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Enantiodifferentiating Photoisomerization of 1,2-Diphenylcyclopropane Sensitized by Chiral Aromatic Esters

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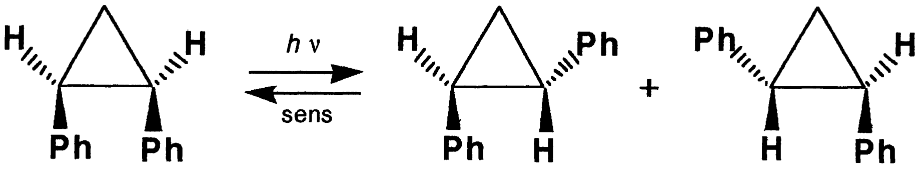
Enantiodifferentiating *cis-trans* photoisomerization of 1,2-diphenylcyclopropane (**1**) in the presence of (-)-tetramenthyl 1,2,4,5-benzenetetracarboxylate as a chiral sensitizer gave (+)-(1*S*,2*S*)-**1*t*** in enantiomeric excesses (e.e.) of 10.4 and 2.8% in pentane and acetonitrile, respectively, while the photosensitization with the corresponding (-)-tetrabornyl ester afforded (+)-(1*S*,2*S*)-**1*t*** (3.8% e.e.) in pentane and, notably, the *antipode* (-)-(1*R*,2*R*)-**1*t*** (2.4% e.e.) in acetonitrile.

Enantiodifferentiating photoisomerization with chiral sensitizer has been an attractive, but really hard, task in photochemistry1) ever since the first asymmetric *cis-trans* photoisomerization of 1,2-diphenylcyclopropane (**1**) reported by Hammond and Cole in 1965.2a) They employed (+)-1-(1-(*N*-acetylamino)ethyl)naphthalene as a chiral singlet sensitizer2b) to effect photoisomerization of racemic *trans*-1,2-diphenylcyclopropane in benzene and isolated optically active (+)-(1S,2S)-**1*t*** of 6.7% e.e. from the photolyzate. Later, Ouannès *et al.* and Kagan *et al.* performed further studies on the same photoisomerization, using optically active aromatic ketones such as 3-methyl-1-indanone3) and 3- or 4-methyl-1-tetralone4) as triplet sensitizers and obtained **1*t*** in lower optical yields of 3.0 and 1%, respectively. Recent mechanistic studies5) on the photoisomerization of diarylcyclopropanes through radical-cation intermediates resulting from the electron transfer within exciplex together with our own result6) on highly enantiodifferentiating *cis-trans* photoisomerization of cyclooctene prompted us to effect this invulnerable photoisomerization through an excited-state charge-transfer system using chiral photosensitizers with electron-withdrawing groups. In this communication, we report that the use of optically active aromatic esters as photosensitizer does enhance the optical yield of the photoisomerization of **1** up to 10% through enantiodifferentiation in the quenching process and, quite interestingly, the product chirality is inverted just by changing solvent polarity.



1c (+)-(1*S*,2*S*)-**1*t*** (-)-(1*R*,2*R*)-**1*t***

A solution (300 mL) of 1,2-diphenylcyclopropane (30 mM) of a given isomer composition containing (-)-tetramenthyl or (-)-tetrabornyl 1,2,4,5-benzenetetracarboxylate (5 mM) as a chiral photosensitizer and cyclododecane (3 mM) as an internal standard was irradiated at 25 °C under an argon atmosphere in an annular Pyrex vessel, using a 300-w high-pressure mercury lamp. The photoisomerization was monitored by GLC analyses (a 3-m silicone OV-101 column at 160 °C) of aliquots removed periodically from the reaction mixture. The major photoreaction observed was the geometrical isomerization of 1,2-diphenylcyclopropane with both sensitizers, and the material balance was excellent (>95% recovery) for the first 24 h and fairly good (80-90% recovery) for 36-100 h irradiations. The resulting mixture was subjected to column chromatography over silica gel with an ethyl acetate/hexane (1:99) eluent and the subsequent preparative GLC over an OV-101 column to give **1*t*** of 73-97% chemical purity. No trace of possible fragments, which could be derived from the decomposition of chiral sensitizer, was detected by GLC and NMR analyses of the isolated sample, and the impurity detected was only the achiral **1*c***, for which the optical yields reported below were corrected appropriately. Specific rotation of the isolated **1*t*** was measured in chloroform and compared with the value reported for the optically pure (+)-(1*S*,2*S*)-**1*t***: $[\alpha]_D^{20}$ +418° (*c* 0.96, $CHCl_3$).7) This isolation and correction procedure was proved valid, since, in some comparative runs, the chemically pure sample obtained by repeated GLC separations showed practically the same specific rotation with the corrected value of the original, chemically less pure, sample obtained by single GLC separation.

Photoisomerizations of both **1*c*** and racemic **1*t*** sensitized by (-)-tetramenthyl benzenetetracarboxylate were performed in pentane. The isomer composition and corrected optical yield of **1*t*** isolated as above are plotted against the irradiation time. As can be seen from Figure 1, the solutions of both isomers appear to approach the photostationary state upon prolonged irradiations, although the ultimate value of 27% *trans* was not attained within this period of irradiation. In the photoisomerization of racemic **1*t***, the optical yield of **1*t*** isolated from the photolyzate increases gradually with the irradiation time and reaches a plateau of *ca.* 8% e.e. at longer irradiation times, as was observed by Hammond and Cole.2a) The slow increase in % e.e. is obviously ascribable to the fact that the sample isolated at the early stages of the photolysis contains a substantial amount of the original racemic **1*t***, along with the photochemically-produced optically active one.

On the other hand, the photoisomerization starting from **1*c*** gives the highest optical yields around 8% within a very short period of irradiation as compared with the **1*t*** case, although the optical yield decreases to some extent with extending irradiation time, probably owing to the decomposition of the chiral sensitizer and/or the building-up of unknown by-product(s) that may act as photosensitizer. The rapidly developing optical yields in the photoisomerization of **1*c*** indicate that the principal enantiodifferentiation step is not the enantiomer-selective decay from the intervening exciplex or radical-ion pair but the enantiodifferentiating quenching of excited optically-active sensitizer by the enantiomers of **1*t***, since, if the decay process is supposed to be enantiomer selective, the optical yield observed should be invariant from the initial stages of photoisomerization as demonstrated in the enantiodifferentiating *cis-trans* photoisomerization of cyclooctene sensitized by the same chiral aromatic sensitizers.6)

Of apparent curiosity, the highest optical yield obtained was shown to depend on the initial isomer composition, as shown in Table 1. Simply according to the above enantiodifferentiation mechanism, the optical yield should reach a common photostationary-state value, which is independent of the initial isomer composition.

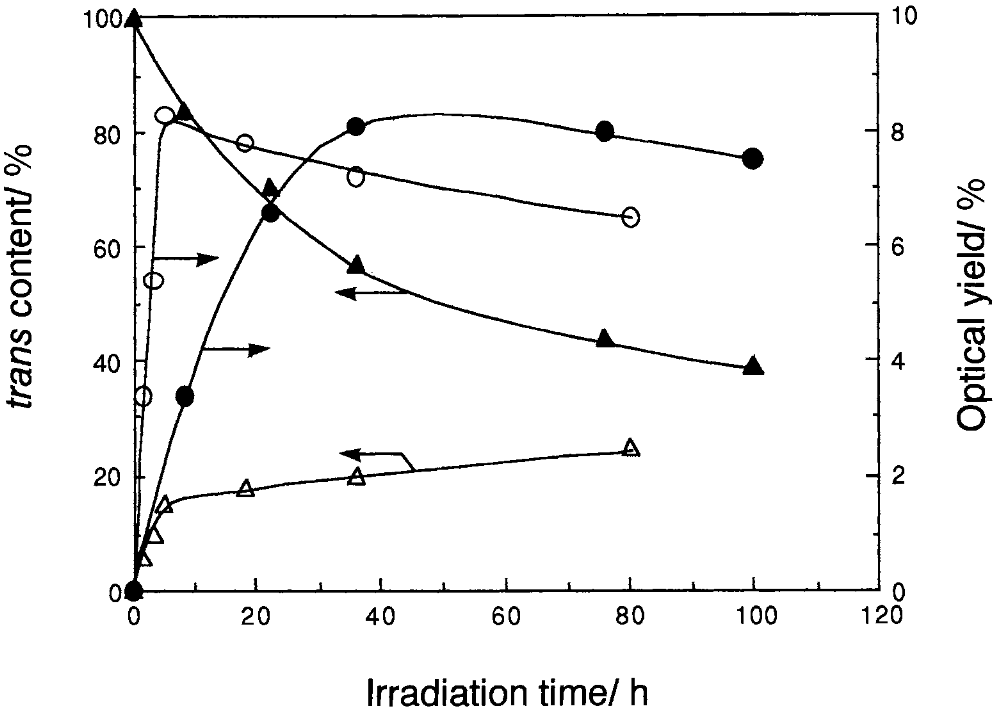


Fig. 1. Isomer composition (△: **1***c*; ▲: **1***t*) and optical yield (○: **1***c*; ●: **1***t*) as functions of irradiation time in enantiodifferentiating photoisomerizations of *cis*- and racemic *trans*-1,2-diphenylcyclopropane (**1***c* and **1***t*; 30 mM) sensitized by (-)-tetramenthyl 1,2,4,5-benzenetetracarboxylate (5 mM) in pentane at 25 °C.

Actually, the obtained value is a consequence of critical balance between the generation of optically active **1***t* by chiral sensitizer and the racemization of it by achiral photoabsorbing by-product(s); the latter becomes dominant, especially upon longer irradiations. Then, the initial isomer compositions of *cis*:*trans* = 22:78 to 38:62 and the irradiation times of 12-13 h gave the optimal optical yields up to 9.8-10.4% with this sensitizer.

The use of (-)-bornyl ester as a chiral sensitizer similarly gave (+)-(1*S*,2*S*)-**1***t* in lower optical yields of 3.8 and 1.2% in pentane and ether, respectively; see Table 1. Unexpectedly, the photoisomerization with the same sensitizer in highly polar acetonitrile yielded the *antipode* (-)-(1*R*,2*R*)-**1***t* in 2.4% e.e. A comparable experiment with the (-)-menthyl ester in acetonitrile did not afford the antipode but merely gave the same enantiomer (+)-(1*S*,2*S*)-**1***t* in a reduced optical yield of 2.8%. Since, in the bornyl case, the solvent of moderate polarity such as ether gave an intermediate optical yield of 1.2%, the solvent effect does not appear to be discrete but rather be continuous in nature. Probably, the sensitizer structure in the excited state changes slightly with solvent polarity, which alters the quenching efficiencies of (+)-(1*S*,2*S*)- and (-)-(1*R*,2*R*)-**1***t* for the chiral sensitizer, or the contribution of radical-ion pair in the decay process would increase especially in the polar solvents. In an extreme case like the bornyl ester, the structural change of excited sensitizer and/or intervening radical-ion pair would be sufficiently large to invert the product chirality.

In addition to the mechanistic interest, the present result provides us with a novel method for controlling product chirality just by changing the solvent polarity without employing the antipodal chiral source.

Table 1. Highest optical yields obtained with varied initial isomer composition and solvent in photoisomerization of 1,2-diphenylcyclopropane sensitized by (-)-tetramenthyl or (-)-tetrabornyl 1,2,4,5-benzenetetracarboxylate[a)]

Sensitizer	Solvent	Initial isomer composition (*cis*:*trans*)	Irradiation time /h	Optical yield /%[b)]
Menthyl ester	Pentane	100:0	5	8.3
		60:40	8	8.2
		38:62	12	9.8
		22:78	13	10.4
		0:100	36	8.1
	CH_3CN	35:65	16	2.8
Bornyl ester	Pentane	35:65	21	3.8
	Ether	35:65	25	1.2
	CH_3CN	35:65	32	-2.4

a) Irradiation conditions: [substrate] = 30 mM; [sensitizer] = 5 mM; 25 °C; argon atmosphere.

b) Sign accords with that of the product's optical rotation.

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