48	4 (52:48)
3	neat	150-170	2	0	—
4	neat	150-170	72	<1	—

^aDetermined by ¹H NMR. ^bDetermined by ¹H NMR. Values in parenthesis are the product ratios of diastereomers of **5**. Left value and right value in parenthesis correspond to integrals at 5.35 and 5.29 ppm in ¹H NMR spectra (CDCl₃), respectively. ^c[**4**] = 0.05 M. ^d[**4**] = 0.01 M.



Scheme 3.

where concerted two carbon-carbon bonds formation occurs through π - π overlapped, sandwich type singlet exciplexes (Scheme 3).⁸ In isotropic environment, since cholesteryl groups disperse, inherent chirality of the cholesteryl group affects the stability of two diastereomers of the singlet exciplexes. In benzene and toluene, relatively tight structure of the π - π overlapped singlet exciplexes gave some de, while face differentiation did not occur in acetonitrile and dichloromethane because of the difficulty of formation of the π - π overlapped singlet exciplexes.^{12a,14} On the other hand, since cholesteryl helical assembly will be constructed at near their melting points,⁷ the twisted assembly of the cholesteric mesophase may bring the diastereodifferentiation to reverse the major diastereomer to another one overcoming the inherent chirality of each molecule.

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