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Asymmetric Photochemical Reactions in Solution

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Contents

I. Introduction

In contrast to the ever-growing asymmetric chemistry in the ground electronic state and the rapidly developing photochemistry, the interdisciplinary asymmetric photochemistry, which introduces the idea of enantio- or diastereodifferentiation into the reactions of electronically excited states or reactive intermediates derived therefrom, has not extensively been explored until recently, except for the pioneering works on the "absolute" asymmetric photochemistry induced by circularly polarized light. This is simply because the photochemical reactions involving highly energetic excited states do not appear to be advantageous over thermal ones as a method for asymmetric induction, where a free energy difference of a few kilocalories per mole is sufficient to give >99% stereodifferentiation. Furthermore, the inter- or intramolecular interaction in the excited states has been believed to be weak and short-lived and also to be difficult to control. However, some recent studies have revealed that these apprehensions are not always realistic, and a high order of regio- and/or stereochemical control has been created in several categories of uni- and bimolecular photochemical reactions. In addition, photochemistry has an inherent advantage that the irradiation can be conducted in principle over a wide range of temperature without affecting the reaction mechanism, although the temperature effect in asymmetry photochemistry has only recently been recognized and demonstrated to be a versatile tool for controlling the stereochemical fate of the excited state. Increasing interest and understanding of the mechanisms and intermediates involved in the molecular recognition in the excited

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state, as well as the conceptual considerations on the asymmetric chemistry, have also made a considerable contribution in developing a variety of methodologies for the photochemical asymmetric induction.

Asymmetric photochemistry in solution phase has already been reviewed briefly by several authors.[1-6] However, in spite of the recent advances in this intriguing field, the latest comprehensive review was written by Rau for *Chemical Reviews* in 1983,[3] which includes a detailed description of the fundamentals and the definitions, as well as a survey of earlier works up to early 1982, of asymmetric photochemistry in solution. On the other hand, the solid-phase asymmetric photochemistry, in which chiral information is provided by the rigid environment, has also been investigated intensively in recent years, but this field has recently been reviewed from various aspects.[7-13] In contrast to the considerable attention focused on the physical and chemical processes in the organized molecular assemblies like Langmuir–Blodgett assembly, micelle, and liquid crystal, the asymmetric photochemistry in these media has not been extensively investigated so far, but both old and relatively new results reported for the asymmetric photochemistry conducted in chiral liquid crystals are highly disappointing and has just been reviewed.[14] Hence, the basic concepts described in the Rau's review[3] or the asymmetric photochemistry in the solid phase or organized molecular assemblies will not be repeated here. We rather concentrate on the asymmetric photochemical reactions carried out in fluid solution. This review covers the literature available through the mid 1991.

II. Historical Background

As early as the late 19th century, Le Bel[15] and, more explicitly, van't Hoff[16] recognized the potential use of right- or left-circularly polarized light (r- or l-CPL) in photochemical reaction for the production of an excess of a particular enantiomer from racemic substrate. This idea gained a physical basis by the discovery of the isotropic circular dichroism (CD) by Cotton,[17,18] who himself performed an attempted enantiodifferentiating photolysis of an alkaline copper tartrate solution with CPL to give no enantiodifferentiation,[19] owing to the insufficient energy of the photon employed as demonstrated later by Byk.[20] After further unsuccessful efforts to verify the prediction of Le Bel and van't Hoff by Freundler,[21,22] Guye and Drouginine,[23] Henle and Haakh,[24] Bredig,[25] Padoa,[26] and Pirak,[27] Kuhn and his collaborators[28-33] reported the first unequivocal asymmetric photolyses in 1929–30, which were followed by the works by Mitchell[34,35] and Tsuchida et al.[36]

In sharp contrast to the unquestionable success in the enantiomer-differentiating photodecomposition of racemic mixtures mentioned above, the enantioface-differentiating photoadditions to prochiral compounds by excitation with CPL, though claimed to give optical activity in the irradiated solution by several investigators,[37-44] lack the theoretical basis for asymmetric induction in the products, and indeed some of them were later revealed not to be reproducible.[45] Another type of CPL-induced asymmetric photochemistry, often called "absolute asymmetric synthesis", flourished in the 1970s; that is the conformational enantiomer-differentiating photocyclization of various diarylethylenes to the corresponding helicenes studied by Kagan's[46,47] and Calvin's groups,[48-50] and the photocyclization of *N*-aryl enamimes by Kagan et al.[51] Recently, Cavazza and Zandomeneghi[52] reported a novel intermolecular asymmetric photocycloaddition of acetylenes to racemic cyclopentenones excited selectively by CPL. Earlier works in this field were reviewed by Henderson,[53] Tai et al.,[54,55] Buchardt,[56] Kagan and Fiaud,[2] and Bonner.[57]

For a long time, the direct asymmetric photochemistry with CPL has been related more or less to the origin of the optically active biomolecules in nature[57-66] and therefore has not been taken seriously as a practical method for synthesizing optically active compounds in high optical yield.[2] Examining the anisotropy (g) factor of various ketones, Kagan and co-workers[67,68] demonstrated that the optical purity (op) of the remaining substrate obtained upon enantiomer-differentiating photodecomposition with CPL can be increased up to 20–30%, but only after most (~99%) of the substrate was decomposed. Recently, Nikogosyan et al.[69,70] reported that the g factor is enhanced by more than 2 orders of magnitude in a two-photon process induced by the CPL irradiation using a high-intensity, short-pulse laser.

In 1965, Hammond and Cole[71] reported the first asymmetric photosensitization with an optically active compound, which is a novel and attractive methodology to transfer and potentially multiply the chirality of an optically active sensitizer in the photoproduct through the photosensitization process, although the product's op was fairly low (6.7%) at that time. After several unrewarded attempts to improve the product's op and to materialize the true chirality multiplication through singlet or triplet photosensitization,[72-81] Inoue et al.[82,83] and Kim and Schuster[84] have recently demonstrated that the product's op can be raised up to 40% in the photoisomerization and 15% in the photosensitized Diels–Alder reaction, respectively. These moderate op's were obtained by utilizing the intimate interaction in the exciplex or triplex intermediate. Unprecedentedly, an evident switching of product chirality was observed by changing the irradiation temperature in the enantiodifferentiating photosensitized isomerization of cyclooctene.[82,83] The asymmetric photosensitization is one of the most intriguing and less explored, but promising, fields in the mechanistic and synthetic photochemistry.

Somewhat unexpectedly, the diastereodifferentiating photochemical reactions induced by built-in chiral auxiliaries or building blocks had not extensively been explored until the mid 1970s. Martin and coworkers[85-88] investigated the diastereodifferentiating photochemical cyclization of diarylethylenes with chiral auxiliaries, which afforded the corresponding hexahelicene derivatives in 28% diastereomeric excess (de), while Green[89-91] studied the intramolecular [2 + 2] photocyclodimerization of polycinnamates of mannitol, erythritol, and their derivatives used as chiral auxiliaries giving rise to the optically active δ-truxinate of as high as 85% de.[90,91] Since then, a number of diastereodifferentiating intra- and intermolecular photochemical reactions have been investigated very intensively. Typical examples include the photoequilibration of diastereomeric metal complexes investigated by Vagg and

Williams,[92-97] and of diastereomeric spirocyclopropanes by Okada and Oda,[98-100] the [2 + 2] photocycloadditions of enones with olefins by Lange,[101-104] Demuth,[105] and Kaneko,[106] and the Paternò–Büchi reaction of ketones with olefins by Gotthardt and Lenz,[107,108] Jarosz and Zamojski,[109-111] and Scharf et al.[112-114] These diastereodifferentiating photoreactions, though inherently require a stoichiometric amount of chemically bonded chiral sources, afford the photoproducts of high de; the product's de often exceeds 90%[98,112,113,115-118] and may well be applied to the practical asymmetric syntheses.

Recently, Ninomiya et al.[119] and Pete et al.[120-129] proposed a new strategy of the photochemical asymmetric induction, in which the enantiodifferentiating photocyclization of enamides or the photodeconjugation of α,β-unsaturated esters is effected in the presence of hydrogen-bonding optically active compounds, affording the product's op up to 42%[119] or 91%.[128] Strictly speaking, these may not be included in the category of asymmetric photochemistry, since the enantiodifferentiation is considered to take place not in the excited state but through the complexation of a photochemically produced labile ground-state intermediate like an enol with an optically active complexing agent. However, this method may be regarded as an advanced modification of the asymmetric photochemistry in the optically active solvents interacting more or less specifically with the substrate in the ground and/or excited states.[130-135]

The broad spectrum of asymmetric photochemistry in fluid solution has been reviewed briefly by Kagan and Fiaud,[2] Griesbeck,[5] Bonner,[6] and Majima[136] or rather extensively by Rau,[3] Jarosz,[4] and Schreiber.[137]

Asymmetric photochemistry in the organized assembly like chiral liquid crystal or in the aggregate or matrix of chiral synthetic or natural polymers like polypeptide or DNA appears to be of great interest and importance, but have not been studied so intensively. In spite of moderate efforts on the photochemistry in chiral cholesteric,[138-141] mechanically twisted nematic,[142] and smectic[143] mesophases, the product's op has not exceeded 1–2%. The asymmetric photochemistry in liquid crystal has been reviewed briefly in a general context.[144,145] It has been quite recent that chiral polymers have been utilized as chiral media in the asymmetric photochemistry[146] and photobiology[147,148] with moderate enantiomer differentiations.

As mentioned above, this review does not deal with the asymmetric photochemistry in the solid state, but some representative investigations and reviews are outlined below.

The solid-state asymmetric photochemistry of chiral crystals of achiral molecules, confusingly sometimes called "absolute" asymmetric synthesis, has been investigated intensely by Lahav's and Trotter/Scheffer's groups since the studies by Schmidt[149] on the photodimerization of crystalline alkenes. In the solid-state photochemistry, various types of asymmetric transformations can be carried out with high op near 100% in some optimized cases, although the rigid environment does not immediately mean such a high stereodifferentiation. Typical enantiodifferentiating photoreactions in pure or mixed chiral crystals reported so far include [2 + 2] cyclodimerization of aromatic olefins,[150-155] di-π-methane rearrangement of dibenzobarrelenes,[156-161] Norrish type II reaction of ketones,[156,162-165] and polymerization of aromatic olefins.[151,154,162,166,167] The diastereodifferentiating photoreactions of crystals of optically active compounds may be represented by the works on di-π-methane rearrangement of chiral dibenzobarrelenes[168-170] and [4 + 4] cyclodimerization of 9-anthracenecarboxylates.[171] This field has frequently been reviewed and discussed.[9-12,162,172-177]

Extensive studies on the solid-state asymmetric photochemistry in chiral host lattice or inclusion complex of synthetic or natural optically active molecular host have also been reported. Apart from the radiation–chemical asymmetric polymerizations in the optically active host lattice of (–)-(*R*)-*trans*,*anti*,*trans*,*anti*,*trans*-perhydrotriphenylene[178] and deoxycholic acid,[179,180] which were reviewed by Farina,[181] various types of enantiodifferentiating photochemical transformations, including addition, cyclization, isomerization, Norrish type II reaction, and oxidation, have been executed, sometimes with nearly quantitative enantiomeric excess (ee), in the cyclodextrin cavity[182-185] or in the host lattice of optically active deoxycholic acid,[186-190] tri-*o*-thymotide,[191] or Toda's "axle and wheel"-type host molecule, and 1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol.[192-201] These reactions have recently been reviewed by several authors.[10,13,174,202-204]

III. Classification

In considering asymmetric photochemistry, both reaction medium and chiral source employed are the most important factors that determine the transfer mechanism of chiral information and practically the optical yield of photoproducts. Subsequently, the stoichiometry of chiral source to substrate and the mode of photoexcitation often become a matter of subordinate or inevitable choice. Thus, the asymmetric photochemical reactions are classified into several categories, primarily according to the phase and the chiral source as shown in Table 1.

In principle, asymmetric photochemical reactions can be performed in any phase from gas to solid, although all possibilities have not been examined experimentally. In practice, no attempts have been reported in the noncondensed phases like gas or supercritical fluid, although included in Table 1. This is probably because the product's op is not expected to be high, since the vapor-phase photolysis at a low pressure, where collisional deactivation is scarce, tends to produce a "hot" electronically excited state and then a ground state carrying excessive vibrational energy. In this aspect, the use of supersonic jet or supercritical fluid as a reaction medium may be worth examining.

Reported asymmetric photochemistry in fluid solution employs a wide variety of chiral sources shown in Table 1. Except for the absolute asymmetric photochemistry by direct irradiation with CPL, the chiral information is usually provided through some intra- or intermolecular interaction with an optically active substituent, complexing agent, sensitizer, or solvent. The absolute asymmetric photochemistry does not necessitate any chiral substance but requires at least one photon of r- or l-CPL per one substrate molecule, but

Table 1. Classified Asymmetric Photochemical Reactions

phase	chiral source	stoichiometry	excitation mode	optical yield
vapor	see below			no examples
supercritical fluid	see below			no examples
solution	circularly polarized light	1	direct	extremely low
	substituent	1	direct/sens	high
	complexing agent	<1	direct	moderate–high
	sensitizer	≪1	sens	low–moderate
	solvent	≫1	direct/sens	low
organized assembly	Langmuir–Blodgett assembly	>1		no examples
	micelle	>1		no examples
	emulsion	>1		no examples
	liquid crystal	≫1	direct	extremely low
	polymer aggregate/matrix	≫1	direct	low–moderate
solid	host molecule	1	direct	low–moderate
	host lattice	>1	direct	moderate–high
	crystal chirality	1	direct	high
	organic glass matrix	≫1	direct	low
	modified clay	>1		moderate
	modified zeolite	>1		no examples

gives an extremely low optical yield determined exclusively by the anisotropy factor of the substrate at the irradiation wavelength. The optically active substrate, possessing a chiral substituent as an auxiliary or building block, inevitably requires a stoichiometric amount of the chiral source, but in several cases, they can be transformed in high de by direct irradiation or photosensitization. An elegant and more chiral-source-efficient modification of the chemically bonded chiral auxiliary is the use of a small amount of chiral complexing agent, producing an optically active product of moderate to high op. Another attractive methodology of much higher chiral-source efficiency is the photosensitization with a catalytic amount of optically active compound, where the chirality multiplication can readily be materialized, although the optical yields reported are not very high in most cases. The use of optically active solvents as a source of chirality is of very poor chiral-source efficiency, and results in low optical yields in the absence of specific solute–solvent interaction in the ground and/or excited states.

Molecular assemblies like monolayer, Langmuir–Blodgett assembly, micelle, emulsion, and liquid crystal, as well as polymer aggregates, are specifically interesting from the viewpoint of the excited-state molecular recognition in chiral organized environment which may be considered as a sort of loosened chiral crystal rather than isotropic fluid solution; the chiral-source efficiency is inherently low. However, only a limited number of attempts in some liquid crystals have been reported with extremely low optical yields, while low to moderate enantiodifferentiation has been achieved with polymer aggregates.

In the solid-state asymmetric photochemistry, the chiral information is transferred from the optically active host molecule like cyclodextrin, the host crystal lattice of optically active compounds, or the chiral crystal of achiral compounds to the guest substrate incorporated in the host cavity, lattice, or crystal. The reported optical yields are generally high in the solid-state asymmetric photochemistry. Low-temperature organic matrices can be used for the enantiomer-differentiating photodecomposition with CPL of thermally unstable chiral compounds or conformers. Little is known about the asymmetric photochemistry in asymmetrically modified clay[205,206] or zeolite.

The asymmetric photochemical and photophysical processes in isotropic fluid solution are classified into the following categories by the physical or chemical chiral source employed: (1) direct asymmetric photochemistry caused by CPL, (2) asymmetric induction by chiral substituents, (3) asymmetric induction by chiral complexing agents, (4) asymmetric photosensitization, (5) asymmetric fluorescence quenching, and (6) asymmetric induction in chiral solvents.

IV. Direct Asymmetric Photochemistry with Circularly Polarized Light

The direct asymmetric photochemistry with CPL is believed to play a crucial role in the abiotic synthesis of optically active molecules in the nature.[6,60–62,64–66,207,208] The natural source of circularly polarized radiation and the possible mechanisms for the amplification of small enantiomeric excess generated in the initial asymmetric photolysis with CPL have also been discussed in considerable detail.[57,60,66,208] In this section, however, only the chemical aspects of the direct asymmetric photochemistry with CPL will be discussed.

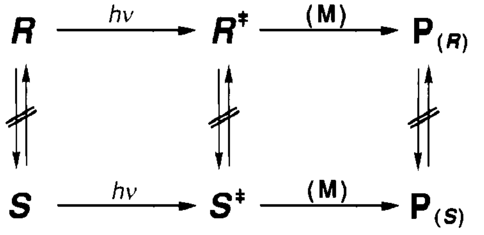
Although all of the asymmetric photochemical reactions induced by the CPL irradiation are brought about through preferential excitation of one, over another, enantiomer, the reported photoreactions may further be divided into three categories, according to the type of the subsequent process in which the chiral center is destroyed, preserved, or apparently created or, more rigorously, fixed:[3,56] (a) asymmetric photodestruction/production, (b) photochemical deracemization, and (c) photochemical asymmetric fixation.

The most important factor that determines product's op in any of these direct asymmetric photochemical reactions is the anisotropy or *g* factor, which was first defined by Kuhn[31,32] as the relative difference of the molar extinction coefficients of an optically pure compound toward l- and r-CPL at a given wavelength:

$$g = (\epsilon_l - \epsilon_r)/\epsilon = \Delta\epsilon/\epsilon \qquad (1)$$

where $\epsilon = (\epsilon_l + \epsilon_r)/2$ and therefore $0 \leq g < 2$. In general, the *g* factors reported are well below unity, typically $<10^{-2}$, for many compounds like aromatics which possess fully allowed π,π^* transition(s) of large oscillator strength ($f \sim 0.5$) or $\epsilon(\sim 10^5\ \mathrm{M^{-1}\ cm^{-1}})$. By contrast,

Scheme 1. Asymmetric Photodestruction/Production



‡ : electronically excited state

some carbonyl compounds, possessing a partially forbidden n,π* transition of very small f ($<10^{-3}$) or ϵ(<100 M^{-1} cm^{-1}), show much higher g factors up to 0.25–0.30.[209-212] Since the g factor varies with wavelength as $\Delta\epsilon$ and ϵ do, the use of monochromatic CPL is desirable in the direct asymmetric photochemistry, otherwise the effective g factor should be calculated by averaging over the entire region of the irradiation wavelengths.

A. Photodestruction/Production

In the CPL-induced asymmetric destruction/production, each enantiomer of a racemic mixture of substrate is consumed photochemically at different rates, leaving the optically active unreacted substrate and simultaneously producing the optically active or achiral product(s). For this purpose, the following conditions are to be met: (a) irradiation is performed at a wavelength where the substrate's $\Delta\epsilon$ is not zero; (b) the substrate undergoes irreversible photochemical transformation(s); (c) each enantiomer does not interconvert thermally or photochemically; and preferably, (d) the product is transparent at the irradiation wavelength. As shown in Scheme 1, the photochemical asymmetric destruction/production can be treated as the independent, parallel unimolecular or bimolecular processes of (R)- and (S)-substrate (R and S), affording the achiral (P) or chiral (P_R/P_S) product(s). Although the concurrent asymmetric destruction and production is possible, in principle, via this method, usually the photoproducts were not identified and only the asymmetric destruction was discussed in most cases, except for some recent studies.

The asymmetric photodestruction of a racemic mixture, if observed, originates solely from the unequal extinction coefficients (ϵ_R and ϵ_S) for CPL of the (R)- and (S)-enantiomers, which in turn afford the different rate constants (k_R and k_S) for the two processes. As formulated by Kuhn and Knopf,[32] the optical rotation (α) of photolyzed solution, which is proportional to the differential concentration ($C_R - C_S$) if the product(s) are optically inactive, is expressed as a function of the extent of destruction (x):

$$\alpha = \Gamma(g/2)(1 - x) \ln [1/(1 - x)] \qquad (2)$$

where Γ represents the rotation that would be observed in an equivalent optically pure substrate. Equation 2 indicates that the optical rotation of the photolyzed solution increases with the progress of decomposition, maximizes at $x = 0.632$ or $1 - 1/e$ ($e = 2.718$), and eventually fades out at the 100% conversion; the maximal rotation is given by $\alpha_{max} = 0.184g\Gamma$ at 63.2% conversion.[32] Experimentally, the optical rotation α, as a measure of ($C_R - C_S$), is usually plotted against the irradiation period rather than the conversion to give a somewhat different curve, showing a maximum accompanied by tailing at the longer irradiation times, as exemplified abundantly.[36,67,213-215] This irradiation-time dependence is a natural consequence of the independent first-order decrease of (R)- and (S)-enantiomers at different rates as analyzed kinetically by Kagan et al.[67,216] and Rau et al.[3,213,214] The time development of the enantiomer concentrations (C_R, C_S) is schematically illustrated in Figure 1 for a model system of $k_S/k_R = 2.0$ or $g = 0.67$.

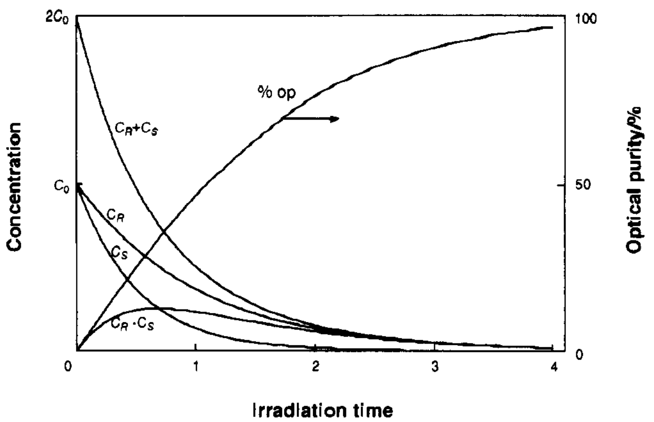


Figure 1. Enantiomer concentrations and optical purity (%op) of the remaining substrate as functions of the irradiation time corrected for decreasing optical density during asymmetric destruction (g = 0.67); $C_R = C_0e^{-k_Rt}$ and $C_S = C_0e^{-k_St}$ (k_S = 2.0; k_R = 1.0).

Tsuchida et al.[36] gave a simple equation for calculating the maximal optical rotation during the asymmetric photodestruction. Rau et al.[3,213,214] derived a more sophisticated but useful equation for evaluating molar ellipticity ([θ]) of any per se chiral, but difficult-to-resolve, substrate by observing the development curve upon the CPL irradiation:

$$[\theta] = 1340\epsilon(\theta_{max}/\gamma A_0)^{1/2} \qquad (3)$$

where ϵ is the molar extinction coefficient of the substrate, θ_{max} is the maximum ellipticity observed during the irradiation, γ is the degree of circular polarization of the light used, and A_0 is the initial optical density of sample solution, all at the irradiation wavelength.

In their pioneering work on the g factor, Kuhn and Knopf[32] further pointed out that, in sharp contrast to the conversion dependence of the observed α fading out at higher conversions, the op of the substrate surviving from the asymmetric photodecomposition increases rapidly as the reaction approaches the completion, as can be seen from the plot of op in Figure 1. Even with a substrate of $g = 0.04$, the op of remaining substrate is calculated as 2.0% at 63.2% conversion, 6.0% at 95% conversion, 20% at 99.995% conversion, and 76% when only 300 out of the Avogadro number (6.02×10^{23}) of the substrate molecules (one mole) are left in the solution.[32] However, the possibility of kinetic resolution through this procedure had not been pursued for more than 40 years. In 1974, Kagan et al.[67] reported a high, but anticipated, op of 20% in the remaining camphor after 99% photodestruction of racemic camphor (g = 0.09 at 310 nm) by CPL irradiation; they later obtained *trans*-bicyclo[4.3.0]nonan-8-one (g = 0.24

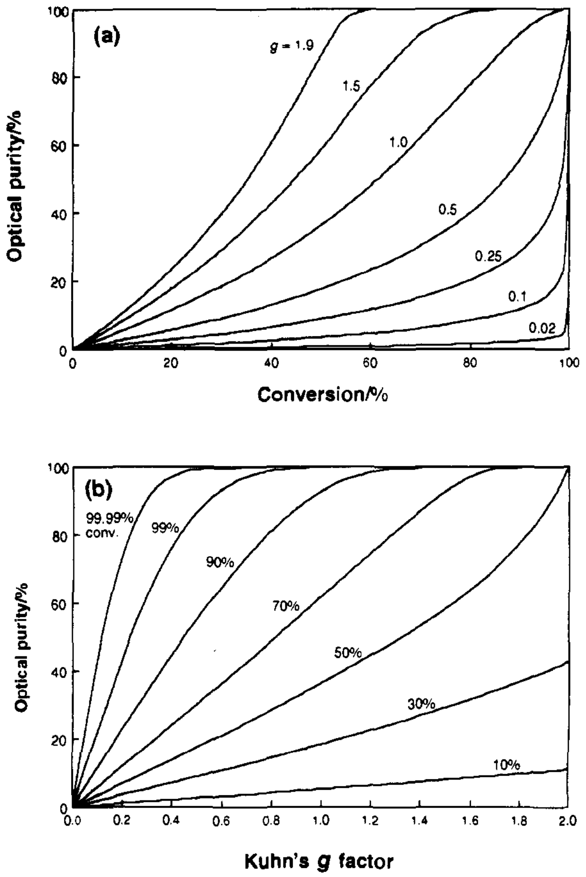


Figure 2. Optical purity of remaining substrate as a function of conversion for some *g* factors (a) or as a function of *g* factor at some % conversions (b) in the CPL-induced asymmetric destruction of racemic substrate.

at 313 nm)[210,211] of 30% op by this method.[68] They also derived an equation for simulating the conversion dependence of op of the remaining substrate for a given *g*:[67]

$$x = 1 - (1/2)\{[(1 + y)/(1 - y)]^{(1/2 - 1/g)} + [(1 + y)/(1 - y)]^{(-1/2 - 1/g)}\} \quad (4)$$

where x and y refer to the extent of decomposition or conversion and the op of the remaining substrate, respectively. In Figure 2a, the optical purity is plotted as a function of the conversion for some selected *g* factors. From the plots, one can readily recognize that the *g* factor plays the definitive role in determining the product's op. It is interesting to point out that the conversion also plays another important role, the op increases with increasing *g* factor more rapidly at the higher conversions, as can be seen from Figure 2b.

Ever since the first experiment by Kuhn and Braun,[28] the direct asymmetric destruction has been conducted with a wide variety of compounds, illustrated in Chart 1 (in this review, bold/hashed wedges are used for optically pure compounds, while bold/hashed lines denote racemic or stereochemically unspecified compounds). The results are summarized in Table 2. Of these reactions, the photodecomposition of ketones afforded the best op's up to 30%,[68] owing to the relatively large *g* factors (~0.24) as well as the high conversion (99%). Thus, the search for a higher *g* factor is a logical consequence, but the highest *g* value hitherto reported is not very high: $g = 0.30$ for a twisted ketone tricyclo[4.4.0.0^{3,8}]decan-2-one.[209,212] In this context, the small, but unambiguous, solvent effect upon the *g* factor of diphenylpyrazoline (**16**), which increases with increasing solvent polarity from 0.0614 in hexane to 0.0863 in acetonitrile,[217] may be used as a convenient tool for further enhancing the product's op in the direct asymmetric destruction.

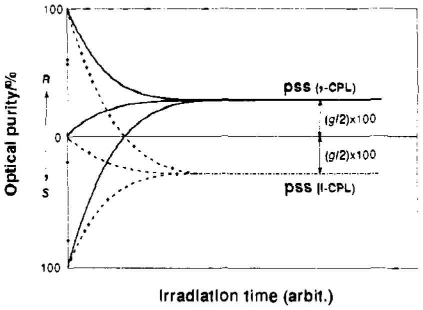


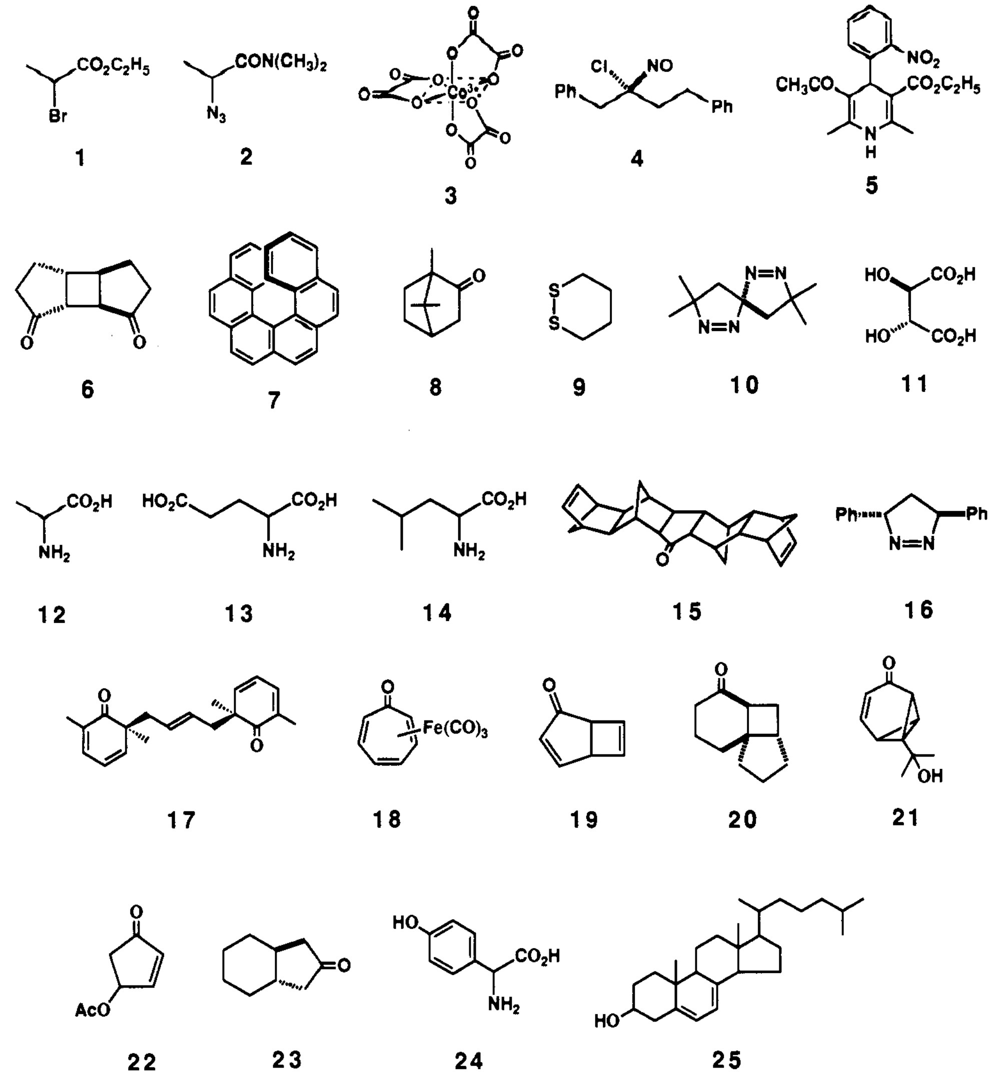
Figure 3. Optical purity as a function of irradiation time during photoenantiomerization upon irradiation with r- (solid lines) or l-CPL (dashed lines) starting with the initial enantiomeric compositions of pure *R*, racemic, and pure *S* (from top to bottom in each case).

Another possibility is the simultaneous operation of asymmetric photodestruction/production and photoderacemization in the same direction. This strategy was examined both experimentally and theoretically by Cavazza et al.[218-222] with bicyclo[3.2.0]hepta-3,6-dien-2-one (**19**) affording the op up to 1.5%. It should be emphasized however that the optical yield, defined as a product of the op and the recovery (chemical yield) of the substrate,[3] is extremely low (~1%) in all of these reported cases. Hence, the asymmetric photodecomposition with CPL, though would have played a significant part in the abiotic synthesis, is not recommended as a practical synthetic procedure.

Recently, Nikogosyan et al.[69,70] have reported that the *g* factors of tyrosine (**24**) and 7-dehydrocholesterol (provitamin D$_3$) (**25**) are enhanced by a factor of ~300 upon CPL excitation with a high-intensity laser of very short pulse duration (100 fs or 23 ps, depending on the singlet lifetime of the substrate **24** or **25**), while only a negligible change in *g* was observed upon excitation with a longer laser pulse of 6–10-ns duration. Unfortunately, the ee of **25** was determined by liquid chromatography, and no chiroptical data were reported. They claimed that this phenomenon may be attributed to the two-photon excitation by the high-intensity, short-pulse laser, in which the first excited singlet and/or triplet state produced absorbs another photon within its lifetime, generating upper excited state(s). The apparent enhancement of the *g* factor would be interpreted by a much larger *g* factor for the first excited state or by the presence of a degenerated state whose sublevels differ slightly in energy.[70]

Only one bimolecular asymmetric destruction/production has been reported by Cavazza and Zandomeneghi.[52] CPL irradiation of racemic 4-acetoxy-2-cyclopentenone (**22**) in the presence of acetylene or 1-hexyne gave optically active cycloadducts, 4-acetoxybicyclo[3.2.0]hept-6-en-2-ones, through the intermolecular [2 + 2] photocycloaddition. But only the chiroptical data are presented.

Chart 1. Compounds Subjected to Direct Asymmetric Destruction



B. Photoderacemization

In the photochemical deracemization, which is often called partial photoresolution or photoenantiomerization, each enantiomer of a racemic substrate interconverts mutually upon CPL excitation, affording a photostationary-state (pss) enantiomeric mixture whose enantiomer ratio is appreciably deviated from unity. The major difference from the asymmetric photodestruction is that the combined enantiomer concentration ($C_R + C_S$) does not change during the photoreaction and the photochemical steady state is attained after prolonged irradiations irrespective of the initial enantiomeric composition, as illustrated schematically in Figure 3.

There may be two minor variations concerning the deracemization mechanism involved, as shown in Scheme 2. In the first mechanism which may be classified as an adiabatic photoreaction,[223] the racemization takes place between the excited (R)- and (S)-enantiomers (R^* and S^*). On the other hand, a common prochiral excited-state or ground-state intermediate $X^{(*)}$ produced upon excitation intervenes in the second case; this process belongs to the diabatic photoreaction or "hot" ground-state reaction.[223] Whatever the deracemization mechanism is, the enantiomeric deviation from unity, if observed, is solely due to the difference of the extinction coefficient (ϵ_R and ϵ_S) of each enantiomer toward the CPL used, since the deactivating reverse reactions, regenerating the starting material, should not be enantiodifferentiating. Detailed kinetic analysis of the photoderacemization was given by Stevenson and Verdieck[224] and Rau.[3] If there is no photochemical side reaction or thermal racemization in the ground state, the enantiomeric pss is attained when $\epsilon_R C_R = \epsilon_S C_S$. Then, the R/S ratio at the pss is equal to the inverse excitation ratio:

$$(C_R/C_S)_{\mathrm{pss}} = \epsilon_S/\epsilon_R \qquad (5)$$

This equation in turn gives the optimum op and ellipticity reached at the pss:

$$\mathrm{op}_{\mathrm{pss}} = (C_R - C_S)/(C_R + C_S) = g/2 \qquad (6)$$

$$\theta_{\mathrm{pss}} = 2C_0[\theta](g/2) \qquad (7)$$

where $2C_0$ is the initial substrate concentration, $[\theta]$ is the molar ellipticity of the pure enantiomer at the analyzing wavelength, and g is the Kuhn's anisotropy factor at the irradiation wavelength. Thus, the g factor may readily be evaluated from the ultimate optical purity at the pss, using the eq 6. Equation 7 enables us to normalize the CD spectrum measured with the

Table 2. Direct Asymmetric Destruction with Circularly Polarized Light in Solution[a]

substrate (*g* factor)[b]	irradiation λ, nm (CPL)	conversion,[c] %	α_{max}[d] or θ_{max},[e] deg	op,[f] %	ref(s)
ethyl 2-bromopropionate (**1**)	280 (r)	50	α_D +0.05	*g*	28
	280 (1)	50	α_D −0.05	*g*	
2-azido-*N*,*N*-dimethylpropionamide (**2**)	ca. 300 (r)	40	$[\alpha]_D$ +0.78	*g*	32, 33
	ca. 300 (l)	40	$[\alpha]_D$ −1.04	*g*	
2 (0.02)	313 (r)	50	*g*	0.6	67
"humulene nitrosite" [h]	ca. 700 (r)	*g*	α_{546} −0.21	*g*	34
	ca. 700 (l)	*g*	α_{546} +0.21	*g*	
potassium trioxalatocabaltate(III) (**3**)	589 (r)	*g*	α_{499} −0.16	*g*	36
	589 (l)	*g*	α_{499} +0.11	*g*	
2-chloro-2-nitroso-1,4-diphenylbutane (**4**)	>600 (r)	90	$[\alpha]_{530}$ −2.50	*g*	35
	>600 (l)	90	$[\alpha]_{530}$ +2.75	*g*	
ethyl 5-acetyl-2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3-carboxylate (**5**)	366 (r or l)[g]	40	α_D −0.056	*g*	*i*
trans-tricyclo[5.3.0.0^{2,6}]decane-3,10-dione (**6**)	330 (l)	*g*	$[\alpha]_{385}$ −0.13	*g*	45
hexahelicene (**7**)	313 (r)	25	$[\alpha]_D$ +2.6	*g*	46
	313 (l)	25	$[\alpha]_D$ −1.1	*g*	
camphor (**8**) (0.09)	313 (r)	99	*g*	20	67
1,2-dithiane (**9**)[j] (0.02)	>290 (r)	32	θ_{300} +0.0025	*g*	*k*
4,4,8,8-tetramethyl-2,3,6,7-tetraaza-spiro[4.4]nona-2,6-diene (**10**) (0.096)	345 (r or l)[g]	59	θ_{345} +0.099	4.3	213, *l*
		83	θ_{345} +0.088	8.4	
tartaric acid (**11**) (0.02)	>200 (r/l)	>20	θ_{210} +42 × 10^{-6}	0.11	58
alanine (**12**) (0.007)	>200 (r/l)	>20	θ_{210} +9 × 10^{-6}	0.06	58
glutamic acid (**13**) (0.008)	>200 (r/l)	52	θ_{210} +36 × 10^{-6}	0.22	58
leucine (**14**) (0.0244)	213 (r)	59	*g*	2.0	59
	213 (l)	75	*g*	2.5	
15 (0.15)	313 (r)	60	$[\alpha]_D$ +8.20	3.0	209
trans-3,5-diphenylpyrazoline (**16**) (0.085)	332 (r or l)[g]	63	θ_{332} +0.036	2.8	214, *l*
		90	θ_{332} +0.019	6.5	
17	365 (r)	40	$[\alpha]_{546}$ −0.004	*g*	*m*
	365 (l)	46	$[\alpha]_{546}$ +0.004	*g*	
tropone–iron tricarbonyl (**18**)	380–500 (r)	3	α_D +0.012	*g*	*n*
	380–500 (r)	3	α_D −0.010	*g*	
bicyclo[3.2.0]hepta-3,6-dien-2-one (**19**)[o]	351, 363 (l)	*g*	*g*	1.5	218–221
tricyclo[5.4.0.0^{1,5}]undecan-8-one (**20**)	334 (l)	54	$[\theta]_{334}$ −1.82	*g*	*p*
1-(1-hydroxy-1-methylethyl)tricyclo[4.1.0.0^{2,7}]-hepta-4-en-3-one (**21**)[q]	351, 363 (r)	35	$[\theta]_{353}$ +43.6	*g*	*r*
	351, 363 (l)	38	$[\theta]_{353}$ +18.5	*g*	
4-acetyl-2-cyclopentenone (**22**)	351, 363 (l)	30	$[\alpha]_{578}$ +0.92	*g*	52
trans-bicyclo[4.3.0]nonan-8-one (**23**) (0.24)	313 (r)	99	*g*	30	68
tyrosine (**24**) (8.8 × 10^{-5}, 0.024[s])	266 (r, 23 ps)[t]	51	*g*	3.6	69, 70
	266 (l, 23 ps)[t]	45	*g*	2.4	
	266 (r, 10 ns)[t]	48	*g*	~0	
	266 (l, 10 ns)[t]	48	*g*	~0	
7-dehydrocholesterol (**25**)[u] (1.5 × 10^{-4}, 0.044[v])	305 (r, 100 fs)[t]	3–18	*g*	*g*	70
	305 (l, 100 fs)[t]	3–16	*g*	*g*	
	308 (r, 6 ns)[t]	23–31	*g*	*g*	
	308 (l, 6 ns)[t]	24–29	*g*	*g*	

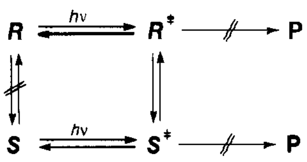
[a] Irradiation performed with racemic substrate at room temperature, unless noted otherwise. [b] Anisotropy (*g*) factor at or around irradiation wavelength, if reported or estimated. [c] Extent of destruction. [d] Maximal observed rotation α of irradiated solution, or specific rotation [α] of isolated sample or of residue obtained upon evaporation. [e] Maximal observed ellipticity of irradiated solution of molar ellipticity of isolated sample. [f] Optical purity of isolated sample. [g] Not reported. [h] Compound (mp 113 °C) of unknown structure, obtained in a reaction of humulene with sodium nitrite, according to the reported procedure: Chapman, A. C. *J. Chem. Soc.* **1895**, *67*, 780. [i] Berson, J. A.; Brown, E. *J. Am. Chem. Soc.* **1955**, *77*, 450. [j] Irradiation performed at 77 K in a hydrocarbon glass matrix. [k] Nelander, B.; Nordén, B. *Chem. Phys. Lett.* **1974**, *28*, 384. [l] Schneider, M.; Schuster, O.; Rau, H. *Chem. Ber.* **1977**, *110*, 2180. [m] Quinkert, G.; Schmieder, K. R.; Dürner, G.; Hache, K.; Stegk, A.; Barton, D. H. R. *Chem. Ber.* **1977**, *110*, 3582. [n] Litman, S.; Gedanken, A.; Goldschmidt, Z.; Bakal, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 983. [o] A mixed case of asymmetric destruction and photoenantiomerization; irradiation performed at 0 °C. [p] Cavazza, M.; Zandomeneghi, M.; Ciacchini, G.; Pietra, F. *Tetrahedron* **1985**, *41*, 1989. [q] Enantiomerically enriched sample used. [r] Zandomeneghi, M.; Cavazza, M.; Festa, C.; Fissi, A. *Gazz. Chim. Ital.* **1987**, *117*, 255. [s] Estimated *g* factor enhanced by two-quantum excitation with high intensity picosecond laser pulse. [t] High-intensity laser of indicated pulse duration used. [u] Optically pure sample photolyzed only to evaluate the enhanced *g* factor. [v] Estimated *g* factor enhanced by two-quantum excitation with high-intensity femtosecond laser pulse.

partially photoresolved substrate obtained in the photoderacemization.

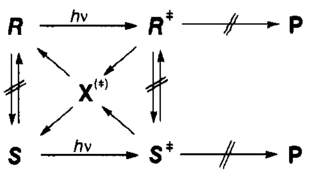
Experimentally, only a limited number of the CPL-induced deracemizations are known. The earlier investigations were executed with a variety of octahedral transition-metal complexes with bidentate ligands like oxalate or acetylacetonate. Stevenson and Verdieck[225] reported the first examples of the CPL-induced deracemization of some octahedral oxalato complexes of chromium(III): trioxalatochromate, di-μ-hydroxytetraoxalatochromate, and *cis*- and *trans*-dioxalatodiaquochromates. In these reactions, an apparent pss of the solution's optical rotation was attained in each case upon prolonged irradiation with CPL at ca. 550 nm, but the ultimate values depended significantly upon the irradiation temperature, owing to the concomitant thermal racemization. Thus the ultimate optical rotation is determined by this competition and therefore

Scheme 2. Photoderacemization

a) Adiabatic path



b) Diabatic or "hot" ground state path



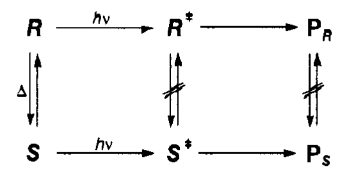
increases at the lower temperatures where the thermal racemization is retarded. Similar competitive photoderacemization/thermal racemization reactions of the same and other chromates(III) were also reported by Stevenson and Verdieck^{224} and by Nordén^{226,227} for tris(dithiooxalato)chromate,^{224} trimalonatochromate,^{224} (ethylenediamido)dioxalatochromate,^{224} trimalatochromate,^{224} and tris(tartrato)chromate.^{224,227} The photoderacemization that is not complicated by the concomitant thermal racemization was also reported for tris(acetylacetonato)chromium(III)^{228,229} and tris(2,2′-bipyridyl)ruthenium(II).^{215}

The first photoderacemization of organic chiral compound was reported by Hayashi and Irie's group.^{230} They showed that a racemic mixture of 1,1′-binaphthyl can be partially photoresolved by the CPL irradiation at 270–310 nm. Cavazza et al.^{221} reported that the photoderacemization and asymmetric photodecomposition of bicycloheptadienone **19** proceed simultaneously in a ratio of 0.61:1 upon CPL irradiation at 351 and 363 nm. They also proposed a methodology for evaluating the chiroptical properties by the asymmetric photochemical reaction.^{222}

As readily recognized from the foregoing works, the photoderacemization of organic compounds, in its strict sense, has quite scarcely been explored. This is partly due to the difficulty in finding an organic compound which undergoes exclusively photoderacemization without giving any side product(s) especially upon excitation at the shorter wavelengths. In this context, the "narcissistic" photoreaction^{231} of, for example, photochromic spiropyrans, nominated previously by Rau,^{3} would still be a possible candidate.

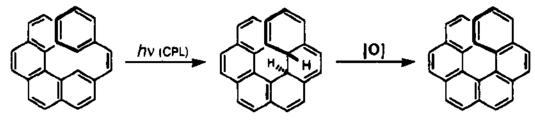
C. Photochemical Asymmetric Fixation

Scheme 3. Photochemical Asymmetric Fixation



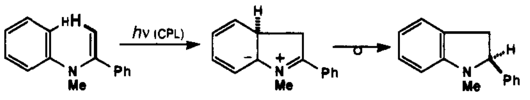
Scheme 4. Photochemical Asymmetric Fixation Exemplified

a) Photocyclization/dehydrogenation

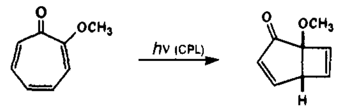


26 27 7

b) Photocyclization/hydrogen shift



c) Photocyclization



In contrast to the asymmetric destruction and the photoderacemization described above, the photochemical asymmetric fixation creates or, more rigorously, fixes the asymmetric element during the photolysis with CPL, producing an optically active product. Appreciable enantiodifferentiation through this process is made possible by preferentially exciting one of thermally equilibrating enantiomeric conformers of the substrate. The required conditions are (a) the thermal racemization is fast enough to keep the substrate racemic during the photolysis; (b) the racemization in the excited state, which is often facilitated, is much slower than the relaxation to product; and (c) the enantiomeric conformer has an perceptible g factor at the irradiation wavelength. It should be emphasized that the enantiomeric conformers are not resolved at the reaction temperature. If the thermal racemization process is absent, such a system may be classified as an asymmetric destruction/production process discussed above. Typical reaction sequences are shown in Scheme 3.

Under these conditions, the R/S ratio of the product is simply equal to the excitation ratio ϵ_R/ϵ_S of the substrate enantiomers, and the optical rotation of the irradiated solution increases with increasing irradiation time. Thus the product's op is given by eq 8:

$$\mathrm{op} = (\epsilon_R - \epsilon_S)/(\epsilon_R + \epsilon_S) = g/2 \qquad (8)$$

Up to now, only a few photocyclization processes are known to satisfy the conditions for the photochemical asymmetric fixation. Of these, the most work has been concentrated on the photocyclization/dehydrogenation of the thermally racemizing enantiomeric conformers of diarylethylenes to hexa- to tridecahelicenes, studied intensively by Kagan's^{46,47,216,232,233} and Calvin's groups in the 1970s.$^{48-50}$ A typical example for the oxidative photocyclization of 1-(2-benzo[c]phenanthryl)-2-phenylethylene (**26**) to hexahelicene (**7**) via dihydrohelicene (**27**) is illustrated in Scheme 4. The maximum op of 0.46% was reported for the synthesis of octahelicene from 1-(2-benzo[c]phenanthryl)-2-(3-phenanthryl)ethylene.^{233} Most of these works, including the mechanistic details, have been reviewed by Buchardt^{56} and by Tai and Imaizumi,^{54,55} and there have been a few works reported on this topic in the recent years. Other photochemical asymmetric fixations include the photocyclization/hydrogen shift of *N*-aryl-*N*-methylenamine to *N*-methyldihydroindoles (Scheme 4b)[51] and, with some reservations, the photocyclization of 2-methoxytropone to 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (Scheme 4c).[234] In the former reaction, the product's op reported was extremely low (0.2%) as was the case with the helicene synthesis. The latter reaction, although complicated by the subsequent rearrangement process,[219,220] showed a steady increase in the optical rotation of the photolysate solution with extending irradiation time. Again, the asymmetric fixation with CPL is not of synthetic interest, but is useful for the CD measurement of partially photoresolved product.[234]

V. Asymmetric Induction by Chiral Substituent

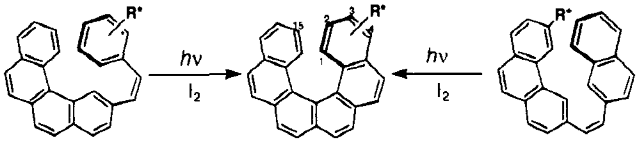
Although the use of CPL as a physical chiral source is unique to the photochemical reaction, chemical chiral sources are much more frequently used in the asymmetric photochemistry. Most frequently employed are the chiral substituents appended to a prochiral substrate as a chiral auxiliary and the chiral unit built into the substrate skeleton as an essential building block of the product. Thus, all of the photoreactions in this category involve the diastereodifferentiating process. The chiral sources are usually selected from the pool of the optically active natural products. Differing from the physical counterpart described above, where the chiroptical property of the substrate is the only determining factor, the chemical asymmetric induction is governed by several factors, including the steric, electronic, and hydrogen-bonding interactions in the excited and/or ground states. In this review, we will concentrate primarily on the photochemical asymmetric induction by chiral auxiliaries and will not extensively refer to the photoreactions of the substrates with built-in chirality, since the asymmetric transfer or induction in the latter case is often inherent to the system or simply regarded as a reaction of the chiral compound.

Several types of intra- and intermolecular photochemical reactions have been utilized in the photochemical asymmetric induction by a chiral handle. These are, chronologically: (a) photocyclization/dehydration of diarylethylenes to helicenes;[85,87] (b) [2 + 2] photocyclodimerization/addition of arylalkenes[89-91,115] or enones[101-106,235-237] to cyclobutanes; (c) Paternò–Büchi reaction of ketones with alkenes giving oxetanes;[91,107,110,112-114,116,238-243] (d) hydrogen abstraction and subsequent radical addition/dimerization of aromatic ketones affording pinacols or adducts with unsaturated compounds such as maleates;[76,244] (e) [4 + 2] photocycloaddition of anthracenes;[245] (f) diastereomeric equilibration of arylcyclopropanes;[98-100] (g) photodeconjugation of α,β-unsaturated esters;[246] and (h) di-π-methane rearrangement.[168] Of these, only the [2 + 2] photocycloaddition and the Paternò–Büchi reaction have been widely investigated.

A. Photocyclization

The diastereodifferentiating photocyclization/dehydrogenation of diarylethylenes possessing chiral substituents was investigated by Martin et al.[85-87] As exemplified for hexahelicene (7) in Scheme 5, various 1-(2-benzo[*c*]phenanthryl)-2-phenylethylene (26), 1-(2-naphthyl)-2-(3-phenanthryl)ethylene (26′), and 1,2-bis-(2-benzo[*c*]phenanthryl)ethylene derivatives possessing a chiral alkyl, alkoxycarbonyl, or hexahelicenyl group (R*) at the peripheral position were cyclized to the corresponding helicenes. The op of the product helicene, though mostly much better than the direct asymmetric fixation with CPL (section IV.C), was shown to depend on the position of the chiral handle introduced and the precursor used. The best de of 28% was recorded for the formation of 1-[(1,2,2-trimethyl-propyloxy)carbonyl]hexahelicene (7a) (R* at C-1), although the (hexahelicenyloxy)carbonyl substituent appears to be a better chiral group since the hexahelicenyl, among the chiral groups examined, gave the highest de of 16% in the 2-substituted hexahelicene 7d (R* at C-2).[87]

Scheme 5. Diastereodifferentiating Photocyclization



26

7a R = $CO_2CH(CH_3)Bu^t$
7b R = $CO_2CH(CH_3)Ph$
7c R = $CO_2menthyl^l$
7d R = CO_2-2-hexahelicenyl
7e R = $CCH_3(OCH_3)Bu^t$

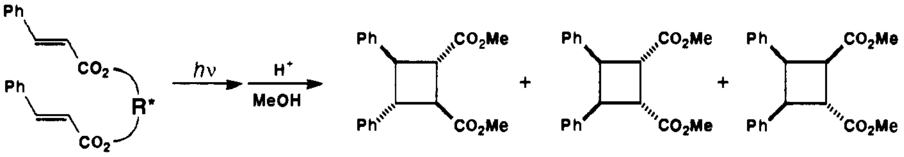
26′

B. [2 + 2] Photocycloaddition

The intramolecular [2 + 2] photocyclodimerizations of di-, tetra-, and hexacinnamates of the protected and/or native D-mannitol and L-erythritol used as a linking bridge and chiral template were studied by Green et al.[89-91] As exemplified for dicinnamate (28) in Scheme 6, the irradiation of di- to hexacinnamates of the chiral polyols and the subsequent ester exchange with acidic methanol gave two major head-to-head cycloadducts, i.e. chiral δ-truxinate 29 and achiral β-truxinate 30, along with a small amount of *neo*-truxinate 31. High de's up to 85–86% were reported for δ-truxinate 29 obtained in the photocyclizations of D-mannitol 1,6-dibenzoate 2,3,4,5-tetracinnamate[89] and also of (−)-2,3-di-*O*-methyl-L-erythritol 1,4-dicinnamate.[91] Somewhat unexpectedly, the polycinnamates of isopropylidene-protected mannitols and erythritol, which carry apparently a more rigid chiral backbone, gave rather lower de's of 48–82%[89] and 6%,[91] respectively. This suggests the considerable contribution of the electronic, rather than steric, interaction, although the product's de's were qualitatively related to the ground-state conformation of the erythritol dicinnamates by computer simulation.[91]

The intermolecular asymmetric [2 + 2] photocycloaddition was first reported by Tolbert and Ali.[115] The photocycloaddition of *trans*-stilbene 32 to chiral dialkyl fumarates 33a–d and the subsequent ester exchange with acidic methanol give optically active dimethyl δ-truxinate 29 and μ-truxinate 34 (Scheme 7). Using methyl *l*-bornyl fumarate (33a), they obtained the best de's for 29 (20%) and 34 (90–94%), while the other fumarates (33b–d) gave much lower de's for 29 (0–20%) and 34 (20%). The high de for 34 indicates the intervention of a highly ordered exciplex intermediate, whereas the much lower or negligible asymmetric induction in another product 29 may be attributed to the involvement of 1,4-biradical producing less crowded cyclodimer 29 rather then congested 34.

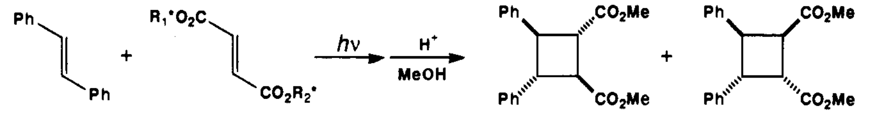
Scheme 6. Photocyclodimerization of Dicinnamate



28 R = D-mannitol or L-erythrithol

29 (δ) **30** (β) **31** (neo)

Scheme 7. Photocycloaddition of Styrene to Fumarate



32

33a $R_1 = CH_3$, R_2 = *l*-bornyl
33b $R_1 = R_2$ = *l*-bornyl
33c $R_1 = CH_3$, R_2 = (*R*)-2-methylbutyl
33d $R_1 = R_2$ = (*R*)-2-methylbutyl

29 (δ) **34** (μ)

More recently, another type of intermolecular asymmetric [2 + 2] photocycloaddition between enones and alkenes has been reported by Lange's,[101-104] Vandewalle's,[238] Scharf's,[235-237] Demuth's,[105] and Kaneko's groups.[106] As illustrated in Scheme 8 for typical enone–ene combinations, the chiral group may be introduced conveniently in the enone and/or alkene moiety in this strategy. The effects of chiral substituent, solvent, and/or temperature upon de have been widely investigated with 2-cyclopentenones (**42**, **46**), 2-cyclohexenones (**35**, **39**, **43**, **47**), furanone (**50**), and 1,3-dioxin-4-ones (**52**, **53**). Some selected results are listed in Table 3. So far, the diastereoface-differentiating photocycloaddition of prochiral enone **43** to chiral spiro-substituted cyclopentene **44** gave the best de of 84% at room temperature.[101] Lange et al.[102] demonstrated that the use of acidic solvents greatly improves the de of anti-adduct **37** from 30% in toluene to 68% in 95% acetic acid/methanol without substantially affecting the de of syn-adduct **38**. They noted that this enhancement may be attributed to the increased content of s-trans conformer of **35** through hydrogen bonding or protonation, since the anti approach is sterically more differentiated by the chiral substituent in the s-trans than in the s-cis conformation. As may be expected, the de increases with lowering the irradiation temperature in the photoreactions of **35**, **39**, **50**, and **52**; see Table 3. It is interesting to note that the doubly chiral combination, in which both enone **47** and ene **48** possess chiral substituents (menthyl or 8-phenylmenthyl), afford much higher de of 47 or 74% than that (27%) obtained in the singly chiral system where only the ene **48** is chiral.[236] Vandewalle and co-workers also reported the competitive cyclobutane and oxetane formation in a ratio of 3.5:6.5 in the photocycloaddition of 2-cyclopentenone to a chiral ketene acetal, (*S*)-2-methyl-(2-methylbutoxy)-1-[(trimethylsilyl)oxy]propene; the de of the cyclobutane formation was evaluated as ca. 30% through a lengthy derivatization.[238]

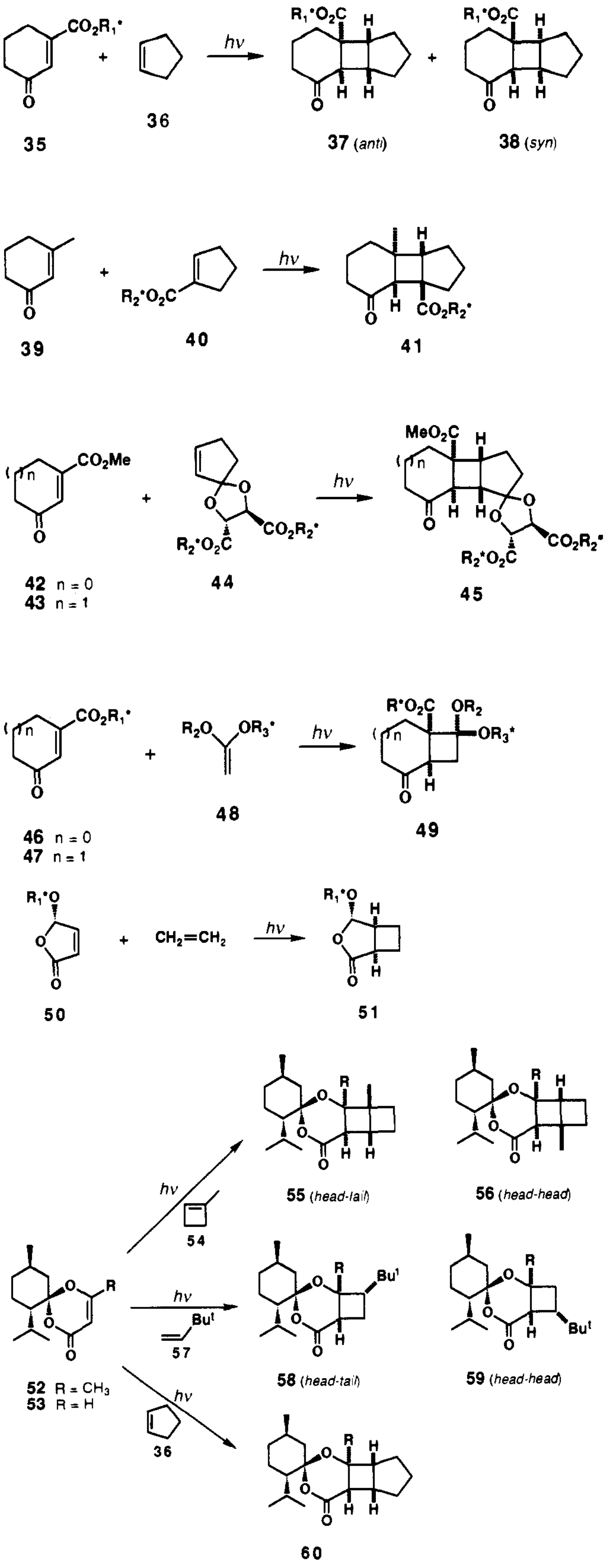
C. Paternò–Büchi Reaction

The Paternò–Büchi reaction of various ketones and thioketones with alkenes has also been used to effect the photochemical diastereodifferentiating oxetane/thietane formation.[91,107,110,112-114,116,238-243] Except for the asymmetric induction by some built-in chiral substituents,[109,111,243,247] the asymmetric Paternò–Büchi reactions induced by chiral auxiliaries may be summarized as shown in Scheme 9. The chiral handle can be introduced in the ketone or alkene moiety as the ester of a chiral alcohol. The chemical yield and the de are usually good to excellent and often exceed 90%, as shown in Table 4.

Gotthardt and Lenz[107] first reported the diastereodifferentiating thiethane formation in the photocycloaddition of xanthione (**61**) and thiobenzophenone **62** with (−)-menthyl methylacrylate (**63**). The photochemistry of thioketones is known to be wavelength dependent, involving both excited triplet (T_1) and singlet (S_2) states that undergo independent processes.[248,249] Interestingly, the de's reported are substantially greater for the product (17–18% de) from the T_1 state (589-nm excitation) than that (4–6% de) from the S_2 state (400-nm excitation), indicating that the diastereodifferentiation is poor in the quenching of S_2 but works more efficiently in the 1,4-biradical intermediate involved in the triplet path.[107]

Subsequently, several aliphatic and aromatic glyoxylic esters (**65**–**68**) of chiral alcohols were shown to undergo the highly diastereodifferentiating photocycloaddition with electron-rich alkenes (**69**–**71**, **74**, **77**–**79**) affording exo and/or endo oxetanes (**72**, **73**, **75**, **76**, **80**, **81**) by Gotthardt's,[108] Zamojski's,[110,250] and Scharf's groups.[112-114,116,239-242] Of these, the phenylglyoxylic esters with some bulky chiral auxiliaries like 8-phenylmenthyl gave excellent de's up to 95% at room temperature, for which the conformation analysis and crystallographic study were reported.[239] Scharf et al. further investigated the substituent[241] and temperature[240-242] effects on the product's de in considerable detail. In the photocycloaddition of phenylglyoxylate **66** with some 1,3-dioxolenes **77**, they found that the Eyring plot of the logarithm of the relative rate constant giving two diastereomers as a function of the reciprocal temperature gives two straight lines crossing at the "inversion" temperature (T_{inv}), limiting the maximal de at that temperature.[241,242] In these photocycloadditions, the diastereodifferentiation was proposed to occur potentially in two successive processes: first in the addition of triplet ketone to olefin forming 1,4-

Scheme 8. Photocycloaddition of Enone to Alkene



biradical, and then in the cyclization to oxetane of the resulting biradical, which is in competition with the bond cleavage regenerating ketone and olefin. In the high-temperature region ($T > T_{\text{inv}}$), mostly the enthalpy-determined diastereodifferentiation was observed, and this behavior was attributed to the early transition states of the bond cleavage in the 1,4-biradical intermediate; i.e. the second step controls the selectivity. Contrarily, in the low-temperature region ($T < T_{\text{inv}}$), the diastereodifferentiation is entropy-determined and may be attributable to the formation of 1,4-biradical, i.e. the first step.[242]

D. Hydrogen Abstraction

Diastereodifferentiating radical dimerization and addition reactions were shown to be initiated by the photochemical hydrogen abstraction by aromatic ketones.[76,244] As shown in Scheme 10 (top), photolysis of (−)-menthyl 2-acetylbenzoate (**82**) in 2-propanol leads to the hydrogen abstraction from the solvent, followed by the dimerization of the resulting arylhydroxyethyl radicals giving unstable diastereomeric pinacols **83** (*dl*) and **84** (*meso*). The pinacols suffer spontaneous lactonization, eliminating the chiral auxiliaries, to a 1:1 mixture of *dl*- and *meso*-dilactones **85** and **86** in good chemical yields (80%). The de of the final product **85** is temperature-independent, ranging 19–22% between 55 and −6 °C.[134] Another photoinduced asymmetric radical reaction is the addition of hydroxyisopropyl radical, generated by the hydrogen abstraction of triplet benzophenone **87** from 2-propanol, to chiral maleate **88** or fumarate **89**[134,244] [Scheme 10 (bottom)]. The addition first gives the regioisomers **90** and **91**, which eventually cyclize to terebic acid (**92**) and/or ester **93**. Although the de's first reported for dimenthyl maleate by Horner and Klaus[134] were fairly low (5.4% maximum), Scharf et al.[244] greatly improved the de of **93** up to 62% by using 8-phenylmenthyl maleate as a substrate.

Other miscellaneous intramolecular diastereomeric photoreactions induced by chiral auxiliaries have also been reported, but they contain only limited examples as discussed in the following sections.

E. [4 + 2] Photocycloaddition

Okada and Oda's group reported that the intramolecular [4 + 2] photocycloaddition of anthracene derivatives **94** and **95** carrying a chiral fumarate or maleate moiety are converted to the corresponding cycloadduct **96** in a low de of 9% at room temperature (rt) for the bornyl ester **95**, and in higher de's of 35% (rt) and 54% (−20 °C) for the menthyl ester **94**[245] (Scheme 11).

F. Diastereomeric Photoequilibration

The same group investigated the diastereomeric photoequilibrium of (*R*)-1-(1-naphthylethyl) amide of spirocyclopropanes **97** and **98**[98] and the related esters **99**–**103**,[99,100] excited directly or sensitized by some aromatic compounds of varying triplet energy (E_T).[99,100] The photoequilibriums studied are illustrated in Scheme 12. In the amide cases, the diastereomer ratio at the pss is a critical function of the sensitizer's E_T; the de increases from 28% (acetophenone, E_T = 73.7 kcal/mol) to 72% (4-phenylacetophenone, 61.1 kcal/mol) for **97** and from 74% (acetophenone) to 96% for **98** (4-phenylacetophenone). In collaboration with Yoshimura and Ohno,[99] they further demonstrated that this photosensitized diastereodifferentiating isomerization proceeds through the consecutive triple-energy transfer from the sensitizer to the naphthyl and then intramolecularly to the

Table 3. **Asymmetric Photocycloaddition of Enone to Alkene**

substrates						product			
enone	R$_1$[a]	ene	R$_2$/R$_3$[a]	solvent	temperature, °C	no.	cy,[b] %	de, %	ref
35	PhMen	**36**	*c*	toluene	rt	**37**	60[d]	30	103
						38	40[d]	79	
				methanol	rt	**37**	*e*	51	102
						38	*e*	78	
					–60	**37**	*e*	68	
				CF_3CH_2OH	rt	**37**	*e*	56	
						38	*e*	78	
				AcOH–MeOH (95/5)	rt	**37**	*e*	68	
						38	*e*	76	
	Men	**36**	*c*	toluene	rt	**37**	70[d]	18	103
						38	30[d]	25	
	Bor	**36**	*c*	toluene	rt	**37**	83[d]	4	103
						38	17[d]	*e*	
39	*c*	**40**	PhMen	toluene	rt	**41**	51	56	104
					–60	**41**	*e*	74	102
				C_6H_{12}	rt	**41**	*e*	62	
				methanol	rt	**41**	*e*	30	
				CF_3CH_2OH	rt	**41**	*e*	12[f]	
			Men	toluene	rt	**41**	54	13	104
			Bor	toluene	rt	**41**	57	19	
42	*c*	**44**	iPr	benzene	rt	**45**	*e*	43	101
43	*c*	**44**	Me	benzene	rt	**45**	*e*	43	101
			Et	benzene	rt	**45**	*e*	64	
			iPr	benzene	rt	**45**	*e*	84	
46	Men	**48**	Et/Et	benzene	rt	**49**	39	10	235
	PhMen	**48**	Et/Et	benzene	rt	**49**	35	18	
	BuBor^{i}	**48**	Et/Et	benzene	rt	**49**	36	5	
	BnBor^{i}	**48**	Et/Et	benzene	rt	**49**	41	8	
47	Men	**48**	Et/Et	benzene	rt	**49**	42	16	235
	PhMen	**48**	Et/Et	benzene	rt	**49**	45	56	
		48	Et/Et	toluene	rt	**49**	75	56	
	BuBor^{i}	**48**	Et/Et	benzene	rt	**49**	44	7	
	BnBor^{i}	**48**	Et/Et	benzene	rt	**49**	46	11	
47	Me	**48**	Me/Men	benzene	rt	**49**	44	27	236
	Men	**48**	Me/Men	benzene	rt	**49**	52	45	
	PhMen	**48**	Me/Men	toluene	rt	**49**	55	74	
50	(+)Men	C_2H_4	*c*	benzene	14	**51**	98	29	237
					–85	**51**	80	75	
52	*c*	**54**	*c*	hexane	20	**55**	50[d]	0	105
						56	50[d]	*e*	
					–78	**55**	82[d]	66	
						56	18[d]	*e*	
		57	*c*	hexane	–78	**58**	75[d]	78	
						59	25[d]	*e*	
		36	*c*	CH_3CN	5	**60**	*e*	80	
					–78	**60**	*e*	82	
53	*c*	**36**	*c*	hexane	rt	**60**	65	72	106

[a] PhMen = (–)-8-phenylmenthyl; Men = (–)-menthyl; (+)-Men = (+)-menthyl; Bor = (–)-bornyl; BuBor^{i} = (1*R*)-*exo*-2-(2,2-dimethylpropoxy)-*exo*-3-bornyl; BnBor^{i} = (1*R*)-*exo*-2-(benzyloxy)-*exo*-3-bornyl. [b] Chemical yield, unless noted otherwise. [c] Not applicable. [d] Relative product ratio of **37** and **38** or **55** and **56**. [e] Not reported. [f] Antipode formed.

fluorenyl group and that the selective, direct excitation of a 9-phenanthryl[99] or 9-anthryl[100] group introduced in the chiral ester moiety of **101–104** give the de's of 84–94%.

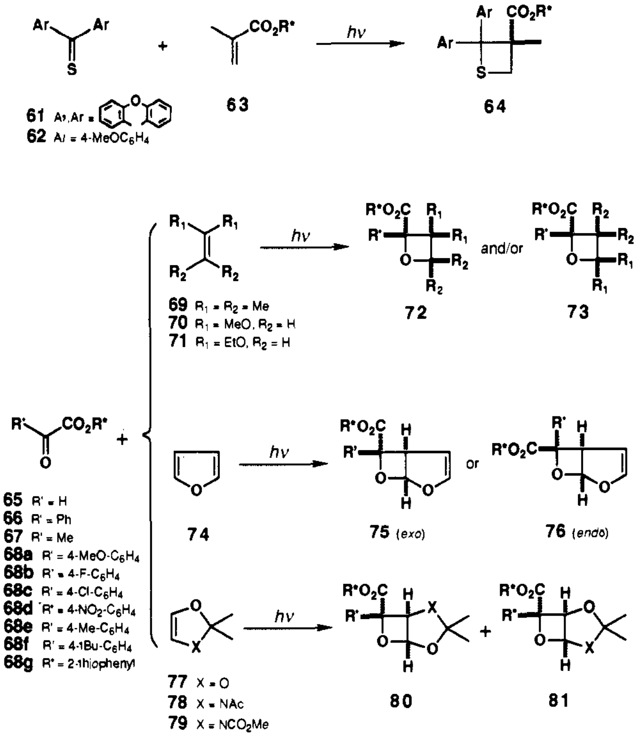
G. Photodeconjugation

In connection with their extensive work on enantiodifferentiating photodeconjugation of α,β-unsaturated esters and lactones described in section VI.D, Pete's group[129,246] reported their results on the diastereodifferentiating photodeconjugation of α,β-unsaturated esters of some chiral alcohols, illustrated in Scheme 13. Upon irradiation in the presence of a proton source (AH) such as achiral alcohol or amine, the chiral esters of highly concaved alcohols **108** and **109** gave the deconjugated β,γ-unsaturated esters **111** of high de up to 88% in good chemical yields at low temperatures (–40 to –78 °C). It is proposed that the observed de is determined by the diastereoface selectivity in the proton transfer of the photochemically produced labile dienol **110**.

H. Di-π-methane Rearrangement

In order to compare the asymmetric photochemical transformation in solution with that in the solid state, Scheffer's group[168] investigated the diastereodifferentiating di-π-methane rearrangement of dibenzobarrelene derivatives **112–116** possessing a chiral auxiliary at various positions (Scheme 14). The position of the chiral handle in relation to the site of the reaction was shown to have a pronounced influence on the product's de. Thus, the menthoxycarbonyl group at the bridgehead in **112** induced moderate de's of 60 and 20% in the rearrangement product **117** in the solid and solution

Scheme 9. Paternò–Büchi Reaction



phase, respectively, whereas the chiral ester group at the vinylic position of **113** resulted in no diastereodifferentiation in **118** in both phases. The solution photochemistry of **114**, where one of the vinylic ester groups is chiral, afforded the best de of 40% for **117** but 0% de again for **118**. The *N*-acetylalanine ester **115** and α-methoxyphenylacetic ester **116** gave a regioisomeric mixture of **119** (major product) and **120** (minor) in low to moderate de's of 0–50%. Interestingly, the solution-phase, rather than solid-state, photolysis of **116** led to the higher de's of 34 and 40% for **119** and **120**, respectively.

A considerable amount of work on the diastereoisomeric photoequilibrium of Δ,Λ-Ru(II) complexes carrying amino acid as a chiral ligand has also been pursued in detail by Vagg and Williams.[92–96,251–253] However the equilibrium is governed not by the chiral auxiliary but by the built-in chiral ligand that constitutes an inseparable block, and therefore we will not discuss it further. This photoequilibrium was reviewed by Vagg.[97]

VI. Asymmetric Induction by Chiral Complexing Agent

The photochemical asymmetric induction does not necessarily require a stoichiometric amount of chiral auxiliary chemically bonded to the substrate molecule. One of the potentially more chiral-source efficient methods for inducing optical activity in prochiral substrates is to use a chiral complexing agent that interacts with the substrate in any stage of the photochemical and subsequent thermal processes. In this strategy, hydrogen or electron donor–acceptor complexes with the ground-state substrate or the reactive intermediate produced photochemically have been utilized to give the diastereomerically differentiated transition states. The chiral complexing agent employed is quite frequently bifunctional, thus working as a chiral template. Naturally, the chiral source/substrate ratio needed, depending drastically upon the strength of the interaction and the lifetime of the intermediate involved, varies from less than 0.1 to as much as 40 in the extreme cases where the chiral complexing agent is used as a solvent.

Table 4. Asymmetric Paternò–Büchi Reaction of Ketone with Alkene

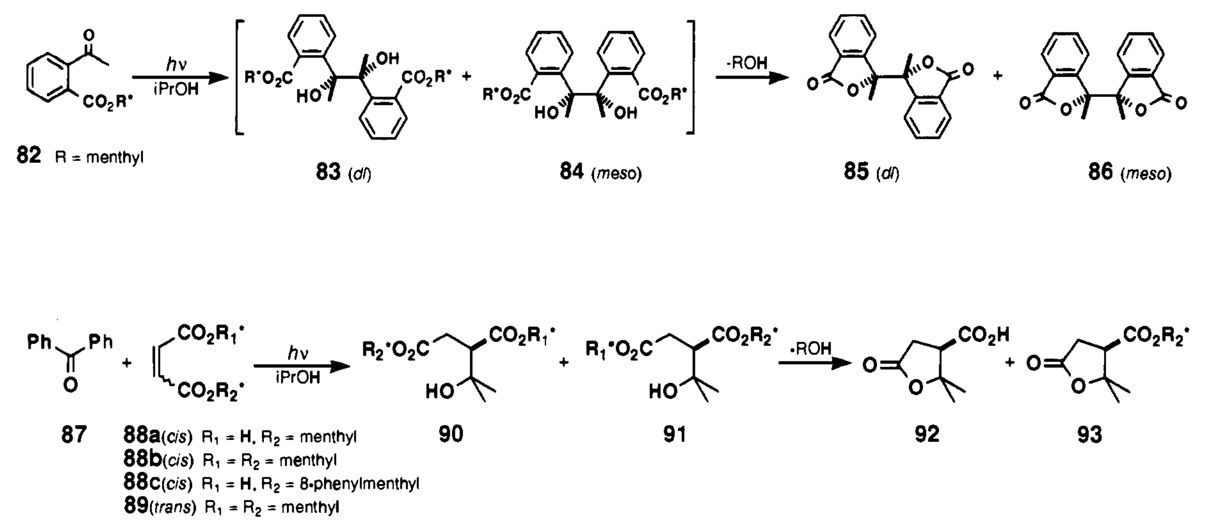
substrates				product			
one	ene	R[a]	*T*, °C	no.	cy,[b] %	de, %	ref
61	**63**	Men	rt	**64**	~100	17[d]	107
			rt	**64**	*e*	6[f]	
62	**63**	Men	rt	**64**	*e*	18[d]	107
			rt	**64**	*e*	4[f]	
65	**74**	Men	rt	**75**	80	7	110
	74	Oct	rt	**75**	71	5	
	74	TMP	rt	**75**	67	2	
66	**69**	Men	rt	**72**	90	53	108
			55	**72**	5	51	116
			20	**72**	20	62	
			–66	**72**	66	75	
		Bor	rt	**72**	59	19	112
		PhMen	rt	**72**	42	>96	112
	70	Men	rt	**72**	60	37	108
	71	Men	57	**72**	34	35	116
				73	25	43	
			24	**72**	47	43	
				73	30	33	
			–70	**72**	61	36	
				73	21	11	
		Bor	rt	**72**	50	3	112
				73	20	9	
		PhMen	rt	**72**	56	90	112
				73	22	76	
		BuBor[i]	rt	**72**	37	>96	112
				73	16	>96	
	75	Glu	rt	**76**	79	48	240
		Ara	rt	**76**	80	80	
	77	Men	rt	**80**	99	57	113
		PhMen	rt	**80**	99	>96	
	78	Men	rt	**80**	23	68	114
				81	11	46	
		PhMen	rt	**80**	30	95	114
				81	38	95	
	79	Men	rt	**80**	53	63	114
				81	>19	66	
		PhMen	rt	**80**	47	95	114
				81	>17	95	
67	**78**	Men	rt	**80**	>18	40	114
				81	>27	57	
		PhMen	rt	**80**	13	67	114
				81	>24	77	
68a	**74**	Men	–23	**75**	93	64	241
68b	**74**	Men	–23	**75**	91	58	241
68c	**74**	Men	–23	**75**	87	57	241
68d	**74**	Men	–23	**75**	19	48	241
68e	**74**	Men	–23	**75**	86	62	241
68f	**74**	Men	–23	**75**	83	62	241
68g	**74**	Men	–23	**75**	90	64	241

[a] Men = (–)-menthyl; Oct = (*R*)-1-methylheptyl; TMP = (*R*)-1,2,2-trimethylpropyl; Bor = (–)-bornyl; PhMen = (–)-8-phenylmethyl; BuBor[i] = (1*R*)-*exo*-2-(2,2-dimethylpropoxy)-*exo*-3-bornyl; Glu = 1,2:5,6-di-*O*-isopropyliden-α-D-glucofuranose; Ara = 1,5-anhydro-4,6-*O*-benzyliden-2-desoxy-D-arabinohexitol. [b] Chemical yield. [c] Not applicable. [d] Irradiation performed at 589 nm; first excited triplet (T_1; n,π^*) involved. [e] Not reported. [f] Irradiation performed at 400 nm; second excited singlet (S_2; π,π^*) involved.

A. Photopinacolization

Seebach and co-workers[130,132,133] reported the first asymmetric photochemical, as well as electrochemical, pinacolization of several aromatic ketones in (+)-1,4-

Scheme 10. Radical Dimerization/Addition



82 R = menthyl

83 (*dl*)

84 (*meso*)

85 (*dl*)

86 (*meso*)

87

88a(*cis*) R_1 = H, R_2 = menthyl
88b(*cis*) R_1 = R_2 = menthyl
88c(*cis*) R_1 = H, R_2 = 8-phenylmenthyl
89(*trans*) R_1 = R_2 = menthyl

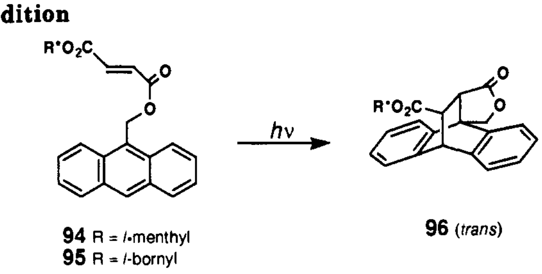
90

91

92

93

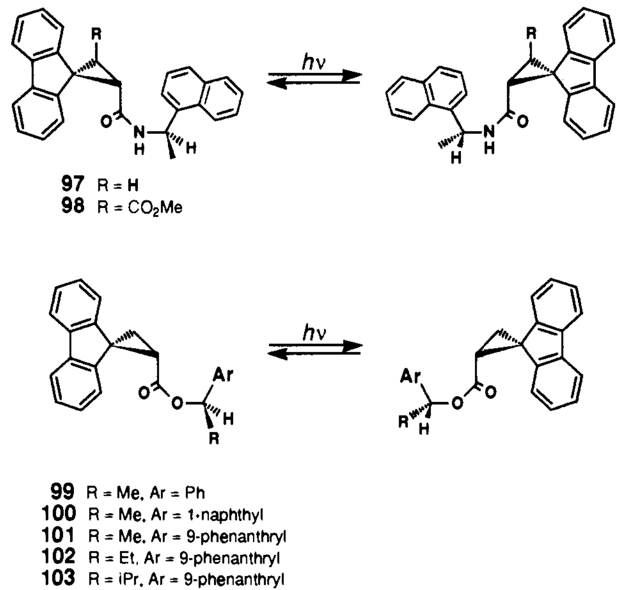
Scheme 11. Intramolecular [4 + 2] Photocycloaddition



94 R = *l*-menthyl
95 R = *l*-bornyl

96 (*trans*)

Scheme 12. Diastereoisomeric Photoequilibrium



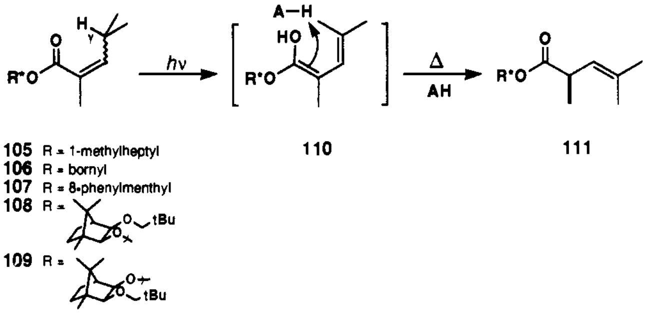
97 R = H
98 R = CO_2Me

99 R = Me, Ar = Ph
100 R = Me, Ar = 1-naphthyl
101 R = Me, Ar = 9-phenanthryl
102 R = Et, Ar = 9-phenanthryl
103 R = iPr, Ar = 9-phenanthryl
104 R = Me, Ar = 9-anthryl

bis(dimethylamino)-2,3-dimethoxybutane (**122a**)[254] used as a solvent or cosolvent. As shown in Scheme 15a, the photopinacolization proceeds through two successive processes. The initial electron transfer from amine **122** to triplet ketone **121**, generated by the irradiation and the subsequent intersystem crossing, produces a radical ion pair [**123**···**124**]. Then the subsequent proton transfer from an *α*-carbon of the radical cation **124** gives a weakly interacting radical pair [**125**···**126**]. Recombination of the resultant radical **125**, which is hydrogen bonded to the chiral amine radical **126**, gives *meso*- and *dl*-pinacol (**127**) in ca. 1:1 ratio, along with the other coupling products. The photolysis of acetophenone was performed in neat **122a** or in a mixture of **122a** and a cosolvent at 25 to −72 °C; the chiral source to substrate ratio varies from 10 to 40. The best result was obtained in a 1:5 mixture of **122a** and pentane; the op's of *dl*-pinacol were 7.6% at 25 °C, 13.4% at −35 °C, and 23.5% at −72 °C.[132] On the other hand, the use of protic cosolvents as diluent or the addition of lithium salts entirely ruined the product's op,[132,133] probably interfering with the complex formation through hydrogen bonding.

Photopinacolization through simple hydrogen abstraction by triplet acetophenone (**128**) in the presence of an equimolar amount of *l*-menthyl *l*- or *dl*-lactate (**129**), added as a hydrogen donor, was reported by Horner and Klaus[76] (Scheme 15b). Although the observed op's were fairly low, the positive participation of the lactate's hydroxyl group in the enantiodiffer-

Scheme 13. Asymmetric Photodeconjugation Induced by Chiral Auxiliary

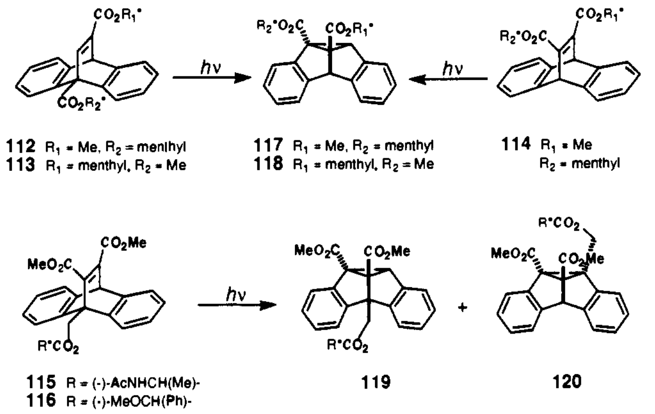


105 R = 1-methylheptyl
106 R = bornyl
107 R = 8-phenylmenthyl
108 R =
109 R =

110

111

Scheme 14. Di-π-methane Rearrangement



112 R_1 = Me, R_2 = menthyl
113 R_1 = menthyl, R_2 = Me

117 R_1 = Me, R_2 = menthyl
118 R_1 = menthyl, R_2 = Me

114 R_1 = Me
R_2 = menthyl

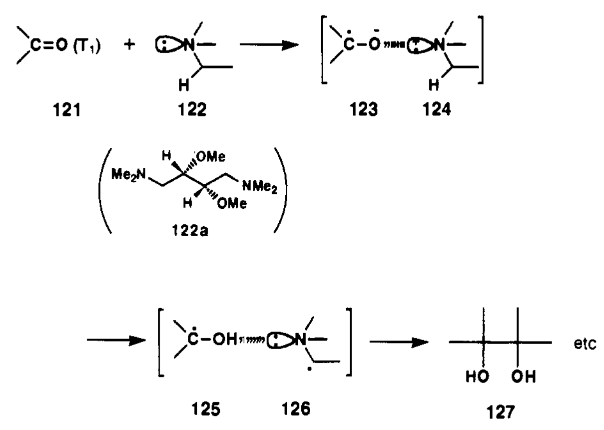
115 R = (-)-AcNHCH(Me)-
116 R = (-)-MeOCH(Ph)-

119

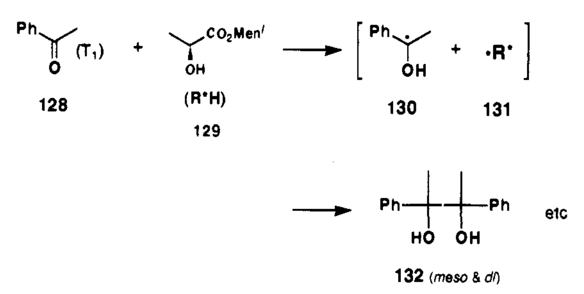
120

Scheme 15. Photopinacolization

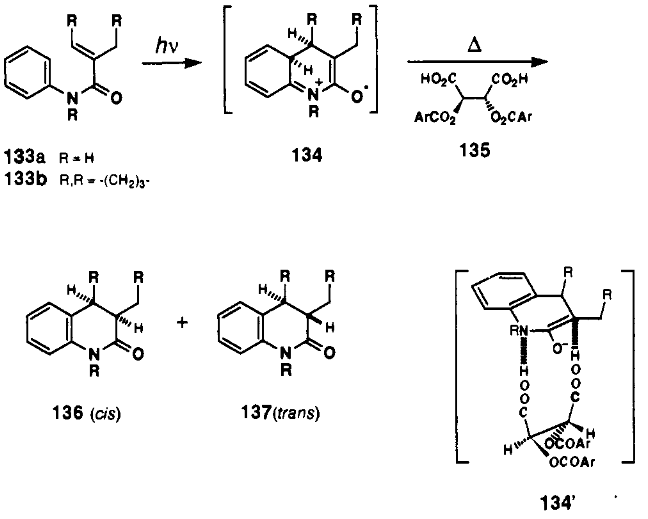
a) Via electron transfer-proton transfer



b) Via hydrogen abstraction



Scheme 16. Photocyclization of Enamide

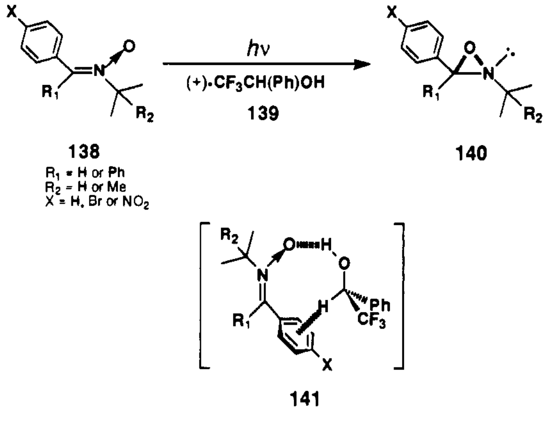


entiating dimerization of **130** is indicated by the observations that the doubly chiral *l*-menthyl *l*-lactate as a solvent gave appreciable op's (1.2–4.7%), while the use of half-racemic *l*-menthyl *dl*-lactate resulted in no enantiodifferentiation.

B. Photocyclization

Naito and Ninomiya[119] reported the photocyclization of aromatic enamides **133** and the subsequent prototropic reaction in the presence of (+)- or (−)-ditoluoyltartaric acid as a chiral template (Scheme 16). The enantiodifferentiation apparently occurs in the second thermal step to give the enantiomeric products **136** and/or **137** of low to moderate op's (9–42%) in good combined chemical yields. A 1:1 complex (**134'**) was proposed for the protonation process, in which the acid protons of **135** are bound to the N-1 and C-3 of the enolate intermediate from the bottom side of the molecular plane.[119] They also investigated the reduction of similar zwitterionic intermediates produced by the photocyclization of enamides with a chiral lithium aluminum hydride–quinine complex.[255] These works were reviewed by themselves.[256,257]

Scheme 17. Photorearrangement of Nitrone to Oxaziridine



C. Photorearrangement

The enantiodifferentiating photorearrangement of aromatic nitrones **138** to the corresponding oxaziridines **140** was studied by Boyd et al[135] (Scheme 17). A chiral complexing agent (*S*)- or (*R*)-2,2,2-trifluoro-1-phenylethanol (**139**) was used as a mixed solvent (1:1) with fluorotrichloromethane to give the optically active oxaziridines **140** in good chemical yields. The op's are low to moderate, varying with the substituents (X, R_1, and R_2) and the irradiation temperature. The introduction of an electron-withdrawing group (X = Br or NO_2) resulted in a substantial decrease in op, while the more bulky substituent at R_1 (Ph rather than H) or R_2 (CH_3 rather than H) and lower temperatures gave much improved op's up to 31% (X = H, R_1 = Ph, R_2 = Me; −78 °C). In analogy with the similar complexes proposed previously for amine oxides, phosphine oxides, and sulfoxides,[258–260] a ground-state complex **141** of nitrone with the chiral alcohol was suggested to be involved in the enantiodifferentiating photorearrangement.

D. Photodeconjugation

An intensive work on the enantiodifferentiating photodeconjugation of α,β-unsaturated esters and lactones has recently been reported by Pete and his coworkers.[120–128] As illustrated in Scheme 18, this photodeconjugation is initiated by the photochemical Norrish type II γ-hydrogen abstraction of α,β-unsaturated ester **142**, giving rise to a labile dienol **143**, and is completed with the subsequent thermal reketonization of the resulting dienol to a chiral β,γ-unsaturated ester **144**. The deconjugating reketonization process, which is in competition with the back hydrogen transfer regenerating the starting material, is the rate-determining step and has been shown to be facilitated in the presence of a protonating agent.[261]

Scheme 18. Photodeconjugation via Norrish Type II Reaction

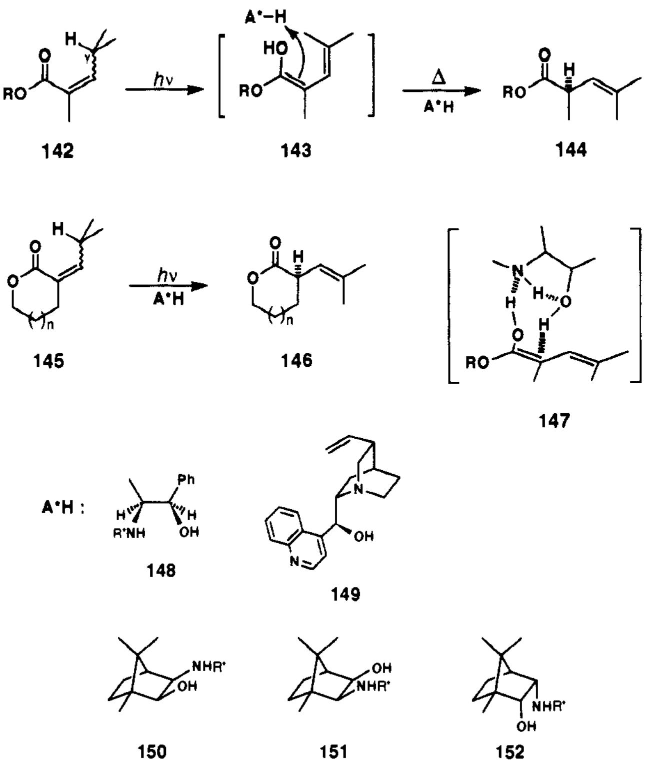


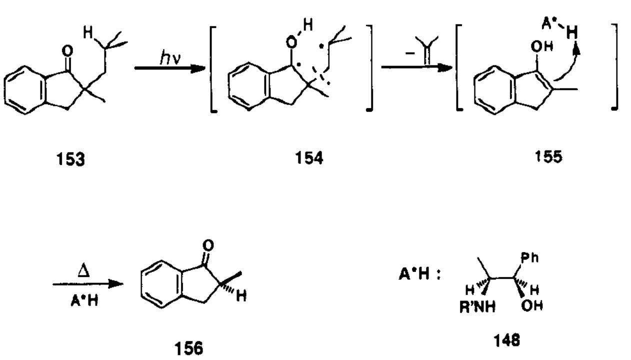
Table 5. Enantiodifferentiating Photodeconjugation of α,β-Unsaturated Esters and Lactones[a]

substrate (R or n)	amino alcohol A*H (R′)	T, °C	cy,[b] %	op,[c] %	ref
142 (Me)	148 (Me)	-78	67	18	123
(iPr)			63	20	
(PhCH$_2$)			78	31	
	(Me)	-40	64	37	125
	(PhCH$_2$)		75	8.4	
	(iBu)		68	32	
	(iPr)		69	70	
(PhCH$_2$)	*l*-menthol	-78	81	0	124
	149	-78	73	37	
	150 (C$_6$H$_{11}$)	-45	52	40	128
	151 (H)	-52	72	10	
	(iPr)	-50	74	16	
	152 (H)	-45	57	54	
	(iPr)	-45	71	83	
	(iPr)	-55	76	89	
	(C$_6$H$_{11}$)	-55	73	80	
	(PhCH$_2$)	-55	75	91	
145 (0)	148 (Me)	25	64	5	120
		-78	85	25	
(1)[d]	148 (Me)	25	*e*	2.3	126
		-78	*e*	26	

[a] Irradiation performed at 254 nm in dichloromethane. [d] Isolated yield. [c] Optical purity or enantiomeric excess determined by NMR spectroscopy or polarimetry. [d] Irradiated in pentane–ether (90:10). [e] Not reported.

Some selected results are listed in Table 5. In the earlier studies, natural β-amino alcohols like (−)-ephedrine (148, R′ = Me) and cinchonidine (149) were employed as a chiral proton-donor/template (A*H) in the photodeconjugation of various α,β-unsaturated esters 142 or lactones 145 to give moderate op's.[123,130] On the other hand, simple optically active alcohols such as menthol or 2-octanol were totally ineffective as for the enantiodifferentiation,[124,127] and the use of polar coordinating solvents like ether, methanol, and acetonitrile drastically diminished the op to almost zero.[127] As compared with the other enantiodifferentiating reactions described in this section, the chiral-source efficiency is excellent. In the photodeconjugation of 142 (R = PhCH$_2$) in the presence of (−)-ephedrine (148, R′ = Me), the product's op rapidly increased from zero to the ultimate value of 30% with increasing the relative molar ratio of the chiral source to the substrate from zero to 0.05 and leveled off thereafter. On the basis of these and additional observations, a nine-membered complex 147 was proposed for the enantiodifferentiating protonation step.[123,127] After further extensive efforts in examining a wide variety of the substituents on substrate and the complexing amino alcohols, they finally found a highly enantiodifferentiating amino alcohol 152, which gives the deconjugation product 144 with the op up to 91% at −55 °C.[128]

Scheme 19. Norrsh Type II Photoelimination



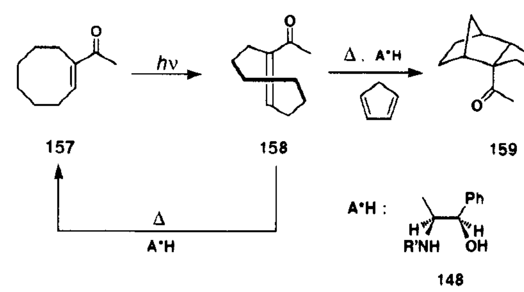
E. Photoelimination

More recently, Pete and Rau's group[262] reported a similar enantiodifferentiating protonation of an enol generated by the Norrish type II photoelimination of 2,2-disubstituted 1-indanone 153. As illustrated in Scheme 19, the intramolecular γ-hydrogen abstraction of excited indanone 153 and the subsequent β-fission of the resulting 1,4-biradical 154 gives enol 155. In the presence of a chiral proton donor (A*H) such as (−)-ephedrine (148), the photoenol 155 suffers enantiodifferentiating reketonization, affording the optically active cleavage product 2-methyl-1-indanone (156) in 42–59% chemical yield. The op obtained varies from 21 to 47% with the solvent and the amount of the chiral source employed. It is noted that the chiral source/substrate ratio as low as 0.01 can give an almost maximal op of 45%, which is comparable to that (47%) obtained with a higher ratio (0.1).[262]

F. Geometrical Photoisomerization

Enantiodifferentiating thermal isomerization of photochemically produced constrained compound in the presence of (+)-ephedrine has also been reported by the same group.[263] (*E*)-1-Acetylcyclooctene (157), possessing a *cis*-cyclooctene skeleton, is known to undergo the geometrical isomerization upon irradiation, affording the highly strained trans-isomer 158[264-266] (Scheme 20). Utilizing an observation that the trans-isomer, though thermally stable at room temperature in the dark, suffers a slow water- or alcohol-induced back-reaction to the cis, they showed that the photochemically produced racemic trans is kinetically resolved during the (+)-ephedrine-catalyzed thermal trans-to-

Scheme 20. Cis–Trans Photoisomerization



cis isomerization, for which only the evolution of CD was reported.[263] They also demonstrated that the irradiation of 157 in the presence of cyclopentadiene and (+)-ephedrine (148) gives an optically active Diels–Alder adduct 159 of >22% ee. In this case, it is likely that the enantiodifferentiation occurs not in the photochemical isomerization process but in the subsequent thermal trans-to-cis or cycloaddition process.

Although the aforementioned reactions involve the electronic excitation by light absorption, the photochemical process is used as a mere tool for making the substrate highly reactive. In this context, it is quite difficult to differentiate these reactions from the purely thermal ones in which highly reactive substrates or intermediates are reacted in the presence of a catalytic amount of chiral complexing agent,[267-271] e.g., the quinidine-catalyzed cycloaddition reaction of ketene to chloral, giving β-propiolactone of 98% ee.[271]

VII. Asymmetric Photosensitization

Photochemical reactions sensitized by optically active compounds provide us with more authoritative examples of the *photochemical* asymmetric induction, in which the enantiodifferentiating interaction occurs indeed in the electronically excited state rather than the subsequent thermal process. The asymmetric photosensitization, demanding merely a catalytic amount of the chiral sensitizer, is in principle a promising method for transferring and multiplying chirality from the sensitizer to the product molecule with a high chiral-source efficiency, although the product's op's hitherto reported are low to moderate.

There is a formal analogy with the direct asymmetric photochemistry described above, since, in the sensitized asymmetric photochemical reactions, the electronically excited optically active photosensitizer, in place of CPL, transfers its chiral information to the substrate during the sensitized excitation process. In the photosensitization, however, the influence of the chiral sensitizer may not be limited to the photophysical excitation process but often lasts throughout the subsequent photochemical process via an excited complex (exciplex) formed from the excited sensitizer and the ground-state substrate. Another distinct difference or choice exists in the excitation mechanism. Depending on the energetic relationship between sensitizer and substrate, the photosensitization may proceed through the singlet, triplet, or electron-transfer mechanism. Despite these critical differences from the direct asymmetric photochemistry with CPL, the asymmetric photosensitized reactions may be classified into analogous categories: (a) photosensitized destruction/production; (b) photosensitized deracemization; (c) photosensitized geometrical isomerization; and (d) photosensitized cycloaddition/dimerization. The first two categories have the straight analogies in the direct photolysis with CPL and are formally represented by Schemes 1 and 2 with some modifications for the presence of chiral sensitizer. Hence, the modified anisotropy factor (g') may be defined for the asymmetrically sensitized excitation, using the experimentally determined excitation, or quenching, rate constants, instead of the extinction coefficients toward CPL, of the (R)- and (S)-enantiomers:

$$g' = (k_R - k_S)/[(k_R + k_S)/2] \qquad (9)$$

This value refelcts the electronic and steric interaction between the excited sensitizer and the substrate. Furthermore, if the enantiodifferentiating interaction occurs only in the excitation step, the eqs 2–7 and Figures 1–3 may also be applied to the enantiodifferentiating photosensitization.

The third category would be taken as a minor variation of the second category, since there is no apparent destruction or production involved, except for the geometrical isomerization. However, the presence of this isomerization process makes a great difference. This unimolecular process enables the simultaneous photoequilibrations among the geometrical and enantiomeric isomers, and therefore the production of chiral trans isomer from achiral cis. Historically, this type of asymmetric photosensitization was the earliest example[71] and has most frequently been investigated. In the last category, the photochemical synthesis of a chiral cycloadduct from two achiral substrates is accomplished through the photosensitization with a chiral sensitizer.

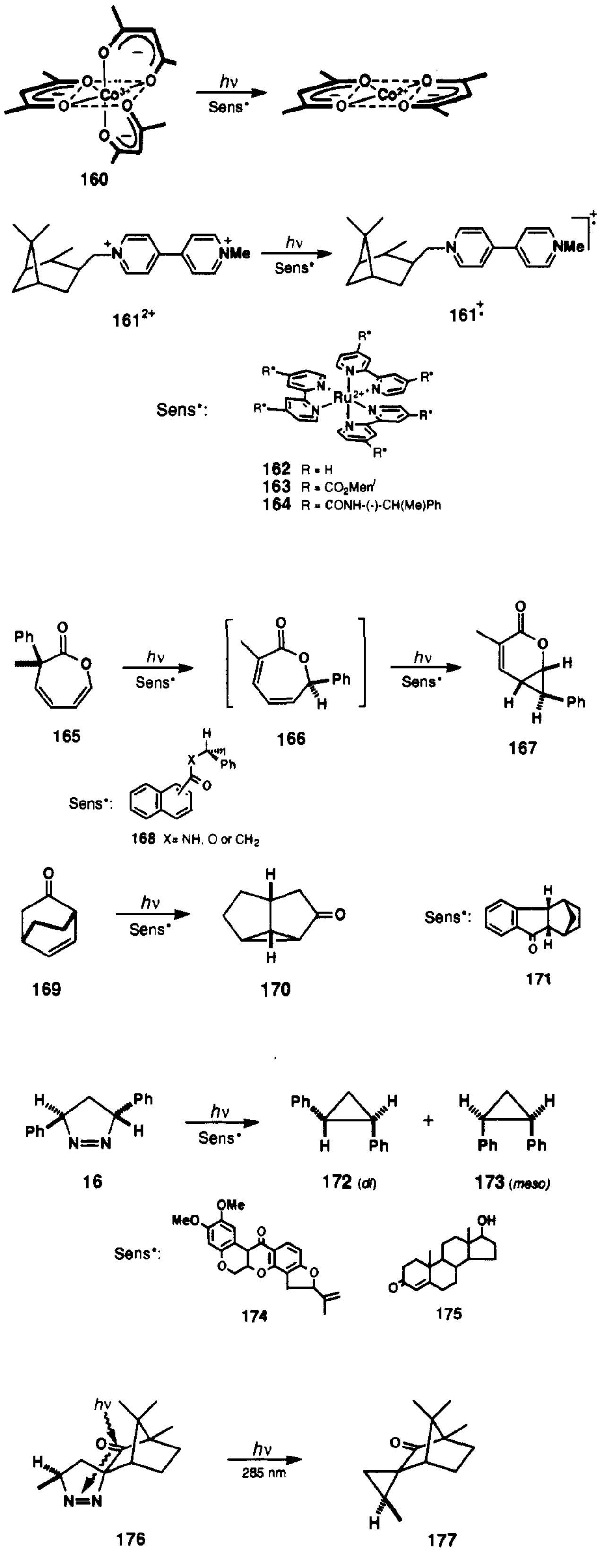
A. Photosensitized Destruction/Production

Several mostly irreversible photochemical transformations, including the reduction through electron transfer, 1,5-phenyl shift, oxa–di-π-methane rearrangement, and molecular elimination of nitrogen, are known to be sensitized by optically active compounds.

Porter and Sparks[272] reported the first enantiomer-differentiating electron transfer from an excited Δ-Ru(bpy)$_3$ 162 to a ground-state racemic Co(acac)$_3$ 160 and the subsequent decomposition of the latter, affording a chiral reduced Co^{2+} complex and oxidation products derived from acac$^-$,[273] as shown in Scheme 21. Upon the selective excitation of Δ-Ru(bpy)$_3$ at 458 nm, an evident evolution of the CD spectrum corresponding to Δ-Co(acac)$_3$ was observed, indicating the selective decomposition of Λ-Co(acac)$_3$.[272] The relative rate constant is not so high: $k_\Lambda/k_\Delta = 1.08$ or $g' = 0.076$. A similar order of enantiodifferentiation ($k_+/k_- = 1.1$–1.2) was reported by Kaizu et al.[274] in the luminescence quenching of Δ-Ru(bpy)$_3$ 162 with optically active (+)- and (−)-[Co(edta)]$^-$.

Using Δ- and Λ-Ru(bpy)$_3$ 162 as chiral electron donors, Rau and Ratz[275] demonstrated that the phosphorescence quenching through electron transfer of 162 with an optically active methylviologen derivative 161^{2+} is highly enantiodifferentiating ($k_\Lambda/k_\Delta = 1.95$; $g' = 0.64$), but the enantiodifferentiation observed in the formation of reduction product 161$^{\bullet+}$ is substantially diminished: $k_\Lambda/k_\Delta = 1.32$. The loss was attributed to the competing

Scheme 21. Photosensitized Destruction/Production



back-electron-transfer from $161^{\bullet+}$ to Ru^{3+} and the dissociation of the geminate ion pair.

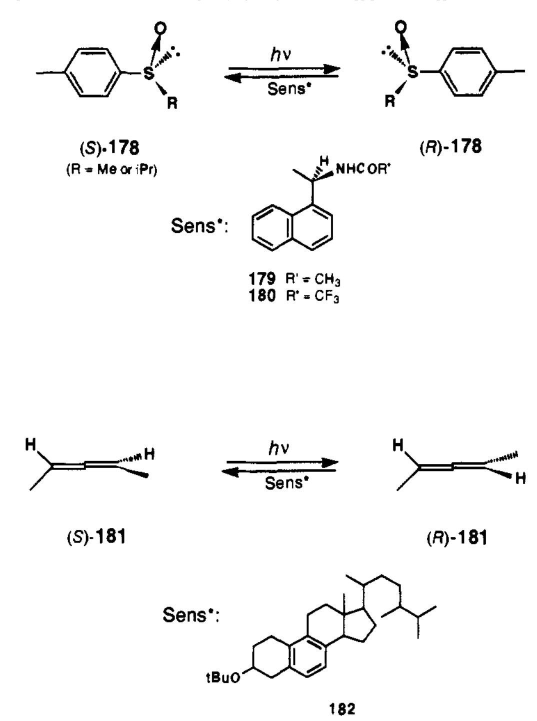
Recently, Ohkubo and co-workers[276] synthesized an optically active ruthenium(II) complex **163**, the chirality of which originates not from the ligand configuration around Ru^{2+} but from the peripheral chiral auxiliaries. Using this complex, they investigated the phosphorescence quenching with Δ- and Λ-Co(acac)$_3$ **160** in aqueous ethanol, along with the photochemical reduction through electron transfer. The quenching rate constants for Δ- and Λ-Co(acac)$_3$, though smaller than that for the unsubstituted **162** ($k_q = 6.6 \times 10^8$ M^{-1} s^{-1}),[272] were distinctly different: $k_\Lambda = 1.68 \times 10^8$ M^{-1} s^{-1}; $k_\Delta = 2.24 \times 10^8$ M^{-1} s^{-1}.[276] The relative rate constants for the reduction of both enantiomers ($k_\Delta/k_\Lambda = 1.33$; $g' = 0.28$) derived from the pseudo-first-order plot nicely coincide with those obtained in the quenching experiment ($k_\Delta/k_\Lambda = 1.33$) or calculated from the evolution of the CD spectrum ($k_\Delta/k_\Lambda = 1.32$). The photoreduction was shown to proceed catalytically with a turnover number of 30–40, regenerating Ru^{2+} through the thermal reduction of the photochemically produced Ru^{3+} by the solvent ethanol. They further demonstrated that Λ-ruthenium(II) complex **164** reduces **160** in 90% ethanol with a higher enantiodifferentiation: $k_\Lambda/k_\Delta = 1.54$ or $g' = 0.43$.[277] The use of lower ethanol contents (70 or 50%) accelerated the reduction rate by about 1 order of magnitude but drastically diminished the k_Λ/k_Δ ratio to 1.03–1.05. Not reported or discussed, the observed g' factor of 0.43 means that the op of remaining substrate **160** may amount to 50% at 90% destruction and even up to 80% after 99% destruction, as can be seen from Figure 2b.

Hoshi et al.[77] reported a typical photodestruction/production sensitized by a chiral compound (Scheme 21). Upon photosensitization with the optically active 1- and 2-naphthalene derivatives **168** (mostly amides), a racemic mixture of 3*H*-2-oxepinone (**165**) first undergoes 1,5-hydrogen shift, affording unstable 7*H*-2-oxepinone (**166**), the di-π-methane rearrangement of which gives oxabicycloheptenone (**167**) as the final product. Unfortunately, no op's were reported, but the specific rotations of the substrate recovered and the product isolated at ca. 50% conversion unambiguously indicate the operation of the preferential destruction of one enantiomer and the formation of the corresponding optically active product. The apparent relative rate constant (k_R/k_S) was estimated as 1.04 in one of the best cases, although it is not clear if the enantiodifferentiation occurs in either or both of the successive photosensitization processes. The corresponding ester or ketone derivatives as sensitizer gave much lower optical rotations.

The photosensitized enantiodifferentiating oxa-di-π-methane rearrangement of bicyclo[2.2.2]oct-5-en-2-one (**169**) was reported in a synthetic context by Demuth et al.[80] (Scheme 21). Upon the triplet sensitization with an optically active indanone derivative **171**, the bicyclooctenone **169** gave the rearrangement product **170** in 4.5% and 10% op at room temperature and −78 °C, respectively, after 7–44% conversion. No op was reported for the remaining substrate.

Rau et al.[81,278] investigated the photosensitized enantiodifferentiating decompositions of pyrazoline derivatives **16** and **176** by means of the inter- and intramolecular triplet and/or singlet energy transfer (Scheme 21). The photodecomposition of *trans*-3,5-diphenylpyrazoline (**16**) was sensitized by the optically active triplet sensitizers, (−)-rotenone (**174**) and (+)-testosterone (**175**), affording chiral *trans*- and *cis*-1,2-diphenylcyclopropanes (**172** and **173**, respectively). The photodecomposition was monitored by the evolution of the CD spectrum, which gave the maximum θ at the 63%

Scheme 22. Photosensitized Deracemization



conversion as was the case with the direct photolysis with CPL. The relative rate constants (k_R/k_S) are 1.080 and 1.016 for 174 and 175, respectively, and the optimum op at 60–63% conversion is 4.05% (174) or 0.75% (175). Thus, the sensitization with 174 gave a 50% improvement as compared with the direct asymmetric destruction of 16 with CPL (k_R/k_S = 1.058; 2.65% op).

On the other hand, the first enantiodifferentiating intramolecular singlet-energy transfer was attempted with (+)-camphor-3-spiropyrazoline (176).[278] The idea is to excite a chiral antenna chromophore (carbonyl in this case) first and then to transfer its singlet/triplet energy to the reaction site (pyrazoline moiety); see 176 in Scheme 21. If the energy-transfer process occurs at different rates for the enantiomers of 176, an appreciable CD may evolve in the course of the photolysis. However, the intramolecular energy transfer is too fast and efficient to differentiate the enantiomers even in the presence of 1 M piperylene added as a singlet, as well as triplet, quencher.

B. Photosensitized Deracemization

Only a few relatively early examples of the photosensitized equilibration between enantiomers are known; see Scheme 22.

Optically active aromatic sulfoxides were known to racemize upon photosensitization with naphthalene.[278–281] Using this reaction, Kagan's group carried out the first photoderacemization of methyl *p*-tolyl sulfoxide (178, R = CH_3) sensitized by (*R*)-*N*-acetyl-1-naphthylethylamine (179).[74] Prolonged irradiation of a solution containing the racemic sulfoxide 178 and the sensitizer 179 gave an apparent pss mixture of 2.25% op. However, the ultimate pss appears to be established at 4.1% op, judging from the experiments starting with the partially optically active mixtures whose *R*/*S* ratios lie on both sides of the ultimate value. For the more bulky isopropyl *p*-tolyl sulfoxide (178, R = iPr), a much improved op of 12% was attained by using (+)-*N*-(trifluoroacetyl)-1-naphthylethylamine (180).[2]

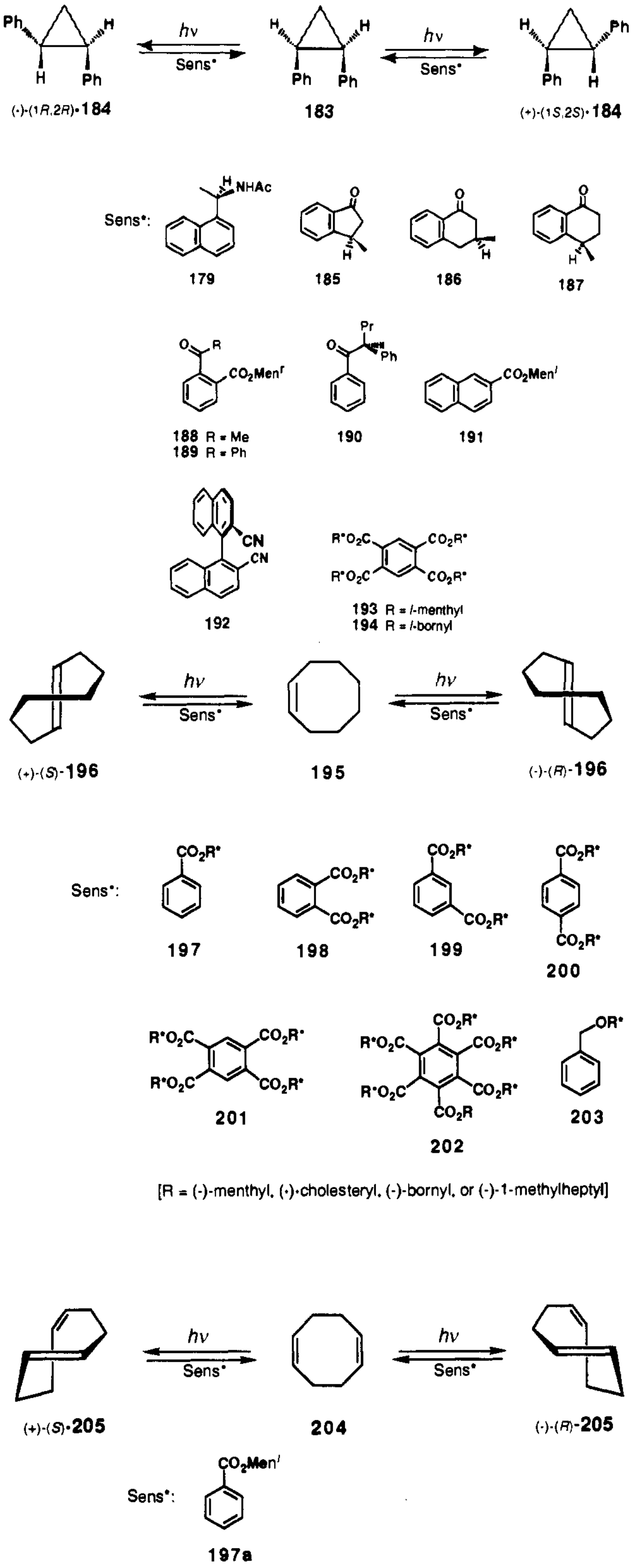
Another example is the sensitized photoderacemization of a chiral allene (Scheme 22). Weiss and coworkers[72] showed that 2,3-pentadiene (181) is partially photoresolved by sensitized deracemization with an optically active aromatic steroid, 21,22-dihydroneoergosterol (182). The optical purity of 3.4% was attained at the pss, from which the relative rate constant k_R/k_S is calculated as 1.07 (g' = 0.067).

C. Photosensitized Geometrical Isomerization

In 1965, Hammond and Cole[71] proposed a novel methodology for the photochemical asymmetric induction other than the CPL excitation. They believed that, on the basis of their foregoing intensive work on the photosensitized reactions,[282–284] there must be significant molecular contact in the energy transfer process, and the "nonvertical" transitions, where the rates of energy transfer fall far below the diffusion-controlled limit, are especially favorable for the stereochemical recognition.[71] Thus the first enantiodifferentiating photosensitized isomerization was performed with 1,2-diphenylcyclopropane (Scheme 23). The irradiation of racemic *trans*-1,2-diphenylcyclopropane (184, 0.12 M) in the presence of a chiral sensitizer (*R*)-*N*-acetyl-1-naphthylethylamine (179, 0.0075 M) led to the development of optical activity in the irradiated solution, along with the concomitant formation of the cis-isomer 183, ultimately giving the pss for both the cis/trans ratio and the optical rotation. The op of the trans isolated in a preparative-scale experiment amounted to 6.7%,[285] as calculated from the specific rotation of pure enantiomer 184 reported later.[286,287] Operation of the singlet energy transfer mechanism was later confirmed.[288]

Since then, a considerable amount of effort has been devoted to this enantiodifferentiating photosensitization, as if this is the system for the bench-mark test of chiral sensitizers. Ouannès et al.,[73] Kagan et al.,[289] and Horner and Klaus[76] employed several optically active aromatic ketones 185–190 and ester 191, working mostly as triplet sensitizers, and merely obtained rather lower op's of 1–3%. Horner and Klaus also attempted the enantiodifferentiating photoisomerization of *cis*-1,2-diphenylcyclopropane sensitized by a chiral naphthylethyl amide bound to silica surface, but obtained a quite low op (~1%).[290] Recently, Vondenhof and Mattay[291] showed that this photoisomerization/deracemization can be sensitized by an electron-accepting sensitizer 192 through a radical ion pair produced in the photoinduced electron-transfer process, but the op's obtained were low: 0.1% in acetonitrile (room temperature) and 4% in toluene (−30 °C). The intervention of a free or solvent-separated radical cation of diphenylcyclopropane in the isomerization process is most probably responsible for the extremely low op in polar acetonitrile solution. More recently, Inoue et al.[292] have shown that the use of *l*-menthyl pyromellitate (193) as a photosensitizer enhances the op of isolated 184 up to 10.4% in pentane solution at room temperature and, interestingly, the product chirality is inverted by changing the solvent from pentane to acetonitrile in the photosensitization with the bornyl ester 194. From the rapidly developing curve of the product's op

Scheme 23. Photosensitized Geometrical Isomerization



obtained in the photoisomerization starting with pure cis (183), they elucidated that the enantiodifferentiating process is not the decay from the intervening exciplex or radical–ion pair but the quenching of the chiral sensitizer by the trans (184).[292]

Much more efficient enantiodifferentiation has been achieved in the cis–trans photoisomerization of cyclooctene sensitized by optically active aromatic esters. In their earlier work, Inoue et al.[75,78] showed that some benzenecarboxylates like 197–200 efficiently sensitize the cis–trans isomerization of cyclooctene through a sinlget exciplex intermediate, and briefly reported that the singlet-sensitized isomerization of the *cis*-195 with *l*-menthyl benzoate (197) or isophthalate (199) gives optically active *trans*-196 in 3–4% op at room temperature. Intending an extensive survey of the temperature effect upon the enantiodifferentiating photosensitization and also a comprehensive understanding of the enantiodifferentiation mechanism, they recently reinvestigated this enantiodifferentiating photoisomerization in further detail at varying temperatures by using a number of optically active benzene(poly)carboxylates 197–202 as chiral sensitizers.[82,83,293] On the basis of the invariable op obtained in the photosensitization of pure cis over a wide range of the conversion and essentially no kinetic resolution occurring in the sensitized photoisomerization of pure trans, they concluded that the enantiodifferentiation occurs not in the quenching of the excited chiral sensitizer but in the decay process, i.e. the rotational relaxation of the cyclooctene moiety in the exciplex intermediate.

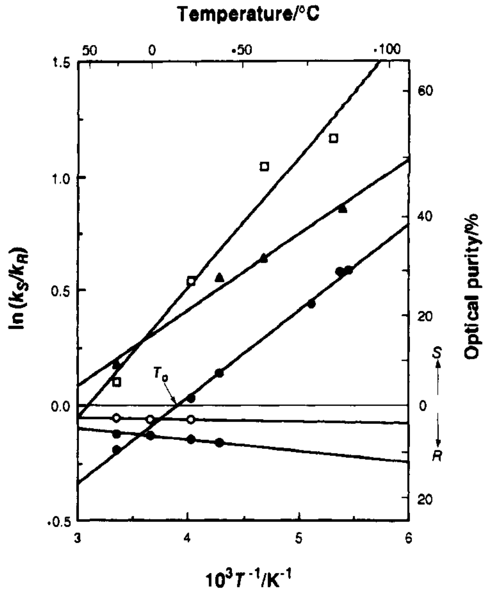


Figure 4. Temperature dependence of ln (k_S/k_R), or ln [(100 + % op)/(100 − % op)], in the enantiodifferentiating photoisomerization of *cis*-cyclooctene (195) sensitized by (−)-menthyl benzoate (197) and terephthalate (○ and **○**, respectively), (−)-menthyl and (−)-bornyl pyromellitates (201) (● and ▲, respectively), and (−)-1-methylheptyl mellitate (202) (□) in pentane.

Quite interestingly, they found an unprecedented temperature switching behavior of the product chirality. As can be seen from the typical plots shown in Figure 4, the direction of the product's rotation inverted at a critical temperature (T_0), called isoenantiodifferentiating or equipodal temperature, specifically in the photosensitization with some sensitizers possessing alkoxycarbonyl groups at the ortho position(s). Thus, above this critical temperature, the op increases with the temperature, apparently conflicting with our tacit understanding. However, this unexpected result is reasonably understood as a natural consequence of the significant contribution of the entropy factor,[293] which will be discussed in the Discussion section. Some of the activation parameters derived from the temperature dependence of op in this photosensitized isomer-

Table 6. Activation Parameters (at 25 °C) and Equipodal Temperatures (T_0) for Enantiodifferentiating Photoisomerization of *cis*-Cyclooctene (195) Sensitized by Some Chiral Alkyl Benzenepolycarboxylates in Pentane[a]

sensitizer		$\Delta\Delta H^{\ddagger}_{S-R}$,[b] kcal mol^{-1}	$\Delta\Delta S^{\ddagger}_{S-R}$,[c] cal mol^{-1} K^{-1}	A_S/A_R[d]	T_0,[e] °C
compd	R				
197	(−)-menthyl	+0.014	−0.027	0.99	*f*
200	(−)-menthyl	+0.092	+0.033	1.02	930
201	(−)-menthyl	−0.77	−1.30	0.52	−17
	(−)-bornyl	−0.61	−0.67	0.71	118
	(+)-1-methylheptyl	+0.54	+0.84	1.52	6
	(−)-1-methylheptyl	−0.52	−0.80	0.67	8
202	(−)-menthyl	−0.96	−1.67	0.43	−24
	(−)-bornyl	−0.86	−1.13	0.56	60
	(−)-1-methylheptyl	−1.13	−1.51	0.47	50

[a] All activation parameters obtained by Arrhenius or Eyring treatment of the optical purity of the *trans*-**196**. [b] Differential enthalpy of activation: $\Delta H^{\ddagger}_S - \Delta H^{\ddagger}_R$. [c] Differential entropy of activation: $\Delta S^{\ddagger}_S - \Delta S^{\ddagger}_R$. [d] Relative frequency factor. [e] Equipodal temperature, at which no appreciable enantiodifferentiation occurs. [f] Does not exist.

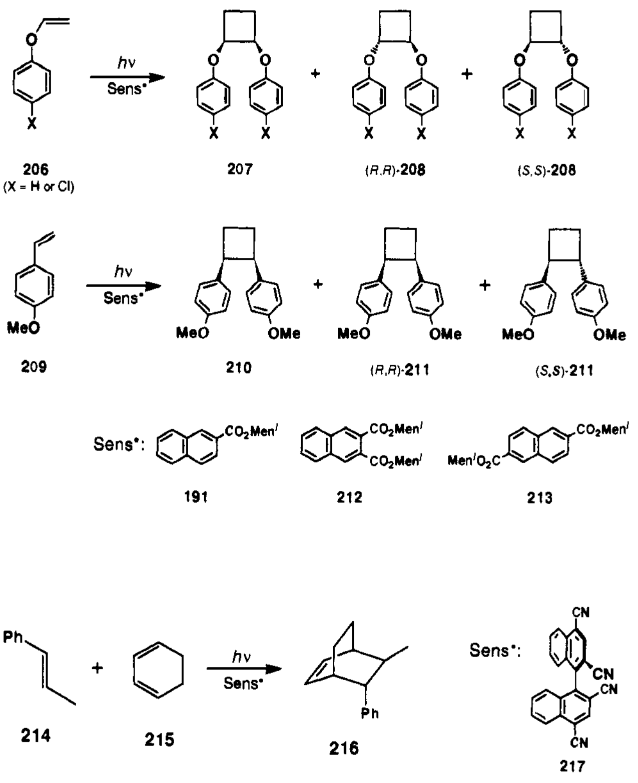
ization are listed in Table 6. Several sensitizers possessing *o*-dicarboxylates gave indeed the equipodal temperatures T_0 within the experimental temperature range. The highest op of 52.7% was obtained in the photosensitization with the highly congested (−)-hexakis(1-methylheptyl) mellitate (**202**) at −87 °C; while the triplet sensitization with benzyl *l*-menthyl ether (**203**) gave almost zero op at the room temperature.[293]

In a related photosensitization of *cis,cis*-1,5-cyclooctadiene (**204**) with (−)-menthyl benzoate (**197a**; Scheme 23), Goto et al. obtained the cis,trans-isomer **205** in a low op of 1.6%.[79] However, this op has been improved greatly up to 70% by employing the efficient sensitizers used in the photosensitization of cyclooctene described above.[294]

D. Photosensitized Cycloaddition/Dimerization

Until very recently, the enantiodifferentiating photosensitization has long been restricted to the unimolecular photochemical transformations as described above. However, some of these formally unimolecular enantiodifferentiating photoreactions are considered to proceed via diastereomeric exciplex intermediates, whether it is stated explicitly or not. In this context, the enantiodifferentiating *bimolecular* photoreaction should logically involve either the attack of yet another substrate molecule to the initially formed exciplex, or contact ion-pair intermediate, or the reaction within the ternary complex (triplex) [A···D···D$^{(\prime)}$] produced in the successive donor–acceptor interaction of an excited sensitizer (A) with two same or different substrate molecules (D and/or D′). The enantiodifferentiating [2 + 2] and [4 + 2] photocycloaddition/dimerizations hitherto reported are shown in Scheme 24.

Scheme 24. Photosensitized Cycloaddition

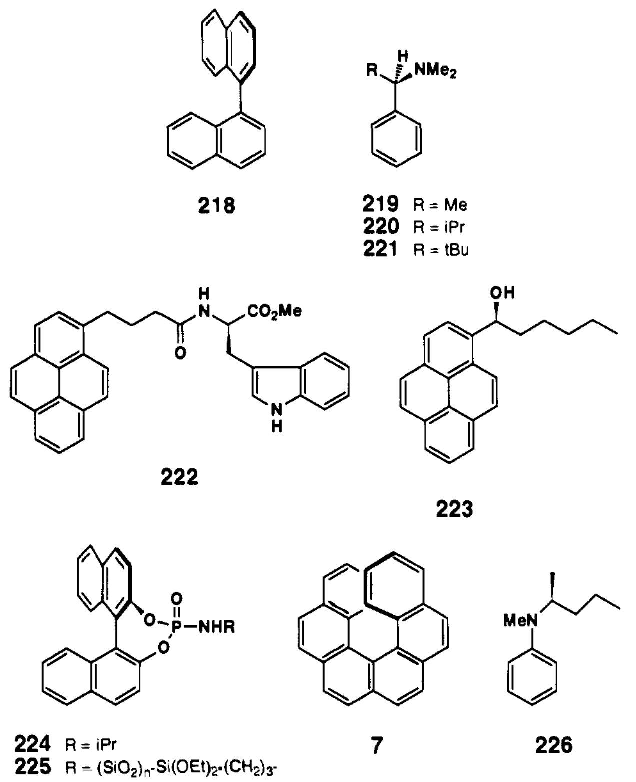


The enantiodifferentiating [2 + 2] photocyclodimerizations of aryl vinyl ethers **206** (X = H or Cl) or 4-methoxystyrene **209** were examined in the presence of some optically active naphthalenecarboxylates (**191**, **212**, **213**) to give the corresponding cyclodimers **207** and **208** or **210** and **211** in good chemical yields only in acetonitrile.[295] However, the optical purities of **208** (X = H) and the specific rotations of **208** (X = Cl) and **211** were extremely low: <1% and <0.2°, respectively. This result may be attributable to the participation of free monomer– and/or dimer–cation radicals and the operation of the quantum chain mechanism[296] in the cyclodimerization process in the polar solvent.

Although Vondenhof and Mattay[297] considered a possible enantiodifferentiating [2 + 2] and [4 + 2] photocycloaddition of 1,3-cyclohexadiene sensitized by several binaphthol derivatives, only a racemic mixture of chiral 1,1′-bis[6-cyano-2-[(trifluoromethyl(or *p*-tolyl)sulfonyl]naphthalene] was used as a sensitizer.

Kim and Schuster[84] reported the first successful enantiodifferentiating [4 + 2] photocycloaddition of *trans*-*β*-methylstyrene (**214**) with 1,3-cyclohexadiene (**215**) sensitized by (−)-1,1′-bis(2,4-dicyanonaphthalene) (**217**). The photochemical Diels–Alder reaction of electron-rich dienes to electron-rich dienophiles has been shown to proceed in the presence of electron-deficient arene sensitizers via triplex intermediates in nonpolar solvent,[298-300] which is a desirable condition for the enantiodifferentiation during the photoreaction. The enantiodifferentiating triplex photocycloaddition of **214** to **215**, sensitized by **217**, gave the cycloadduct **216** of 15% ee at −65 °C, 9% ee at −5 °C, and 1% ee at the room temperature in toluene.[84] In contrast, the photocycloaddition in acetonitrile afforded a low yield and no enantiodifferentiation. The fluorescence of the sensitizer **217** (λ_{max} 400 nm; τ 6 ns) was quenched by *trans*-*β*-methylstyrene (**214**) at the diffusion-controlled rate in toluene at room temperature, forming an exciplex that fluoresces at 470 nm (τ 26 ns). The exciplex formed was in turn quenched by the second donor **215** with a rate constant of 4×10^{-9} M^{-1} s^{-1}. Hence, the optically active product is deduced to arise from the triplex formation through selective capture of the diastereomeric exciplexes by **215**, although the attempts to detect

Chart 2. Compounds Used in Enantiodifferentiating Fluorescence Quenching or Excimer Formation



218

219 R = Me
220 R = iPr
221 R = tBu

222

223

224 R = iPr
225 R = (SiO$_2$)$_n$-Si(OEt)$_2$-(CH$_2$)$_3$-

7

226

the biexponential decay involving two diastereomeric exciplexes were unsuccessful presumably due to their trivial difference in lifetime.[84]

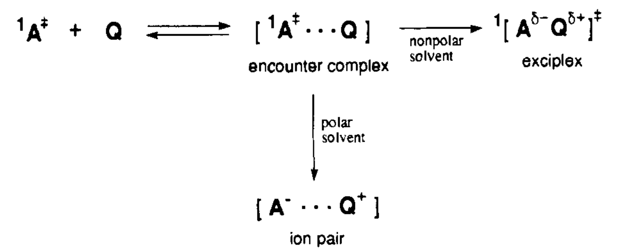
VIII. Enantiodifferentiating Fluorescence Quenching

We have seen that not only the reactivity of an excited state but also the fluorescence quenching behavior play the crucial roles in the enantiodifferentiating photosensitized reactions. In connection with the photosensitized enantiodifferentiation discussed above, it is interesting and useful to review briefly the enantiodifferentiation in the fluorescence quenching process.

Apart from the enantiodifferentiating phosphorescence quenching and redox reaction of the chiral ruthenium(II) complexes **162–164** described above,[272,275–277] some fluorophore-quencher pairs, shown in Chart 2, are known to constitute the enantiomer-differentiating fluorescence quenching systems that do not give rise to any photoreactions.

Irie et al.[301,302] investigated the enantiodifferentiating fluorescence quenching of (*R*)-1,1′-binaphthyl (**218**) with optically active, as well as racemic, *N*,*N*-dimethyl-α-alkylbenzylamines **219–221** possessing an α-substituent of varying bulkiness: R = Me, iPr, tBu. The relative quenching rate constant (k_S/k_R) was shown to be a critical function of the solvent polarity. Although no enantiodifferentiation was observed in acetonitrile for any of the chiral amines used, the k_S/k_R ratio dramatically increased with decreasing solvent polarity, affording the optimal values of 1.9, 2.7, and 4.0 in hexane at 22 °C for **219**, **220**, and **221**, respectively. They proposed a general scheme for the fluorescence quenching process. As shown in Scheme 25, an excited binaphthyl ($^1A^*$) and a ground-state amine (Q) are thought to be in equilibrium with an encounter complex [$^1A^*\cdots Q$] and no quenching is supposed to occur at this stage. The actual quenching takes place in the subsequent process producing an ion pair [$A^-\cdots Q^+$] in polar solvents or a singlet exciplex $^1[A^{\delta-}\cdots Q^{\delta+}]^*$ in nonpolar solvents.[302] In acetonitrile, the dominant ion-pair path via the electron transfer is very fast ($\sim 1.3 \times 10^{10}$ M^{-1} s^{-1}) and produces a free or solvent-separated ion pair, so that no chiral recognition is expected to occur during the electron-transfer process. In nonpolar solvent, where the decay path to ion pair is not available in general, the alternative exciplex path via the partial charge transfer is at least 1 order of magnitude slower than the diffusion and the two components are located in a close distance within the exciplex. Hence, the fluorescence quenching becomes sufficiently enantiodifferentiating to form a diastereomeric exciplex pair of the *R*–*R* and *R*–*S* combinations, which are different in energy and configuration. They further examined the temperature dependence of the relative rate constant (k_S/k_R) at 22 to −10 °C to give the highest k_S/k_R values of 2.9, 4.7, and 7.9 at −10 °C for **219**, **220**, and **221**, respectively. The differential enthalpy change of activation ($\Delta\Delta H^*$) for the *R*–*R* and *R*–*S* combinations increased from 2.0 for **219** to 3.4 kcal/mol for **221**, while the differential entropy change of activation ($\Delta\Delta S^*$) compensated the change in $\Delta\Delta H^*$ to some degree. The isokinetic temperature of 420 K, at which the k_S/k_R ratio becomes unity, was calculated from the plot of $\Delta\Delta H^*$ versus $\Delta\Delta S^*$.[302]

Scheme 25. Fluorescence Quenching Mechanism



Substantial enantiomer differentiation in the excimer formation was reported for pyrene derivatives. Pyrene is well known to form a face-to-face dimer in the excited singlet state at the concentrations higher than 10^{-4} M.[303,304] Using the steady-state and time-resolved spectroscopy, Tran and Fendler[305] determined the parameters for the excimer formation and dissociation of the pyrene derivative **222** (Chart 2). For **222**, which carries a D- or L-tryptophan moiety in the side chain, no intramolecular exciplex formation between the pyrene and indole moieties was observed and only the intermolecular pyrene–pyrene excimer was shown to be formed. The observed rate constant for the excimer formation of the pure D- or L-enantiomer (4.0×10^9 M^{-1} s^{-1}) is somewhat smaller than that for the racemic mixture (6.9×10^9 M^{-1} s^{-1}), while the quantum efficiency of the excimer fluorescence relative to that of monomer is larger for the pure enantiomer than for the racemic mixture. These results indicate the stronger interaction between the complimentary D/L, rather than D/D or L/L, pair. They also demonstrated that the excimer formation of the pure D-enantiomer is differentiated to a smaller extent in an optically active solvent, (*R*)- or (*S*)-2-octanol, through the formation of a hydrogen-bonded diastereomeric fluorophore-solvent complex.[305]

Brittain, Fendler, and co-workers[306] employed the circularly polarized fluorescence spectroscopy[131,307] as a method for investigating the excimer structure of optically active pyrene derivative **223** (Chart 2). Dramatically enhanced optical activities associated with the excimer formation of (+)- or (−)-**223** were observed at the excimer emission region. The observed fluorescence anisotropy factor (g^*) critically depends on the concentration of **223**, displaying a sudden evolution around 10^{-4} M and subsequent drastic growth at the higher concentrations. Since the g^* factors for monomeric chiral aromatics are known to zero,[307] the evolution of the g^* factor associated with the excimer formation of **223** indicates that the excimer formed is highly optically active and has a definite preferred orientation of the pyrene rings.

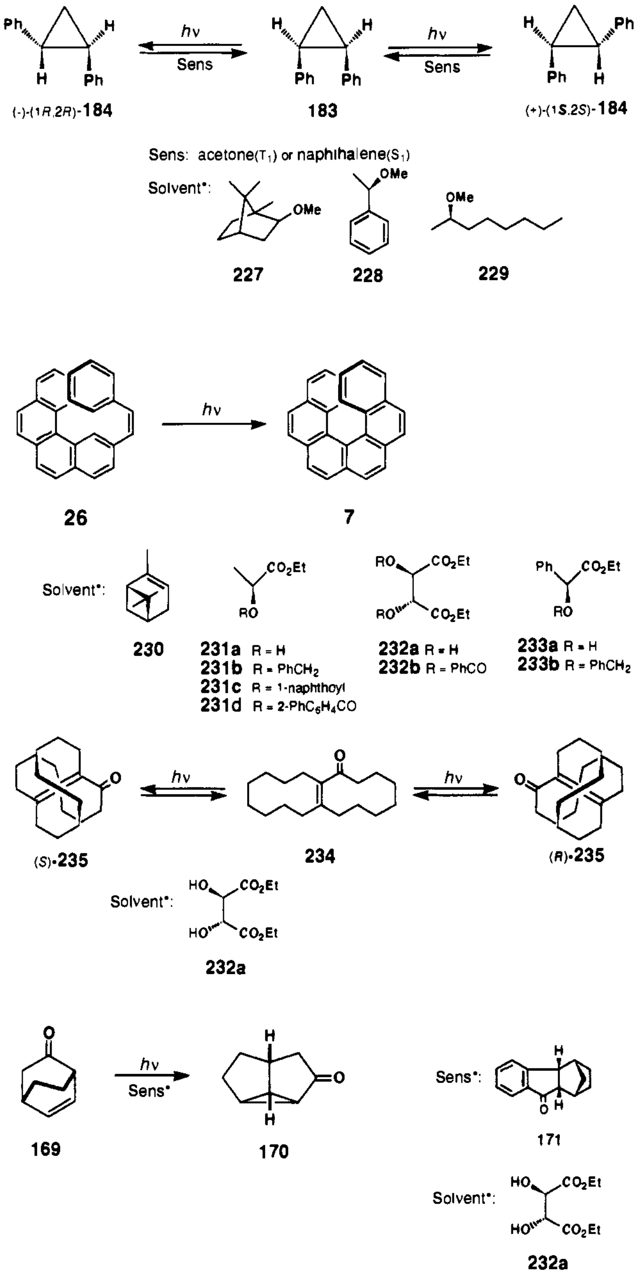
A recent report from Ottolenghi's group[308] revealed that, differing from the Irie's binaphthyl case,[301] no enantiodifferentiation occurs upon the fluorescence quenching of (*R*)-1,1′-binaphthyl 2,2′-dihydrogen phosphate **224** with (*R*)- and (*S*)-phenethylamine **219** (Chart 2) in a toluene solution, although the enantiomers of chiral amine **219** are moderately differentiated on the silica surface modified with the related binaphthyl derivative **225**; $k_S/k_R = 1.3$ in hexane slurry; $k_S/k_R = 1.0$ in methanol slurry.

The enantiodifferentiating fluorescence quenching of optically active hexahelicene (**7**) with (*S*)-*N*-methyl-*N*-(1-methylbutyl)aniline (**226**; Chart 2) was attempted by Rau and Totter.[309] Although the competing exciplex and ion-pair quenchings (Scheme 25) were shown to occur in highly polar solvents like alcohol or acetonitrile, no quenching was observed in less polar solvents and the enantiodifferentiation upon fluorescence quenching was negligible in the polar solvents.

As first indicated by Irie et al.[302] and subsequently demonstrated by other workers, the fluorescence quenching via exciplex path is the essential condition for appreciable enantiodifferentiation, which takes precedence over any other steric and electronic fluorophore–quencher interactions in the excited state.

The enantiodifferentiating fluorescence quenching technique has been used as a tool for elucidating the chiral recognition in crown ethers by Tundo and Fendler.[310]

Scheme 26. Asymmetric Induction in Chiral Solvent



IX. Asymmetric Induction in Chiral Solvent

This category is closely related to and sometimes hard to be distinguished from the asymmetric induction by selectively complexing chiral agents discussed in section VI. In this review, the discrimination was made based on a tentative criterion whether the chiral solvent plays an active role as an electron or hydrogen/proton donor in the enantiodifferentiating step(s) (section VI) or just behaves as passive chiral environment even if weak hydrogen bonding is supposed to be involved (this section). Photochemical reactions performed in optically active solvents are summarized in Scheme 26.

Weiss et al.[311] examined the sensitized cis–trans photoisomerization of 1,2-diphenylcyclopropane (**183**), a bench-mark test compound in the asymmetric photosensitization (section VII), in some optically active solvents. The triplet and singlet sensitization with acetone (T_1) and naphthalene (S_1) were performed in chiral solvents **227**–**229** to give no detectable optical rotation in the isolated *trans*-**184**.

More positive results were reported by Laarhoven and Cuppen.[312,313] The direct irradiations of 1-(2-benzo[*c*]phenanthryl)-2-phenylethylene (**26**) in the presence of iodine in a variety of optically active solvents **230**–**233** gave optically active hexahelicene (**7**). The product's op ranges from 0.2 to 2.1%, depending on the solvent used; the best op (2.1%) was obtained with (*S*)-ethyl mandelate (**233a**), while the irradiation in (*R*,*R*)-diethyl tartrate (**232a**) afforded **7** of 1.1% op. These op's are much greater than those obtained in the direct excitation of **26** with CPL. Since the dilution with benzene led to a proportional decrease in op, no specific solute–solvent interaction other than the van der Waals interaction is involved in the differentiation process.

Nakazaki et al.[314,315] investigated the direct cis–trans photoisomerization of (*Z*)-bicyclo[8.8.0]octadec-1(10)-en-2-one (**234**) in (*R*,*R*)-diethyl tartrate (**232a**) to give a 1:7 *Z*–*E* mixture of **234** and **235** at the pss. The isolated

(*E*)-isomer **235**, which may be called [8.8]betweenanen-2-one,[316] was shown to be optically active: $[\alpha]^{24}_D$ −13°. They estimated the product's op as 0.5–1.0% by comparing the specific rotation ($[\alpha]^{24}_D$ −2.3°) of the corresponding hydrocarbon, [8.8]betweenanene, derived from the Wolff–Kishner reduction of the obtained "*trans*"-**235** with that of the structurally related *trans*-cyclooctene ($[\alpha]^{25}_D$ −426°).[317]

In a review,[318] Demuth and Schaffner briefly stated the dual chiral induction system, in which both sensitizer and solvent are optically active. The oxa-di-π-methane rearrangement of racemic bicyclooctenone **169** sensitized by optically active indanone **171** was performed in (*R*,*R*)-diethyl tartrate (**232a**) to give an op of 12%,[318] which is comparable with that (10%) obtained in achiral ethyl acetate at −78 °C, described in their earlier work.[80]

X. Discussion

In his previous review,[3] Rau declared a decade ago that, as compared with its thermal counterpart, the asymmetric photochemistry is but a narrow field; he even deplored that the limited enantioselectivity seems to be a basic feature of the asymmetric photochemistry. But the situation has changed dramatically in these 10 years. As we have seen in the preceding sections, the area of the asymmetric photochemistry in solution, as well as that in the solid state and organized assemblies, has been expanding quite rapidly in the recent years. The optical yields have also been improved greatly in several categories of the asymmetric photochemistry. Some unprecedented findings enable us to utilize novel strategies for controlling the enantiodifferentiating photochemical reactions, or more practically for enhancing the optical yield.

One of such findings is the anomalous enhancement of the absorption anisotropy (*g*) factors observed upon two-photon CPL excitation by a high-intensity, short-pulse laser (section IV.A).[69,70] This is quite impressive in view of the extensive efforts which have continued for 60 years since Kuhn's day in order to find a chiral compound of higher *g* factor. Although the detailed mechanism is not necessarily clear at present, the *g* factor was enhanced by 2 orders of magnitude.[70] A plausible explanation is the much larger *g* factor for the first excited state, since smaller ϵ and larger $\Delta\epsilon$ would be anticipated for the excited-state molecule which possesses a spatially dispersed distribution of the antibonding electrons as compared to the ground-state molecule. Another possibility is the cumulative anisotropy effect in both ground and excited states in the same direction; if so, the multiphoton ionization through the excitation with a high-intensity laser would be much more effective. In any event, further verifications and mechanistic elucidation of this phenomenon should be executed using a variety of chiral compounds with high original *g* factors.

It is however inevitable that the anisotropy factor still plays the definitive role in the direct asymmetric photochemistry with CPL even in the two-photon process. Then, the search for high *g* molecules or molecular systems will continue. A simple guideline for high *g* is to inspect compounds possessing a low ϵ transition. The n,π^* transition of ketones, which satisfies this criterion ($\epsilon < 100$ M^{-1} cm^{-1}; $g \sim 0.3$), has been examined and gave partial success (section IV.A). Other possible candidates in this line include the n,σ^* transition of oxygen and nitrogen compounds, the spin-forbidden S_0–T_1 transition of extremely low ϵ ($\ll 1$ M^{-1} cm^{-1}), and the charge-transfer band of weakly interacting donor–acceptor pairs such as oxygen complexes of organic compounds. The CD Cotton effect induced by the exciton coupling and its temperature dependence[319] may also be used to enhance the *g* factor.

In the direct asymmetric photochemistry, the choice of wavelength and bandwidth of CPL radiation used is also crucial. In the earlier studies, CPL of fairly broad bandwidth was used, so that the *g* factor has to be averaged over the entire irradiation wavelength and often becomes smaller than the peak value.[67,68,216] High-intensity excimer laser is a desirable monochromatic light source for the direct asymmetric photochemistry with CPL, but the available wavelengths are discrete and difficult to tune into the desired wavelength at which the *g* factor is optimized. Recently, Onuki et al. proposed[320] and later constructed indeed[321,322] a novel polarizing undulator with crossed and retarded magnetic fields, which was installed in the electron storage ring of a synchrotron radiation facility. This helical undulator can produce high-intensity circularly polarized radiation of variable wavelength and fairly narrow band, and therefore be best suited as a CPL source for the direct asymmetric photochemistry.[323]

In the asymmetric photosensitization of cyclooctene **195** (Scheme 23, second example),[82,83,293] we have seen another apparently striking phenomenon that, just by changing irradiation temperature, the direction of product's optical rotation is inverted at the equipodal temperature (T_0), above which the product's op increases with the temperature. Thus, the op can be improved through an apparently paradoxical approach of raising temperature. Although essentially no systematic investigation of the temperature effect upon the enantiodifferentiating photoreactions had been made until 1989, the fragmental evidence available at that time appeared to support our tacit understanding that lowering temperature leads in general to higher optical yield, as is still the case with the asymmetric ground-state chemistry. However, this is not a logical consequence.

The Arrhenius and Eyring treatments of the enantiodifferentiating photochemical reaction as independent parallel processes of or to each enantiomer lead to the following equation for the relative rate constant:

$$\ln (k_S/k_R) = -\Delta E_{S-R}/RT + \ln (A_S/A_R) = -\Delta\Delta H^{\ddagger}_{S-R}/RT + \Delta\Delta S^{\ddagger}_{S-R}/R \quad (10)$$

where ΔE_{S-R}, $\Delta\Delta H^{\ddagger}_{S-R}$, and $\Delta\Delta S^{\ddagger}_{S-R}$ refer to the differential activation energy, enthalpy, and entropy, respectively, while A_S/A_R stands for the relative frequency factor. The activation parameters reported for the enantiodifferentiating photoisomerization of cyclooctene (**195**) (Table 6) clearly indicate that the switching of the product chirality originates from the unequal frequency factor ($A_S/A_R \neq 1$) or, synonymously, the nonzero differential entropy of activation ($\Delta\Delta S^{\ddagger}_{S-R} \neq 0$).[293] Equation 10 indicates that the relative rate constant, or the product's op, is governed predominantly by the enthalpy factor at low temperatures, whereas the entropy factor dominates at high temperatures. Hence, when the differential activation entropy ($\Delta\Delta S^{\ddagger}_{S-R}$) has a significant value, the temperature switching of the product chirality is the logical consequence.

In the actual case of the photosensitized isomerization of cyclooctene, the observed $\Delta\Delta H^{\ddagger}_{S-R}$ and $\Delta\Delta S^{\ddagger}_{S-R}$ values, bearing the same sign, cancel each other to give no enantiodifferentiation at the equipodal temperature, which is characteristic of the chiral sensitizer used. Usually, the deviation of A_S/A_R from unity, or the entropic contribution ($\Delta\Delta S^{\ddagger}_{S-R}$), is thought to be trivial in most photochemical, as well as thermal, reactions, as is the case with the photosensitizations with benzoate **197** and terephthalate **200** (Table 6). Since the exceptionally high op and the unique temperature-switching behavior have been observed only with the congested *o*-benzenepolycarboxylates like **201** and **202**, the substantial structural change during the rate-determining geometrical isomerization within the exciplex intermediate is thought to be responsible for the substantial deviation of the A_S/A_R ratio from unity.[293]

This explanation sounds plausible in view of the fact that the highly congested benzenehexacarboxylates **202** exhibit steric hindrance-induced dual fluorescence that is caused by the restricted rotational relaxation of the adjacent bulky *o*-alkoxycarbonyl groups in the excited state.[324] It is likely that a similar situation is encountered in the photosensitization with benzenepolycarboxylates. Thus, the enantiodifferentiating rotational relaxation of cyclooctene moiety in the exciplex experiences severe steric hindrance caused by the chiral alkoxycarbonyl group(s) of the sensitizer, enforcing a synchronized motion of both components. This in turn leads to the global structural changes within the exciplex, producing a large entropy difference between the diastereomeric transition states. This strategy to induce dynamic structural changes in the exciplex intermediate may also be applicable to the other enantiodifferentiating photosensitizations as a working hypothesis for higher op, as far as not the excitation but the decay process is enantiodifferentiating.

As discussed above, the temperature switching of product chirality is not only the theoretical consequence of eq 10 but also observed indeed within the actual experimental temperature range. This warns us that *we cannot necessarily deduce the preferred diastereomeric transition state or the favorable reaction path merely from the enthalpic contribution evaluated by the steric hindrance considerations using molecular models*, although such kinds of illustrations may be found amply in the literatures. Instead, especially in the temperature region above T_0, we should give priority to the major entropic, over enthalpic, contributions arising from the changes in the substrate conformation and the solvent coordination.

The unfavorable effect of polar solvents observed in the photosensitized enantiodifferentiating isomerization and cycloaddition/dimerization reactions may provide us with useful general instructions: the highly enantiodifferentiating photosensitization should involve (a) singlet, rather than triplet, excited state, (b) exciplex, rather than free or solvent-separated ion-pair, intermediate, and (c) no quantum chain mechanism.

The "inversion" temperature, found in the Paternò–Büchi reaction of chiral phenylglyoxylates **66** with cyclic olefins **77** (section V.C; Scheme 9),[242] does not indicate the inversion of product chirality, but means the inversion of the sign of slope in the Eyring plot, which originates from the switching of the dominant diastereodifferentiation mechanism involved in the low- and high-temperature regions. In most of these photoreactions, the inversion temperature, though mechanistically interesting, is phenomenally preventing the product's de from further augmentation beyond this critical point. A key observation to break this dilemma may be found in the high de of >95% obtained in the Paternò–Büchi reactions of the highly bulky alkyl phenylglyoxylate with various olefins at room temperature (Table 4).[112-114] This is probably achieved by raising the energy level of the 1,4-biradical intermediate through introduction of the highly bulky group as a chiral auxiliary.

An alternative approach to high product op's may be found in the asymmetric induction through the diastereomeric complexation of the excited state or reactive intermediate derived therefrom with a chiral template (section VI). A fairly reliable strategy for high op has been developed recently for the enantiodifferentiating photodeconjugation of α,β-unsaturated ketones with chiral α-amino alcohols.[127,128] Although this particular chiral template does not appear to be applicable in general to the other systems, we may extend this idea to the enantiodifferentiating photosensitization, in which the substrate and the sensitizer interact more intimately through not only the steric effect but also the hydrogen bonding, as is the case in the enzymatic system. In this context, the enantiodifferentiating photochemical or photochemically-induced reactions in the chiral polymer matrix,[146] peptide,[325,326] and DNA[147,327] may be interesting as models of the site-specific interaction.

XI. Conclusions

In conclusion, the direct asymmetric photochemistry with CPL, being restricted in principle by the Kuhn's g factor, is not for the synthetic purpose at present, but it provides us with a convenient and irreplaceable tool for evaluating the molar ellipticity or g factor of the difficult-to-resolve sort of compounds (section IV). However, the anomalous enhancement of the g factor upon two-photon excitation would open a new frontier of the direct asymmetric photochemistry with CPL, provided that its scope and limitations were manifested with various chiral substrates. On the contrary, a high level of asymmetric induction up to 95% de has been achieved in several diastereodifferentiating photoreactions of the substrates possessing chemically bonded chiral auxiliaries. Nevertheless, from the viewpoint of chiral-source efficiency, the asymmetric photosensitization and the use of chiral complexing agents in the photochemical and/or subsequent thermal processes are the most promising strategies. However, we have only recently found some clues to the highly enantiodifferentiating photoreactions in these two areas of the asymmetric photochemistry, as discussed above. Further mechanistic and synthetic efforts have to be devoted to the investigations in these fields for the comprehensive understanding of the differentiation mechanism as well as the expansion of the scope of the enantiodifferentiating photoreactions.

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