Asymmetric Photochemistry in Solution

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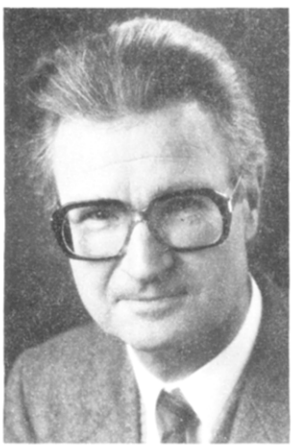
Contents



Hermann Rau is professor and head of the section of Physical Chemistry at the Institute of Chemistry of the University of Hohenheim in Stuttgart, West Germany. He earned his Diploma (1961) and his Ph.D. (1964) at Tübingen University working with Gustav Kortüm on the problem of determination of the complex dielectric constant of water and electrolyte solutions in the microwave region. He was Research Assistant Professor with Leroy Augenstein in Biophysics at Michigan State University, East Lansing, MI, in 1964–1965 and studied emission properties of aromatic amino acids. He returned to G. Kortüm at Tübingen University and received his Habilitation in 1970, became a Dozent in 1971, and joined Hohenheim University in the same year. His research interests are spectroscopy and photochemistry of azo compounds, light-induced electron transfer in microheterogeneous systems, and asymmetric photochemistry.

I. Introduction and Scope

Optically active molecules are abundant in nature. In fact, the nearly exclusive utilization of one form of the optical antipode pair may be considered to be a characteristic feature of living systems. Optical activity has always stimulated the chemist's imagination, the substitution and modification of natural products is not only a challenge but also of high practical importance.

Up to now photochemistry has not become important for industrial mass production of chemicals. But it has its firm stand in laboratory synthesis, in kinetic and mechanistic work, and in the development of general concepts. Asymmetric photochemistry unites the problems and potentials of enantioselective thermal chemistry and photochemistry. This review article on asymmetric photochemistry has been written under the aspects of optical yield, kinetics, and mechanism.

The scope of this review is asymmetric photochemistry in solution where the chiral information is not provided by a solid environment. A short survey has been given in 1978 in a general context on asymmetric synthesis.[1a] Photoreactions in chiral crystals have been reviewed recently.[1b] However, the influence of chiral solvents and in a few examples the influence of chiral substituents on the creation of new chirality in a photoreaction has been included.

Work in the field of asymmetric photochemistry has been intensified only in the past 2 decades. Although already Le Bel[2] and van t'Hoff[3] have realized the potential of circularly polarized light in the last century it was not until 1929 that W. Kuhn provided the experimental proof and the kinetic treatment of an asymmetric photoreaction.[4] In 1965 Hammond and Cole published the first example of an asymmetrically sensitized reaction.[5] Since then, stimulated by the availability of new spectropolarimeters, the field is ex-

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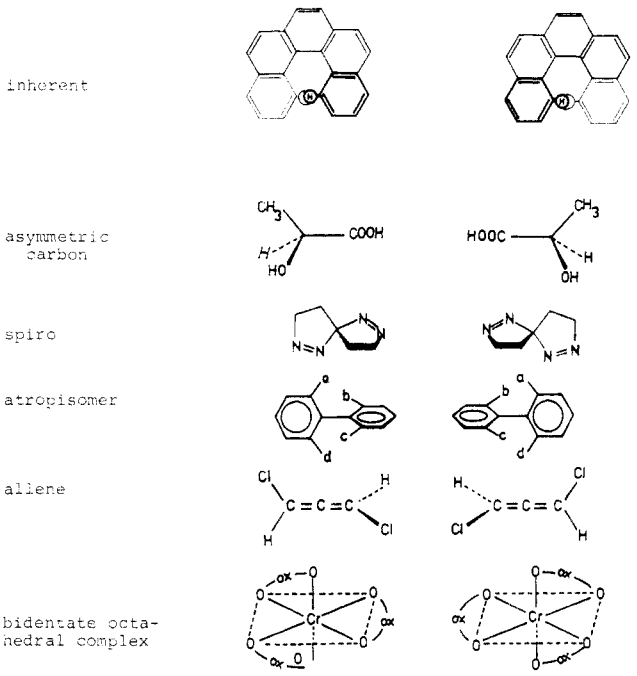


Figure 1. Some chiral structures.

panding. In this review the literature is covered until early 1982.

II. Fundamentals and Definitions

A. Chirality and Diastereomerism

Chirality of a molecule is a symmetry property: chiral molecules are either asymmetric, i.e., they do not have any symmetry element (point group C_1) or they are dissymmetric, i.e., they have only axes of rotation (point groups C_n and D_n). In this article there will be no discrimination of asymmetry and dissymmetry as this is insignificant for asymmetric photochemistry.

If the symmetry operation of reflection is performed with a chiral molecule this is transformed into a different chiral system of equal energy and other nonvectorial properties. This new molecule is called the mirror image, the optical antipode, or the enantiomer. Molecular systems that show chirality have an obvious or hidden screw property, a handedness. Some prototypical structures of chiral molecules are collected in Figure 1.

The simplest asymmetric unit comprises four different elements in a nonplanar configuration, and the asymmetric carbon atom bearing four different substituents is the most common realization of that model. The nomenclature now generally accepted to characterize the configuration at an asymmetric C atom is the R and S notation of Cahn–Ingold–Prelog.[6]

Laboratory procedures normally give a 1:1 mixture of the enantiomers, called the racemic mixture. In normal preparative chemistry neither right nor left is privileged. Moreover, a solution of pure enantiomers is thermodynamically unstable. There is a driving force for racemization, for forming the 1:1 mixture: $\Delta G = \Delta H - T\Delta dS$. As, however, the heats of formation of both enantiomers are identical (only the sign of bond angles is different) racemization is purely an entropy driven reaction, and it is essentially the entropy of mixing that is important. Separation of enantiomers, called optical resolution, requires the work of $T\Delta S$ and it can be only successful if the enantiomers have a high activation energy of interconversion, i.e., if they are kinetically stable.

TABLE I. Chiroptical Constants[a]

ORD
instrument reading: angle of rotation α
$\alpha = 180(d/\lambda)(n_l - n_r)$ [deg] (d and λ in cm)
specific rotation
$[\alpha] = \alpha/(dc')$ [deg cm^3 g^{-1} dm^{-1}] (d in dm; c' in g/cm^3)
molar rotation $[\psi]$
$[\psi] = 100\alpha/(dc)$ [deg cm^2 dmol^{-1}] (d in cm; c in M)
CD
instrument reading: ellipticity θ
$\theta = cd \ln [10(\epsilon_l - \epsilon_r)]/4$ [deg] (d in cm; c in M)
molar ellipticity $[\theta]$
$[\theta] = 100\theta/(dc)$
$= 3300\ (\epsilon_l - \epsilon_r)$ [deg cm^2 dmol^{-1}] (d in cm; c in M)

[a] d = cell length, c = concentration in M, c' = concentration in g cm^{-3}, n = refractive index, ϵ = absorption coefficient in M^{-1} cm^{-1}, λ = wavelength of analyzing light.

In solution the individual enantiomers cannot be discriminated as in crystals by means of X-ray analysis. What is needed is a probe that interacts differently with both enantiomers. This probe must recognize the handedness and therefore must have a handedness of its own that is known. The difference of interaction of a pair of enantiomers with a probing system is rationalized in the principle of diastereomerism. The two interacting enantiomer/probe couples are called diastereomers. Because of the different interactions of probe and R or S enantiomers the diastereomers differ in energy and are distinguished by normal procedures of molecular analysis. The discrimination of enantiomers, which is often called "chiral recognition" or "chiral discrimination",[7] may be very pronounced as, e.g., in enzyme–substrate complexes, or poorly defined as in many chemical reactions.

B. Circularly Polarized Light and Chiroptical Constants

The most important probe for identification of the enantiomers is circularly polarized light (cpl).[8] It is from this that chirality, a symmetry property, is often identified with optical activity, a spectroscopic property, in a sort of relaxed use of terms.

Optical activity of molecules in solution is detected and quantified by the different interactions of one enantiomer with l- and r-cpl. The difference in interactions is characterized by the optical rotatory dispersion (ORD), derived from the rotation of the plane of linearly polarized light by the active sample and by the circular dichroism (CD). The relations of ORD and the refractive indices and of CD and the absorption coefficients are stated in Table I. The same ORD and CD effects are observed if the R and S enantiomers interact with one kind of cpl. ORD and CD are wavelength dependent and related to the UV spectrum but in contrast to absorption they may be positive or negative (Figure 2). ORD and CD spectra contain the same information and can be interconverted by means of the Kramers–Kronig relation.[8]

In order to determine the molar ellipticity or rotation the pure enantiomer usually is isolated. Residual concentration of the other enantiomer does not change the shape of the CD spectrum but the CD values. There

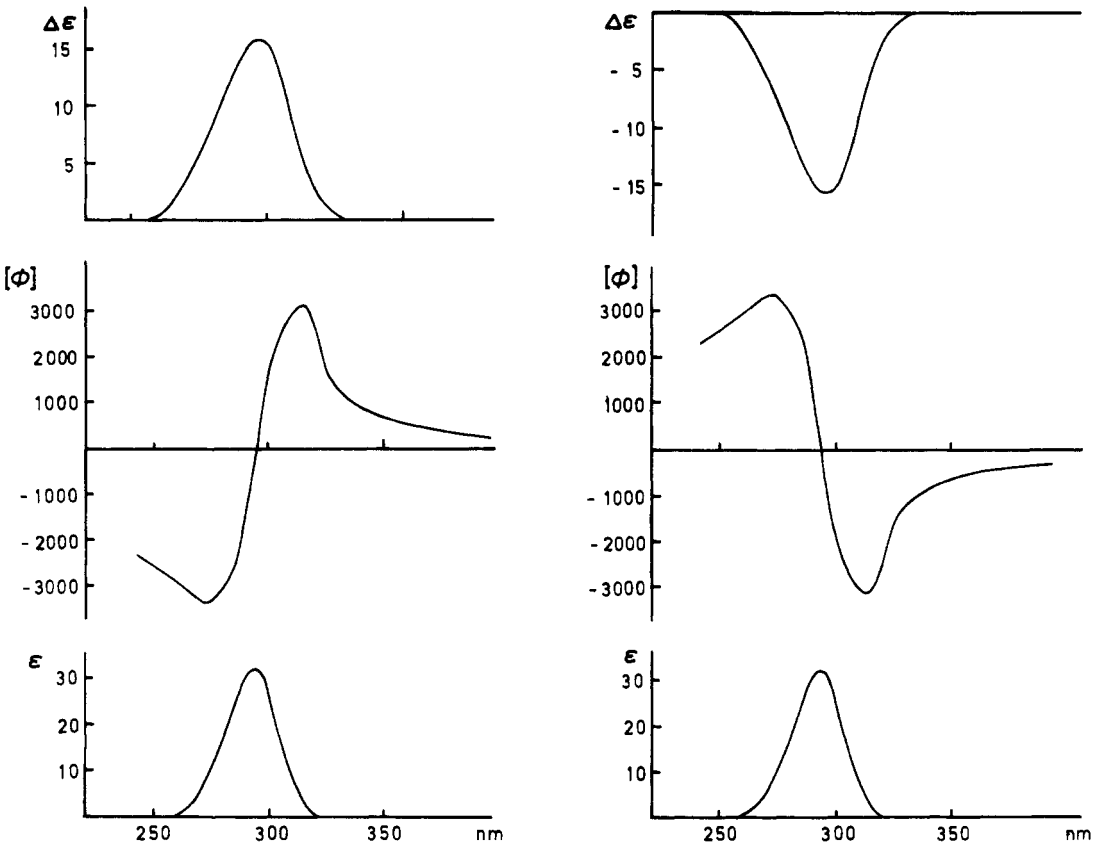


Figure 2. ORD, CD, and UV spectra of the enantiomers of (+)- and (−)-camphor.

are many examples in the literature of compounds whose $[\theta]$ or $[\alpha]$ values have increased from paper to paper published just because resolution techniques improved with time. On the other hand with $[\theta]$ or $[\alpha]$ known for the pure enantiomer the purity of an optically active sample can be calculated in terms of what is called optical purity (op), enantiomeric purity (P_{en}) or enantiomeric excess (e.e.)

$$P_{en} = 100\frac{c_R - c_S}{c_R + c_S} = 100\frac{\theta}{[\theta]}\frac{100}{c_R + c_S} = 100\frac{[\theta]^*}{[\theta]}\% \quad (1)$$

with $[\theta]^*$ being the apparent molar ellipticity (viz. Table I).

The close relation of optical activity with electronic excitation is obvious from Figure 2. The combined ORD and CD phenomena of an electron transition are called a Cotton effect. The sheer value of molar ellipticity, however, is not the best way to characterize the optical activity as the strength of the corresponding electronic transition is not taken into account. Therefore the relative CD value called anisotropy or g factor has been defined by W. Kuhn[9]

$$g = \frac{(n_l - n_r)}{n - 1} = \frac{(\epsilon_l - \epsilon_r)}{\epsilon} = \frac{\Delta\epsilon}{\epsilon} \quad (2)$$

Optical activity is a relatively small effect compared to absorption: generally g factors are less than 10^{-2}. This is important for photochemistry.

C. Asymmetric Photochemistry

1. Direct Asymmetric Photochemistry

The use of cpl closely mimics that of nonpolarized light (npl). Both kinds of radiation are useful for spectroscopy at low intensities and both can be used to induce photoreactions at high intensities. No asymmetry is observed in the photochemistry of a racemic mixture of optically active molecules on irradiation with npl. However, if a racemic mixture of enantiomers is irradiated by either r- or l-cpl the enantiomers will behave differently. In fact, one realizes diastereomerism in the system.

What is this difference in behavior? It is the different absorption of the enantiomers. In photochemistry different absorption means different reaction rates and so the chiral information in the irradiating light is transformed into a chiral information of the solution, expressed in terms of the concentrations of the enantiomers. This will be carried out later.

2. Sensitized Asymmetric Photochemistry

In sensitized photochemistry energy or an electron is transferred between the sensitizer and the reacting acceptor which form a loosely coupled system for some time. Asymmetry can be induced by use of a chiral sensitizer molecule. Again diastereomerism is introduced into the system leading to different transfer rates and, consequently, reaction rates.

3. Asymmetric Photochemistry vs. Photochemistry of Chiral Molecules

Pure enantiomeric solutions may be irradiated by normal light. The enantiomers will react and the optical activity will change. In many cases no optical activity is induced by the reaction itself; this is photochemistry of an optically active molecule, not asymmetric chemistry. This reaction system, however, has gained practical importance for the elucidation of reaction mechanisms. The transfer of optical activity

from educt to product gives information on the configurational stability of possible intermediates. This information can also be drawn from true asymmetric photoreactions; we shall present an example later.

Asymmetric photochemistry to our understanding are photoreactions by which new optical activity is created (asymmetric induction). This may lead to partial or total photochemical resolution of a racemate or to formation of new chirality centers. This means that the enantiomers of chiral molecules react at different rates or that the reactions of chiral and prochiral molecules lead to new enantiomers at different rates. So the asymmetry of a photoreaction is based on the competition of the enantiomers and this suggests kinetic treatment according to

$$R \text{ enantiomer} \xrightarrow{k_R} \text{products}$$

$$S \text{ enantiomer} \xrightarrow{k_S} \text{products} \qquad (3)$$

The asymmetry of the reaction is defined by

$$\kappa = k_S/k_R \qquad (4)$$

4. Experimental Techniques

There are basically two ways to obtain information about the asymmetry of a photoreaction. The same reaction is conducted consecutively with the R and S enantiomers and the same mode of excitation (e.g., r-cpl) or with one enantiomer and the two different modes of excitation. The ratio of suitable reaction data determined in these separate reactions may be used to characterize the asymmetry of the reaction. Alternatively, an optically inactive racemic mixture is used and a simultaneous reaction of both the enantiomers is induced by one mode of excitation. The asymmetry is determined directly by use of a suitable property of the system.

The second option is to be preferred if possible as the optical activity emerges from a zero background, and small asymmetries may be registered. The method of separate reactions requires large effects and pure enantiomers. The resolution of racemic mixtures has only lately become more convenient by the use of chromatographic methods and chiral stationary phases.

III. Monomolecular Reactions: Direct Asymmetric Photochemistry

A. General Remarks

Asymmetry can be induced in a reaction system of chiral molecules by intense cpl. If, say, the R enantiomer should absorb r-cpl more strongly than the S form of the molecule does, and if one were to look at the fluorescence of the two enantiomeric forms in separate experiments then the fluorescence intensity of the R enantiomer would be higher on r-cpl excitation than the fluorescence of the S enantiomer and vice versa. The information contained in the asymmetry of the exciting light is transformed into a difference in the number or concentration of excited R and S molecules.

The same experiment done with the racemic 1:1 mixture would not show any change of fluorescence intensity when the sense of the cpl is inverted, as the total of excited molecules stays constant. For this photophysical process we needed a chiral probe for the excited state in order to detect the difference in the concentration of excited R and S molecules, and it is the degree of circular polarization of the fluorescence that might serve as such a probe.

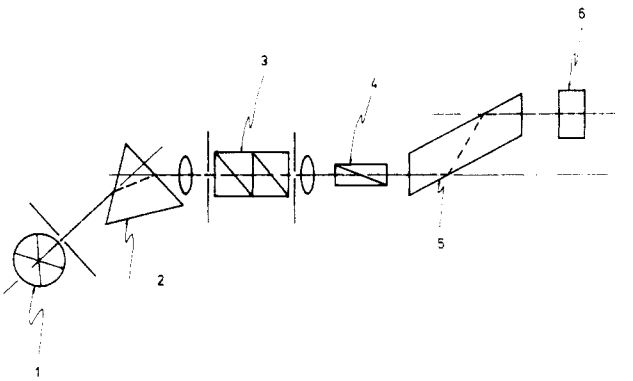


Figure 3. Experimental setup for direct asymmetric photochemistry: (1) irradiation source, (2) predispersion (eliminates IR and much of UV/VIS), (3) monochromator, (4) linear polarizer in 45° position to 5, (5) Fresnel rhomb, (6) sample cell.

If, however, excited molecules are leaving the excitation—deactivation cycle of the racemic mixture by taking part in a chemical reaction, a difference in R and S forms of the educt will develop as a consequence of the different concentration of excited enantiomers. Depending on the reaction mechanism the product may also contribute to the emerging optical activity of the reaction mixture. Here the advantage of the use of CD as an analytical tool compared to the use of ORD becomes obvious. Usually in CD there can be found a spectral region that is characteristic for only one molecular species whereas the ORD spectra are a superposition of the individual spectra at all wavelengths. The kinetic analysis of these asymmetric photoreactions treats the system as one of two independent parallel reactions of the R and S forms as has been mentioned earlier.

The experimental setup is shown in Figure 3.[10] If the irradiation is to be made with reasonably narrow bandwidths at arbitrarily selected wavelengths then a very intense arc lamp (e.g., 1600-W Xenon) is required. A predispersion system is recommended in order to keep most of the irradiation energy off the monochromator which might be damaged in long-term experiments. A Fresnel rhomb should be used in broad-band irradiation experiments. Its polarization is weakly dependent on wavelength in contrast to a quarter wavelength device.

B. Types of Asymmetric Photoreactions

Photochemists have observed several types of asymmetric monomolecular reactions:[17d] photoenantiomerization, asymmetric photosynthesis, and asymmetric photodestruction.

1. Photoenantiomerization

The reaction of photoenantiomerization is represented by the reaction scheme

$$R \underset{h\nu,\, k_{-1}}{\overset{h\nu,\, k_1}{\rightleftharpoons}} S \qquad (5)$$

There are few examples reported in the literature: the octahedral transition-metal complexes with bidentate

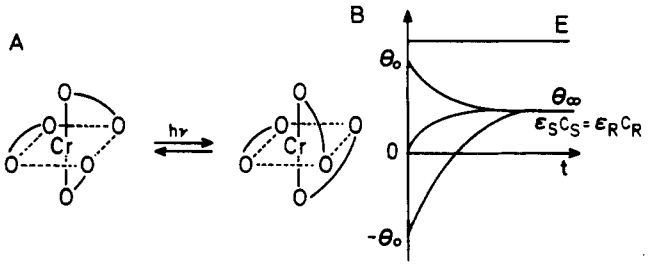


Figure 4. (A) Photoenantiomerization of the $Cr(ox)_3^{3-}$ ion. (B) Time development of ellipticity and absorbance in photoenantiomerization.

ligands $Cr(ox)_3^{3-}$ ion,[11,12] $Cr(acac)_3$,[13] and $Ru(bpy)_3^{2+}$ ion[14,15] (Figure 4A).

The rate equation for photoenantiomerization is

$$dc_R/dt = -dc_S/dt = -k_1 c_R + k_{-1} c_S \quad (6)$$

leading to a photostationary state (pss) at long irradiation times. The pss is identical with the racemic mixture if npl is employed. Cpl, however, causes the accumulation of one enantiomer, independent of the enantiomeric composition of the starting mixture (Figure 4B).

The kinetic analysis of this photochemical system given by Stevenson[11] is uncomplicated as the total concentration $c_R + c_S$ is maintained during the reaction. The photochemical rate equation in a 1-cm cell is

$$\frac{dc_R}{dt} = -\frac{dc_S}{dt} = -1000 I_o[(1 - 10^{-A'})/A'][\epsilon_R' \phi_R c_R - \epsilon_S' \Phi_S c_S] \quad (7)$$

ϵ_R' and ϵ_S' are the absorption coefficients of the enantiomers towards r- *or* l-cpl at the irradiation wavelength (indicated by the primes). The interconversion quantum yields must be identical for symmetry reasons (otherwise npl would induce optical activity).

The photostationary state is reached when $dc_R/dt = dc_S/dt = 0$. Then

$$\epsilon_R' c_R = \epsilon_S' c_S \quad (8)$$

This leads, since $\epsilon_R' = \epsilon' - \Delta\epsilon/2$ and $\epsilon_S' = \epsilon' + \Delta\epsilon'/2$, to

$$c_R - c_S = (\Delta\epsilon'/\epsilon')[(c_R + c_S)/2] \quad (9)$$

The maximum optical yield is limited by the *g*-factor at the irradiation wavelength, and the yield is equal to the enantiomeric purity of the solution since $c_R + c_S = c_{R,o} + c_{S,o}$ = constant.

$$P_{en} = 100(c_R - c_S)/(c_R + c_S) = 100g'/2 = [\theta]'/66\epsilon'\% \quad (10)$$

The asymmetric induction of the reaction can be evaluated, of course, at any wavelength. The derivation of the stationary state's ellipticity is as follows:

$$\Delta A = A_l - A_r = \epsilon_{R,l} c_R + \epsilon_{S,l} c_S - (\epsilon_{R,r} c_R + \epsilon_{S,r} c_S) \quad (11)$$

As from symmetry reasons $\epsilon_{R,l} = \epsilon_{S,r}$ and $\epsilon_{R,r} = \epsilon_{S,l}$

$$\Delta A = (\epsilon_{R,r} - \epsilon_{R,l})(c_R - c_S) = \Delta\epsilon(c_R - c_S) \quad (12)$$

with (9) one obtains for the pss

$$\Delta A_{pss} = \Delta\epsilon(\Delta\epsilon'/\epsilon')(c_R + c_S)/2 = \Delta\epsilon(c_R + c_S)g'/2 \quad (13)$$

or, expressed in ellipticities $\theta = 3300\Delta A$

$$\theta_{pss} = [\theta](c_R + c_S)g'/2 = 2c_o[\theta]g'/2 \quad (14)$$

The CD value measured at long irradiation times is dependent on the molar ellipticity at the analyzing wavelength, the relative absorbance difference at the irradiation wavelength, and the total concentration of both enantiomers. Of course, thermal racemization reduces the CD reading in the pss[11] and also introduces intensity and temperature dependence of the pss.

A photoenantiomerization system that is thermally stable and photochemically well defined and has reasonable quantum yields, i.e., reasonable irradiation times for reaching the pss, could be used as a convenient actinometer for the degree of polarization of cpl. If this is less than 100% then the CD of the pss is, of course, lowered. If the degree of polarization is defined by $I_o = I^{cpl} + I^{npl} = \gamma I_o + (1 - \gamma)I_o$ then one can derive a simple linear relation

$$\gamma = \theta_{pss}(\gamma)/\theta_{pss}(\gamma = 1) \quad (15)$$

Experimentally it is not easy to achieve 100% circular polarization for the expanded beams necessary for photochemical use. Therefore such an actinometer would be very important.

Candidates are "narcissistic" photoreactions[16] as, e.g., the light-induced suprafacial 1,3-H shift of 1,3-disubstituted indenes or the photoreaction of chiral spiro compounds as, e.g., the photochromic spiropyrans. In this latter case a nonchiral intermediate is photochemically produced by cpl at different rates from the enantiomers but the thermal back reaction is not enantioselective.

2. Asymmetric Synthesis

In asymmetric synthesis the product mixture is optically active, the educt mixture may or may not become active during irradiation with cpl. Asymmetric synthesis has been reviewed by Buchardt.[17d]

If the educt mixture stays racemic during irradiation with cpl there must be a racemization process active. The general scheme is given in Figure 5. Such an educt system is often met in a mixture of chiral enantiomers that cannot be resolved. Examples are the diarylethylenes.

Excitation is much faster than molecular motion, therefore one of the thermally labile enantiomers is preferentially excited. If the reaction of the excited molecule is faster than its enantiomerization then we observe asymmetric synthesis. However, the activation energy of racemization may be much smaller in the excited state than in the ground state. So the photoreaction step must be very fast. No wonder, that only few monomolecular asymmetric syntheses are found in the literature, mainly cyclization reactions. The most important type is the asymmetric synthesis of helicenes from diarylethylenes as investigated by the groups of Calvin and Buchardt[17] and Kagan and Martin.[18]

In asymmetric syntheses there are different definitions for asymmetric induction. The optical yield is

$$P_{oy} = 100\,\frac{c_{R\text{-Pr}} - c_{S\text{-Pr}}}{c_{o,R\text{-Ed}} + c_{o,S\text{-Ed}}} = 100\,\frac{100\theta_{prod}}{2c_o[\theta]_{prod}}\% \quad (16)$$

i.e., the excess of one product enantiomer in reference to the total concentration of the starting material. θ_{prod} is the ellipticity measured. Unfortunately optical yield sometimes is defined without reference to the reaction

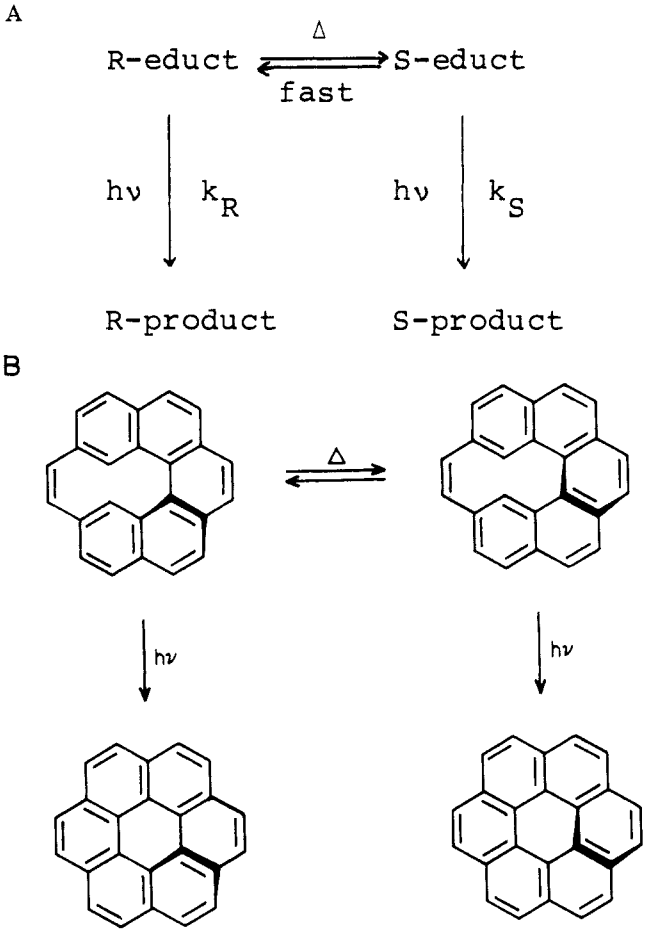


Figure 5. (A) General scheme of asymmetric synthesis. (B) Hexahelicene photosynthesis as an example.

and has the essential features of enantiomeric purity:[17-19]

$$100[\alpha]_{\text{product}}/[\alpha]_{\text{pure enantiomer}}\ \% \qquad (17)$$

By multiplication with the chemical yield, which usually is given as a second number, P_{oy} can be calculated. If there are no side reactions $c_{R\text{-Pr}} = c_o - c_{R\text{-Ed}}$ and now the enantiomeric purity is

$$P_{en} = 100\frac{c_{R\text{-Pr}} - c_{S\text{-Pr}}}{c_{R\text{-Pr}} + c_{S\text{-Pr}}} = 100\frac{c_{R\text{-Pr}} - c_{S\text{-Pr}}}{2c_o - (c_{R\text{-Ed}} + c_{S\text{-Ed}})} = 100\frac{100\theta_{\text{prod}}}{[\theta]_{\text{prod}}}\frac{\epsilon_{\text{Ed}}}{A_{o,\text{Ed}} - A_{\text{Ed}}}\% \qquad (18)$$

So it is necessary to be careful with literature data on optical yields. Buchardt has given a maximum optical yield for asymmetric synthesis of $g_{\text{Ed}}'/2$.[17d]

It has been shown that the asymmetric synthesis of helicenes is due to the different cpl absorption of the parent diarylethylene enantiomers.[17c] Many helicenes, up to undecahelicene, have been prepared photochemically by this ring-closure method. However, all the cpl-irradiation experiments have not given more than 0.2% of optical yield.

3. Asymmetric Destruction

In asymmetric destruction the educt mixture becomes optically active during cpl irradiation, the products may or may not be optically active.

Most of the cpl photochemical experiments are asymmetric destructions,[20-29] starting from the classical work of Werner Kuhn in the thirties. He investigated

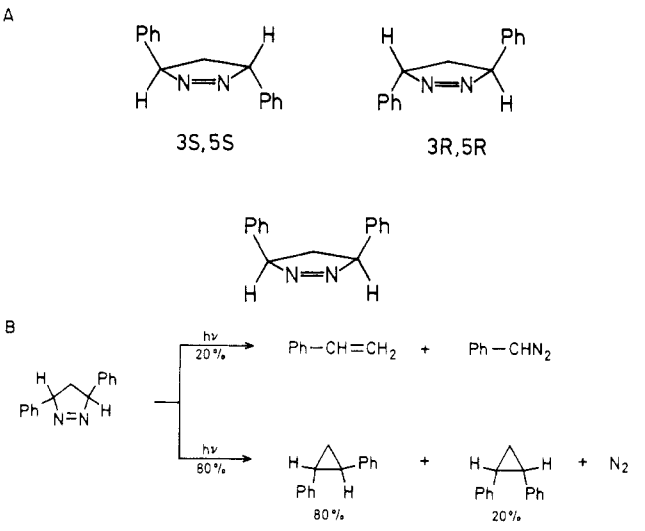


Figure 6. (A) Isomers of DPY. (B) The photoreaction of *trans*-DPY in benzene solution at room temperature.

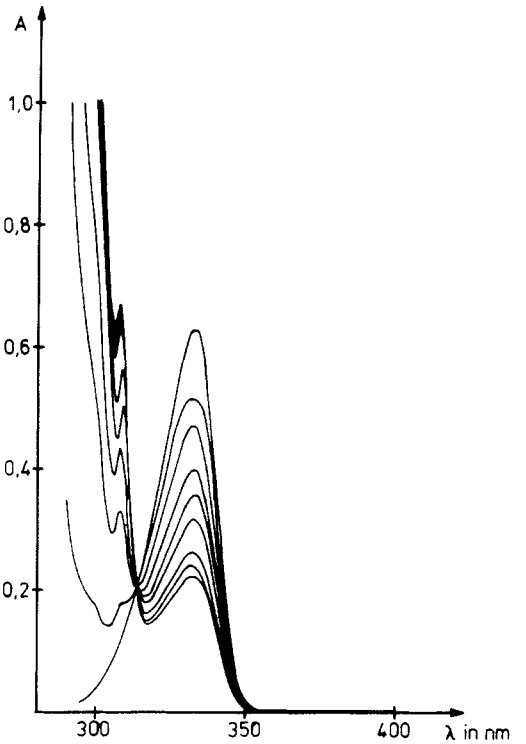


Figure 7. Reaction spectra of photolysis of *trans*-DPY in hexane. Irradiation at 330 nm and room temperature.

the photolysis of α-azido-[20] and α-bromopropionic esters[4] and gave the basis of the kinetic treatment of asymmetric destruction as independent parallel reactions of the enantiomers.[20] These experiments were repeated and extended to camphor cpl photolysis by Kagan et al.[24] in order to prove the potential of asymmetric destruction for reaching high enantiomeric purity.

Rau et al.[21] have chosen the nitrogen extrusion from *trans*-1,3-diphenyl-1-pyrazoline (DPY) as a model photoreaction. DPY (Figure 6A) has two asymmetric carbon atoms, the cis compound being the meso form. The photoreaction scheme is shown in Figure 6B, the absorption spectra of the reaction in Figure 7. On monochromatic irradiation at 330 nm, right at the wavelength of the azo n → π* absorption band (ϵ = 300) the reaction proceeds uniformly,[30] which is indicated

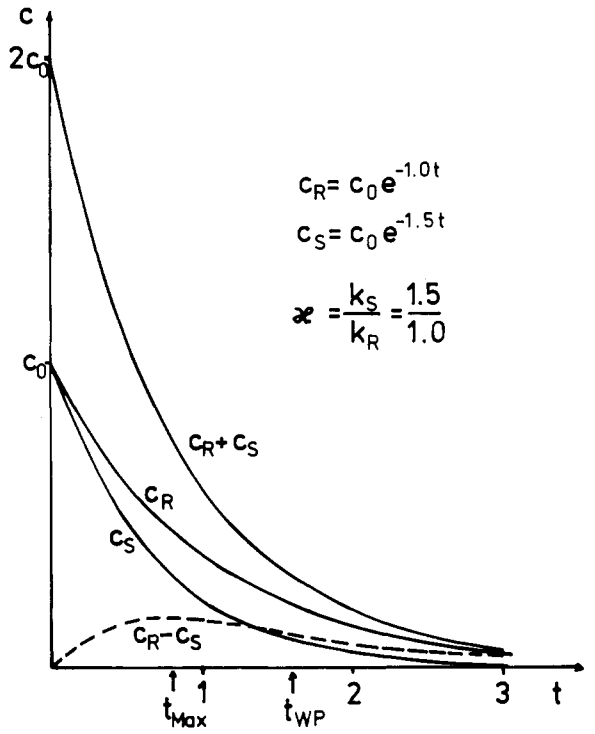


Figure 8. Time development of the concentrations of the enantiomers in asymmetric photodestruction.

by the isosbestic point at 312 nm. The CD spectrum mimics the 330-nm band of the UV spectrum in shape, the 330-nm CD band emerges in the early stages of irradiation and disappears later again.

The important features of the time development of the concentrations of the enantiomers, as realized already by Kuhn[20] and later by Kagan,[24] are obvious from the plots in Figure 8 which have been calculated for $\kappa = 1.5$. The two enantiomers disappear at different rates. Their individual concentrations cannot be determined. But $c_R + c_S$ (which shows a monotonic decrease) can be measured, e.g., by UV or gas chromatographic methods, and also $c_R - c_S$ (which shows a maximum curve) by CD spectroscopy. The kinetic analysis can be conducted rigorously for first-order independent parallel reactions.[21,22] Photochemistry is not first order in irradiation time as the absorption changes during the reaction. A transformation of the time axis[20,21] to $t' = \int_0^t (1 - 10^{-A'(t)})/A'(t)\, dt$ restores the exponential form of the concentration changes.

From this photolysis experiment UV and CD information are obtained and so two properties can be calculated from the kinetic analysis: the asymmetry of the reaction κ and the molar ellipticity $[\theta]$ of the educt. The determination of this important constant otherwise requires total resolution of the enantiomers.

This procedure, however, works only for $\kappa > 1.5$. For $\kappa < 1.5$, which is the case of all direct photoreactions, the nonexponentiality of the UV curve is lost in the error margin. There is a way out if the CD evaluation is made at the wavelength of excitation as then the asymmetry of the reaction is dependent on the different absorption of the R and S forms, i.e., the ellipticity of the solution:[22]

$$3300\Delta\epsilon' = [\theta]' \tag{19}$$

and

$$(\kappa - 1)/(\kappa + 1) = \Delta\epsilon'/2\epsilon' \tag{20}$$

TABLE II. Optical and Photolysis Data of *trans*-DPY

solvent	ϵ_{330}	$[\theta]_{330}$	$10^2 g_{330}$	P_{oy}, %	κ
hexane	306	62 000	6.34	0.99	1.064
benzene	370	79 000	6.43	1.03	1.066
α-pinene	306	68 000	6.76	1.06	1.070
ethanol	310	82 000	7.81	1.23	1.082
acetonitrile	314	90 000	8.63	1.34	1.090

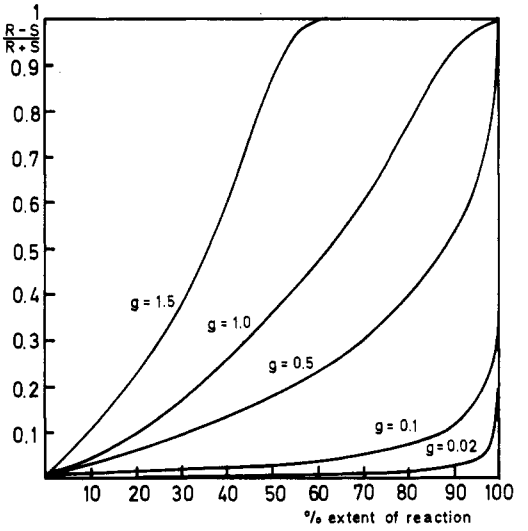


Figure 9. Enantiomeric purities of the educt in cpl-induced photoreactions.[24]

Rau et al.[21] have given a simple equation for determining the molar ellipticity at the excitation wavelength[31]

$$[\theta]'^2 = 66e10^4\epsilon'^2\theta'(\max)/\gamma' A_0' \tag{21}$$

where $e = 2, 71, ...$, A_0' is the initial absorption, γ' is the degree of circular polarization, and θ' (max) is the maximum value of CD during the reaction, all taken at the excitation wavelength. For $\kappa < 1.5$ the maximum of CD is reached at 63% extent of reaction $(1 - (1/e))$.

In Table II the results of the direct asymmetric photolysis of *trans*-3,5-diphenyl-1-pyrazoline are presented.[23] κ is very close to 1.0, the maximum optical yield P_{oy} of DPY is about 1%, higher though than that of asymmetric synthesis. Unfortunately, this yield is limited by the difference in absorption at the irradiation wavelength to $P_{oy}(\max) = 100(c_R - c_S)/2c_o = 37g'/2\%$. g factors are in the order of 10^{-2}–10^{-5}, so direct asymmetric photochemistry is not a preparative method although the optical yield increases with g'.[24] On the other hand, the enantiomeric purity of the educt DPY ever increases with the extent of reaction. Kagan et al.[24] have calculated the curves in Figure 9 and one realizes that direct photochemistry may ultimately reach high enantiomeric excesses, but only if most of the material is destroyed. This may be of practical interest in pharmaceutical preparations.

C. Mechanistic Aspects

Asymmetric synthesis and asymmetric destruction are two sides of the same coin. If there is neither racemization of the educt or excited educt nor racemization during the reaction we find total transfer of asymmetry to the product. This can be calculated from the theoretical enantiomeric purities of educt and product.[23] By comparison of observed and calculated CD data the

extent of configurational retention can be determined. Side reactions can be taken into account.

This method has been used by Rau, Schneider, and co-workers[23] to show that the *trans*-1,2-diphenylcyclopropane molecules formed by cpl photolysis from *trans*-3,5-diphenyl-1-pyrazoline have the same configurationally stable intermediates, a result important for the discussion of the trimethylene problem. The formation of ca. 15% *cis*-diphenylcyclopropane indicates, however, that there is some inversion of the configuration at C atoms 3 and 5. This is in agreement with Walborsky's photolysis of an asymmetric pyrazoline.[32] An interesting application of an asymmetric ring cleavage of the dialkylcyclohexadienone system in the synthesis of dimethylcrocetin is reported by Quinkert et al.[33] They succeeded in determining the configuration of an important synthetic intermediate by an asymmetric destruction/asymmetric synthesis step.

IV. Monomolecular Reactions: Asymmetric Induction by a Chiral Substituent

A chiral substituent in a photosensitive molecule may induce preferential formation of one diastereomer in a photoreaction induced by nonpolarized light if a new chiral element is created in the reaction.

This principle has been used by Martin and co-workers[34-37] in photocyclization of diarylethylenes made optically active by attachment of a chiral substituent. The position of the chiral substituent in the molecule is important for the helicene enantiomer formed preferentially[34-36] and so is temperature.[37] Optical purities of up to 96% have been achieved![37] The same principle of asymmetric induction governs Green's[38,39] [2 + 2] cycloadditions of cinnamic acids oriented to one another by attachment to the OH groups of sugar molecules by an ester bond. The optical purity of the products is up to 85%.[39]

In these reactions asymmetric induction is thought to emerge from a difference in the energy of the diastereomeric transition states. Salem has given a theory for thermal reactions which in principle applies to photochemical reactions, too.[40]

V. Monomolecular Reactions: Asymmetrically Sensitized Photoprocesses

A. General Remarks

In direct photochemistry the yields are limited by the magnitude of g'. Such a limitation is not valid in sensitized reactions.

In sensitized reactions one enantiomer of the sensitizer is irradiated by npl. The rates of energy or electron transfer to the two acceptor enantiomers are different. The scheme of the kinetically controlled parallel reaction is:

$$^3D_R + A_R \xrightarrow{k_{qR}} D_R + {}^3A_R \rightarrow D_R + R \text{ products}$$

$$^3D_R + A_S \xrightarrow{k_{qS}} D_R + {}^3A_S \rightarrow D_R + S \text{ products} \qquad (22)$$

There are two indicators for the asymmetry of energy transfer: one is the emission which is a property of the excited state of the enantiomeric sensitizer. Energy

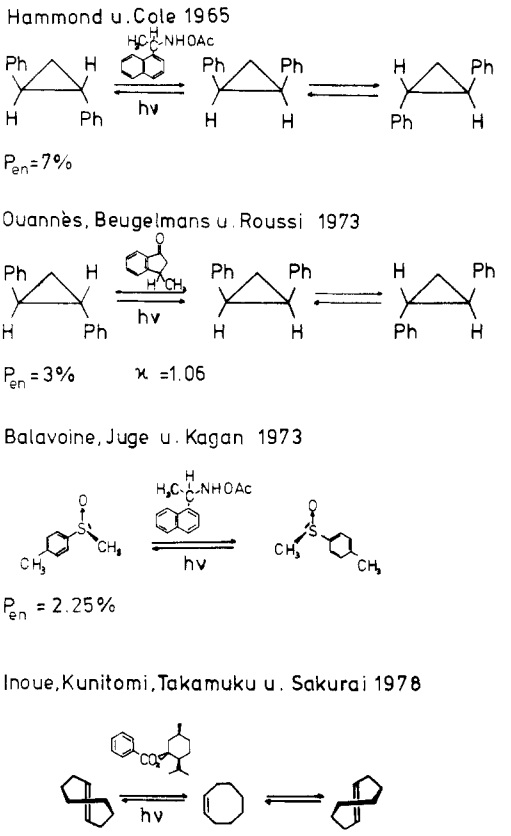


Figure 10. Asymmetrically sensitized trans–cis isomerizations.

transfer is a competitive process, emission quenching should be different for the two acceptor enantiomers. This indicator can be used in the separate reaction system. The other indicator is, of course, the photoreaction of the acceptor. This response to excitation is used for reactions in racemic mixtures. The same general kinetic equations are valid as those used in direct photochemistry. As the sensitizer concentration is constant, pseudofirst order of the reactions can be restored by a time axis transformation in a similar way as used in direct photochemistry (vide infra).

B. Asymmetrically Sensitized Photoreactions

Although there is much interest in asymmetric photochemistry there are only few reports, mostly short communications, on asymmetric sensitization. Four reaction types have been reported: trans–cis isomerizations, nitrogen elimination from pyrazolines, rearrangements in cyclic compounds, and emission quenching and photoredox reactions.

1. Trans–Cis Isomerizations

The asymmetrically sensitized trans–cis isomerizations[5,41-46] are compiled in Figure 10. The trans–cis isomerization of diphenylcyclopropane was the first asymmetrically sensitized reaction to be reported on.[5] In this reaction as well as in the octene system the enantiomers are interconverted via the symmetric cis form. In the photostationary state one of the optically active trans forms is in excess. Basically this reaction is a photoenantiomerization with a stable symmetric intermediate. The isomerization of methyl *p*-tolyl sulfoxide is an example of a reaction leading through a symmetric transition state.

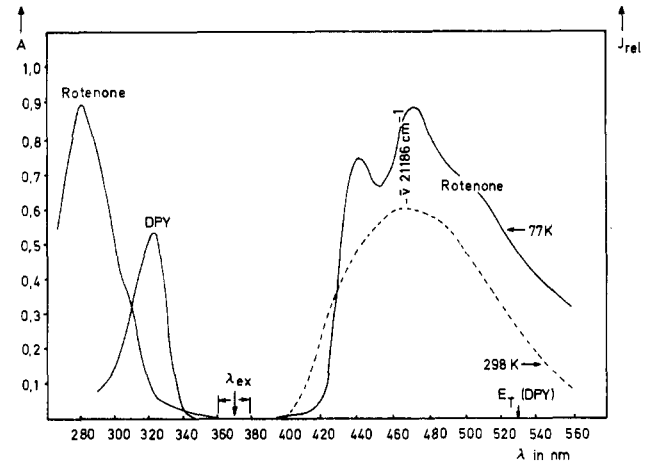
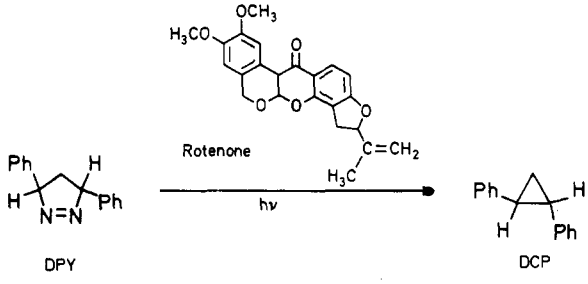


Figure 11. Spectroscopic data of the DPY–rotenone photoreaction system.

The enantiomeric excess in the reactions of Figure 10 is in the same order as can be achieved in direct photoenantiomerization with cpl. Only Hammond's result is clearly higher and proves the potential of the method.

2. Nitrogen Elimination from Pyrazolines

Rau and Hörmann[47] have used the *trans*-3,5-diphenyl-1-pyrazoline photodestruction model system for sensitized nitrogen extrusion. Rotenone, a natural



(23)

product, has been selected from a large number of ketone sensitizers because of its unique properties in benzene solution (Figure 11): (a) Rotenone can be selectively excited. (b) Triplet energy transfer is exothermic. (c) Rotenone phosphoresces at room temperature. Furthermore: (d) There is no energy transfer to the reaction product diphenylcyclopropane. (e) Rotenone is sufficiently stable when irradiated in benzene solution. (f) Rotenone can be removed easily when the reaction mixtures are worked up for analysis.

The Stern–Volmer plots of the dynamic and stationary phosphorescence quenching experiments are coincident at low (racemic) quencher concentrations but they diverge at higher quencher concentrations. This is important for the mechanism of energy transfer discussed later. The kinetic analysis of the nitrogen elimination reaction also requires a time axis transformation: $t' = \tau_0^{-1}\int_0^t \tau(t)dt$, for the lifetime of the sensitizer is increased as more of the quencher has disappeared. Then the general scheme of independent parallel reactions of the enantiomers can be applied. As $[\theta]$ of the pyrazoline is known κ can be obtained. Table III demonstrates for two sensitizers that the sensitized reaction may lead to higher as well as to lower asymmetry than is reached by direct excitation by cpl. Still the yields are small in this case.

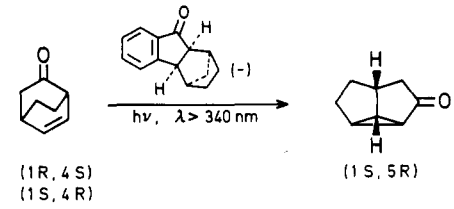
TABLE III. Asymmetric Photolysis of DPY

	κ	P_{oy}, %	P_{en}, %[63]
rotenone sensitized	1.080	1.5	4.05
testosterone sensitized	1.016	0.3	0.75
direct (cpl)	1.062	1.0	2.75

3. Rearrangements in Cyclic Compounds

There are two reports on asymmetrically sensitized di-π-methane rearrangements in the literature.

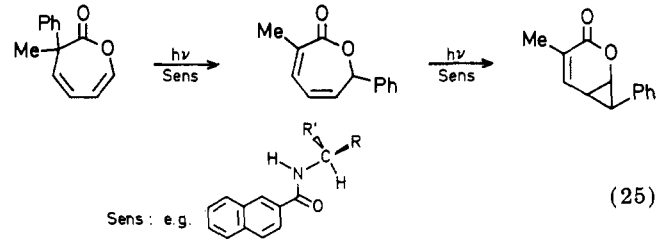
Schaffner and Demuth et al.[48] tried to synthesize (1*S*,5*R*)-(-)-tricyclo[3.3.0.0]octan-3-ones by the sensitized photoreaction



(24)

In this asymmetric oxa-di-π-methane rearrangement 4.5 ± 0.7% enantiomeric excess of the 1*S*,5*R* form of the tricyclic compound was reached at room temperature in benzene solution. At −78 °C in ethyl acetate the enantiomeric excess could be increased to 10 ± 3%. Still this is not enough for synthetic purposes.

Hoshi et al.[49] have observed the asymmetric rearrangement of the cyclic lactone



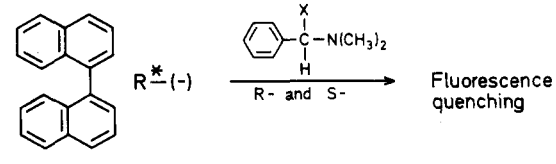
(25)

in a two-step reaction. Both the 1,5-phenyl shift and the subsequent di-π-methane rearrangement steps are asymmetrically sensitized by chiral acetonaphthone derivatives. It is claimed that "enantiomeric differentiation took place at the stage of the initial photosensitization". κ was found to be in the order of 1.04.

4. Emission Quenching and Photoredox Reactions

Emission quenching is not a photochemical but a photophysical process. But it is considered an indicator of asymmetric energy or electron transfer, the first step of a sensitized photoreaction.

Irie et al.[50,51] have investigated the quenching of excited (*R*)-(-)-1,1′-binaphthyl by asymmetric amines in different solvents and at different temperatures (Table IV). This system



(26)

exhibits a high degree of asymmetry. κ = 7.9 is the

TABLE IV. Solvent and Temperature Dependence of the Asymmetry of Emission Quenching of 1,1'-Binaphthyl by Differently Substituted Amines $PhCHXN(CH_3)_2$

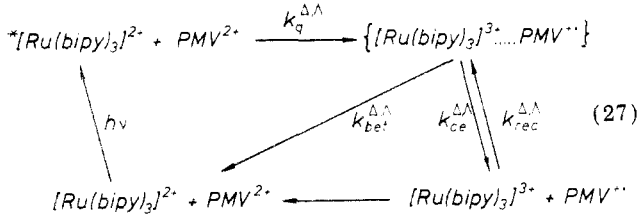
X	κ, CH_3CN, 295 K	κ, $C_2H_4Cl_2$, 295 K	κ, hexane 295 K	283 K	273 K	263 K	$\Delta(\Delta H^{\ddagger}_{hexane})$, kJ mol^{-1}	$\Delta(\Delta S^{\ddagger}_{hexane})$, J mol^{-1} deg^{-1}
CH_3	1.0	1.5	1.9	2.2	2.4	2.9	8.4 ± 0.8	23.0 ± 3.3
$CH(CH_3)_2$	1.0	2.2	2.7	3.3	3.7	4.7	11.3 ± 1.6	29.7 ± 5.9
$C(CH_3)_3$	1.0	2.5	4.0	5.0	6.2	7.9	16.7 ± 1.3	36.4 ± 5.0

highest value of asymmetry known in photochemistry and photophysics. The quenching reaction is thermally activated, the differences of the activation parameters are given in Table IV. The solvent dependence is remarkable and will be discussed later.

Quenching of (+)- and (-)-camphor with optically active amines did not result in unequivocal asymmetry.[52]

From the energy values of the excited states of binaphthyl or camphor and aliphatic amines an electron-transfer quenching mechanism is derived. There is no net photoreaction, though, which is considered the other indicator of asymmetric induction.

In order to compare the degree of asymmetry of the quenching reaction and the photoreaction Rau and Ratz have investigated the $Ru(bpy)_3Cl_2$–viologen system.[53] They used the enantiomers Δ-(-)-$Ru(bpy)_3Cl_2$ and Λ-(+)-$Ru(bpy)_3Cl_2$ as donors and 1-methyl-1'-((*S*)-(-)-3-methylpinanyl)-4,4'-bipyridinium dichloride ($PMV-Cl_2$) as an acceptor. The reaction is assumed to proceed according to the reaction scheme[54]



(27)

The quenching constants k_q^{Λ} and k_q^{Δ} have been determined from Stern–Volmer plots of separate stationary and dynamic quenching experiments. The concentration of the pinanylviologen radical ion $PMV^{+\cdot}$ formed in the quenching reaction has been measured in separate laser flash experiments. The asymmetry of emission quenching $\kappa = k_q^{\Lambda}/k_q^{\Delta} = 1.96$ ($\kappa - 1$ accurate to ±5%) is much higher than the asymmetry of the photoreaction $\kappa = (k_q^{\Lambda}/k_q^{\Delta})(\phi_{redox}^{\Lambda}/\phi_{redox}^{\Delta}) = 1.32$ where $\phi_{redox} = k_{ce}/(k_{ce} + k_{bet})$ and $\kappa - 1$ is accurate to ±40%. It becomes clear that electron back transfer in the geminal ion pair is a quite asymmetric reaction, too, which partly compensates the asymmetry of exciplex or ion pair formation.

In the realm of inorganic chemistry the photoreduction of Δ- and Λ-$Co(acac)_3$ by Δ-$Ru(bpy)_3^{2+}$ ions is reported to be asymmetric with $\kappa = 1.03$.[14]

C. The Mechanism of Sensitization

Normal energy transfer in sensitized photochemistry is by either the Förster mechanism[55] (by long-range coupling of the transition moments of donor and acceptor which is most important in singlet–singlet energy transfer) or the Dexter mechanism[56] (short-range coupling of the electron systems of donor and acceptor by electron distribution overlap, which is most important in triplet–triplet energy transfer). However, there is not

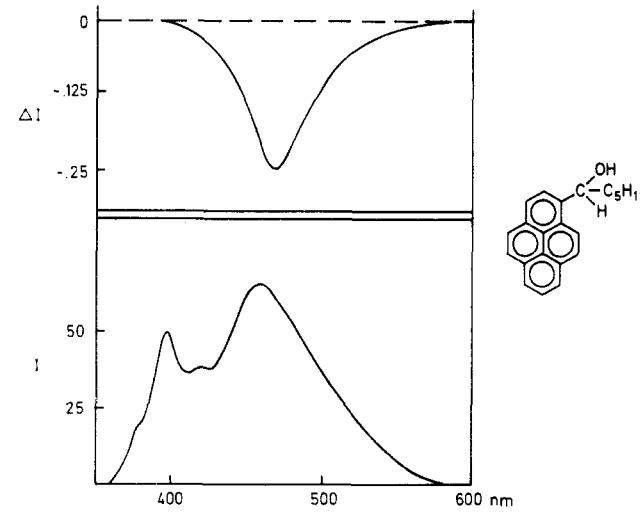


Figure 12. Emission and circular emission polarization spectra of 1-(1-pyrenyl)pentan-1-ol.[58]

one example of asymmetric sensitization in the literature where—if any comment on the mechanism is made at all—one of the two mechanisms is considered.

Basically one expects chiral recognition to be observed when the exchange mechanism is operative. The Förster mechanism is predicted to give very low asymmetry. Formally the Förster mechanism may be treated in a way similar to the trivial (emission–reabsorption) mechanism. So the asymmetry of energy transfer will be of the order of the product of emission and absorption anisotropies, and g_{em} and g_{abs} are usually not greater than 10^{-2}. Energy transfer via the Dexter mechanism requires first diffusion of donor and acceptor and then energy transfer in a collisional complex in which the partners' electron clouds penetrate partly. All asymmetrically sensitized reactions observed hitherto have transfer rates below the diffusion-controlled limit. This is easily rationalized: if the transfer occurs in every collision there is no discrimination of the *R* and *S* forms of the quencher.[57] But this requirement of transfer rates below the diffusion-controlled limit seems not to be sufficient. Nearly all of the authors in the field assume an exciplex mechanism for asymmetric sensitization. In a very new paper[44c] the reasoning is inverted: as asymmetric sensitization is observed an exciplex mechanism is assumed.

Exciplexes may emit and be observed by their fluorescence or phosphorescence. An optically active pyrene derivative may be used to demonstrate how high asymmetry may be in an excited complex in relation to the excited monomer:[58] monomer emission is nearly not polarized, excimer fluorescence, however, is strongly polarized (Figure 12). But even nonemitting exciplexes are tracked down by their effect on the donor emission. It has been shown[47,59] that nonidentical stationary (linear) and dynamic (leveling off to a constant value)

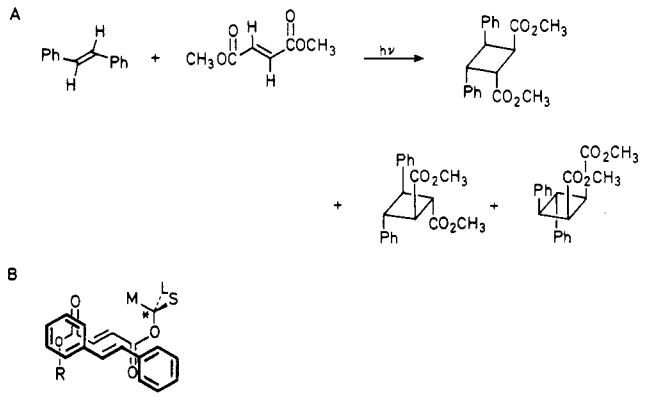
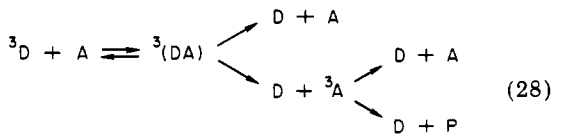


Figure 13. (A) Photoreaction of *trans*-stilbene and dimethyl fumarate. (B) Assumed arrangement in the exciplex.[60]

Stern–Volmer plots are consistent with the exciplex scheme



(28)

The solvent dependence of asymmetry in the case of binaphthyl quenching by amines has been explained by an alternative exciplex or ion pair formation. The electron transfer favored in polar solvents should be effective at distances too large for chiral discrimination.[51] This cannot be a general feature of photoredox reactions as demonstrated by the asymmetry of the $Ru(bpy)_3^{2+}$–PMV and the $Ru(bpy)_3^{2+}$–$Co(acac)_3$ system,[14,53] the photoredox reactions of which have been observed in water.

VI. Asymmetric Bimolecular Photoreactions

In this part reactions between nonchiral excited species with chiral partners that lead to the production of new chiral centers are reviewed.

There are not many reports in this field. Tolbert and Ali[60] present the most impressing one in the direct [2 + 2] cycloaddition of *trans*-stilbene, which is excited, and fumarate esters of chiral alcohols, e.g., borneol (Figure 13A). Enantiomeric excess of the truxinate products of up to 90% (μ-truxinate of 1-bornyl fumarate) are observed and the reaction proceeds via a highly ordered exciplex (Figure 13B). This exciplex can be observed by its emission. There are several interesting features: (a) No increase in enantiomeric excess is observed when the diester products are compared to those of the monoester. (b) Quenching constants of stilbene fluorescence are independent of the ester–alcohol and nearly diffusion controlled. (c) The exciplex emission is sensitive to substitution of the fumaric acid. Tolbert and Ali conclude from their work that asymmetry is induced not in the formation but in the reaction of the exciplex and that competition between cyclization (which may be via 1,4-diradical) and the radiationless decay determines the degree of asymmetry of the photoreaction. Asymmetrically photoinduced cycloadditions leading to the oxetane[61] and thietane[62] systems have been reported by Gotthardt and Lenz to give 37% and 17% enantiomeric excess in the products, respectively.

Horner and Klaus report the photoreduction of acetophenone, which is excited, by the methyl ester of L-lactic acid.[46] The resulting pinacol shows enantiomeric purity of up to 4.7%, which is in the same range as that reached in cpl-induced photochemistry. The same authors also report a sensitized bimolecular reaction with asymmetric induction:[46] the addition of isopropanol to the menthyl ester of maleic acid with benzophenone as a sensitizer. According to Horner's formulation of a radical mechanism benzophenone is reduced and reoxidized, so this reaction is essentially a photocatalytic and not a sensitized one. Enantiomeric purities of up to 3.8% are achieved.

Tran and Fendler have investigated the formation of excimers of tryptophan-substituted pyrene.[63] This is a different type of reaction: an excited chiral molecule associates with another chiral molecule in the ground state. There are considerable differences in pyr-D-Trp/pyr-D-Trp and pyr-D-Trp/pyr-L-Trp excimer kinetics and thermodynamics.

It is astonishing that this type of reaction, which is so closely related to thermal chemistry, has not been used more extensively.

VII. Effect of Chiral Solvents

Asymmetry in the environment of the reacting species has been used to introduce asymmetry into chemical reactions. Photoreactions in chiral crystals[1] as well as the use of chiral cavities of, e.g., cyclodextrins[64] and twisted nematic[65] and cholesteric[66] mesophases are examples for this type of reactions. This review, however, is restricted to asymmetry induced by liquid solvents.

The literature reports the same type of reactions as have been performedd by cpl or asymmetric sensitization. *cis*-Diarylethylenes have been cyclized by Laarhoven and Cuppen in different chiral solvents to give helicenes with enantiomeric purities of up to 2.0%, 10 times more than by direct cpl cyclization.[67] The effect is thought to be on the equilibrium of the two enantiomeric conformations of the ground-state *cis*-diarylethylenes. Cis–trans isomerizations of an α,β-unsaturated ketone induced by direct excitation in diethyl L-(+)-tartrate gave an optical purity of 0.5–1%.[68] Seebach[69,70] has used an optically active amine as a solvent *and* hydrogen donor in acetophenone reduction and has found an enantiomeric purity of 6% (at room temperature)[69] to 11.5% (at −35 °C).[70] When cosolvents such as pentane, methanol, or toluol were used enantiomeric purities of up to 23.5% have been reached.[70]

Chiral solvents influence excimer formation as demonstrated for tryptophan-substituted pyrene. From the temperature dependence of emission Tran and Fendler calculate a difference of excimer stabilities of pyr-D-Trp in *S*-(+)- and *R*-(−)-2-octanol of 2.5 kJ mol^{-1}.[63] Emission may also be rendered circularly polarized by a chiral solvent as is shown, e.g., for fluorescein in α-phenylethylamine.[71]

VIII. Discussion and Conclusions

Compared to the spacious areas of thermal enantioselective chemistry asymmetric photochemistry is but a narrow field. The reason for this is the limitation of enantioselectivity which seems to be a basic feature of asymmetric photochemistry.

It has been shown in section III that the enantiomeric excess in direct photochemistry is locked to the relative

absorption difference at the irradiation wavelength and that high enantiomeric purity in the residual educt can only be achievedd at the expense of loss of most of the starting material.

In sensitized photochemistry the high asymmetry of emission quenching observed in some cases is promising at first sight (Table IV). $\kappa = 4$ corresponds to more than 60% enantiomeric purity of the educt at 63% extent of reaction if this degree of asymmetry can be transferred to the photodestruction reaction. But the high asymmetry of emission quenching seems to be lost partly in the competition between the deactivation routes leading back to the starting material and to photoproducts.[52] If this is a general feature, and there are reasons for it, then sensitized photochemistry has no general perspective in synthetic work.

There is, however, some chance that the temperature effect may be exploited, not in direct, but in sensitized photochemical reactions. No systematic investigation has been made hitherto, but all the pieces of evidence available reveal an increase of enantioselectivity at low temperatures. As stated in section I the kinetic scheme of asymmetric photochemistry normally is that of independent parallel reactions. Asymmetry is introduced in every elementary reaction step according to transition-state theory

$$\kappa = \frac{k_S}{k_R} = \frac{(kT/h)\exp[-(\Delta H_S^{\ddagger} - T\Delta S_S^{\ddagger})/RT]}{(kT/h)\exp[-(\Delta H_R^{\ddagger} - T\Delta S_R^{\ddagger})/RT]} = \exp\left[-\frac{\Delta(\Delta H^{\ddagger})}{RT} + \frac{\Delta(\Delta S^{\ddagger})}{R}\right] \quad (29)$$

If the activation enthalpy and the activation entropy are assumed to be independent of temperature then at high temperatures the asymmetry is determined by $\Delta(\Delta S^{\ddagger})$ and at low temperatures by $\Delta(\Delta H^{\ddagger})$.[51] As the terms of $\Delta(\Delta H^{\ddagger})$ and $\Delta(\Delta S^{\ddagger})$ are different in sign there is an isokinetic temperature above which one and below which the other enantiomer is accumulated. Above this isokinetic temperature the asymmetry of the reaction should be nearly temperature independent. These predictions have not yet been verified experimentally. The experimental data suggest, however, that $\Delta(\Delta S^{\ddagger})$ is not very important compared to $\Delta(\Delta H^{\ddagger})$. Lowering of the temperature in nearly all cases has improved enantioselectivity.

Of course, low solubility and increased viscosity at low temperatures are detrimental for large-scale enantioselective photochemistry but in special synthesis problems enantioselective photoreactions should not be excluded from the synthesis plan offhand.

One may suspect that many a researcher has tried to use an asymmetric photoreaction step in a synthesis sequence in vain, and that some of the short reports do not result from experiments where the conditions have been optimized. In fact, reproduction of published results sometimes is cumbersome, at least in the quantitative aspect. This may be due to the lack of experimental details in the publication. Experiments in the field of optical activity even with the new spectropolarimeters are not foolproof. Often the ellipticity produced in a photoreaction is small and the underlying optical density is high. Then there is the danger of fake CD spectra and the deviation from the true spectrum is a feature of the individual instrument. ORD data are more reliable in this respect but $[\alpha]$ values in many cases are calculated on the basis of minute angles of rotation and published without margins of error. Kagan et al.[66b] point out another difficulty which they have been faced with in futile attempts to reproduce asymmetric induction in cholesteric phases and which has to be paid attention to in sensitized photochemistry, too. It is the isolation and purification of final products. The completeness and reliability of these procedures is of tantamount importance if ORD techniques are used for the analysis of asymmetric induction. So handling of CD and ORD data requires a critical attitude.

One type of asymmetric photoreactions, however, is interesting for synthetic purposes. The bimolecular reaction of a chiral and a nonchiral molecule, one of them being excited may lead to considerable asymmetric induction (section VI), as may monomolecular photoreactions of molecules with a chiral substituent (section IV). There are parallels to thermal chemistry and this leads to the question of the molecular mechanism of asymmetric photoreactions.

In direct photochemistry and in collisional energy or electron transfer the asymmetry is in the production of the reactive excited species. If an exciplex is formed the reaction may take place from the independent dissociated energized acceptor molecule or it may start before the dissociation of the exciplex. It is in this direction that efforts to reach higher asymmetries should be lead. The longer the diastereomeric influence along the reaction coordinate the higher the asymmetry. The extreme case would be a chiral photocatalyst acting like an enzyme, at the same time energizing and arranging the reacting molecule or molecules. The asymmetric bimolecular photoreactions are landmarks on that way. The excited transition states or exciplexes in which new chiral centers develop are diastereomeric entities in which the steric requirements persist and become even more rigorous on deactivation to the ground state. This is in contrast to most normal exciplexes where the steric requirements are loosened on dissociation.

In conclusion: Asymmetric induction in direct photochemistry is limited by the CD value of the educt at the irradiation wavelength. Direct photochemistry is a method for the determination of the molar ellipticity of the educt of a photodestruction reaction without resolution of the enantiomers. In direct and sensitized photoreactions the transfer of optical activity from educt to product provides information about the conformational stability of transient states or intermediates.

In sensitized photoreactions asymmetric induction is not limited in principle, it may be high in exciplex formation. Part of the asymmetry of exciplex formation seems to be compensated by an opposite asymmetry of the exciplex's further reaction. The asymmetry of sensitized photoreactions is quite sensitive to temperature changes. Asymmetrically sensitized reactions at low temperatures, asymmetrically sensitized bimolecular reactions, and reactions made asymmetric by chiral substituents of one reactant have the potential of satisfactory or even good optical yields.

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IX. References and Notes

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