

Theoretical Insights Into Photochemical Reactions Initiated With Circularly Polarized Light

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ABSTRACT A theoretical analysis of several hypothetical photoreactions initiated with circularly polarized light has been carried out to determine the factors influencing the enantiomeric excess of recovered reactant. The anisotropic g value is the dominant influence, although quantum yields and F values may be important in certain cases. *Chirality* 18:419–425, 2006. © 2006 Wiley-Liss, Inc.

KEY WORDS: asymmetric photochemistry; enantiomeric excess; mathematical analysis

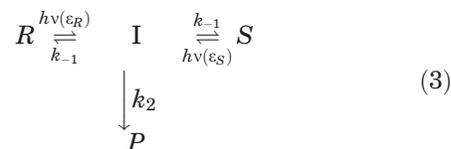
The ability to carry out organic reactions involving stereogenic centers with high enantiomeric excesses (ee's) is certainly one of the triumphs of modern organic chemistry. There is nonetheless the desire to improve these results by the use of new optically active reagents and catalysts. Circularly polarized light (CPL), a chiral form of light which can be used to initiate photochemical reactions, is potentially such a reagent. Unfortunately, it has rarely been used successfully to generate optically active products (or recovered reactant) with high ee's.¹ Why is this so? Is there an innate impediment which prevents such photoreactions from working well?

The first person to delve into these issues theoretically was Kagan.² He showed that for a reaction of a racemate (R/S), the ee of recovered reactant goes to 1 as the amount of reactant goes to zero [see eq. (1) below]. The rate at which the ee goes to 1 depends on the magnitude of g , which is $2(\epsilon_R - \epsilon_S)/(\epsilon_R + \epsilon_S)$, where the epsilons are the extinction coefficients for the enantiomers absorbing CPL. Unfortunately, g is usually small because the numerator, which can be obtained from circular dichroism (CD), is usually small and the denominator, which can be obtained from UV-Vis spectroscopy ($\epsilon_R + \epsilon_S = 2\epsilon$, where ϵ is the extinction coefficient obtained from UV-Vis spectroscopy), is often large. The situation is no better if chiral products are produced in the reaction. For the photoequilibration of R and S , i.e., $R \rightleftharpoons S$, the situation seems better because R and S are not consumed [see eq. (2) below]. The ee of recovered reactant is still low because it also depends on g .



Recently, we published a paper describing a reaction which has characteristics of both of the above systems.³ In this reaction, the R and S enantiomers equilibrate

through an achiral intermediate such as a radical pair or ion pair [see eq. (3) below]. This intermediate in turn reacts to give product(s). Mathematical analysis of this system shows that the ee of recovered reactant depends on g , as in the previous two cases, and F , the fraction of the intermediate which reacts to give the product. Because F requires, at least in part, that the components making up the intermediate diffuse into the bulk solution, its value should depend on the viscosity of the solvent. If this is true, one then has a new method for controlling the ee of the recovered substrate. The imagined connection between F and solvent viscosity has been tested experimentally and shown not to hold.^{4,5} This is a consequence of the fact that the radical or ion pair reacts internally to give products far more readily than its components diffuse into the bulk solution.



There are many other photochemical schemes involving R and S which may afford higher predicted ee's of recovered reactant or chiral products than for the three schemes described above. It is the purpose of the present work to describe several of these systems mathematically and deduce if higher ee's indeed are possible. Even for photoreactions where the resultant ee's are low, the results are still useful. The evolution of the R and S enan-

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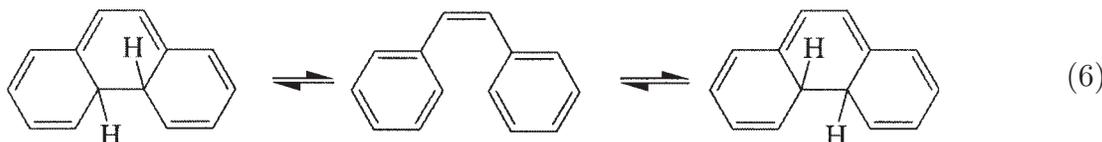
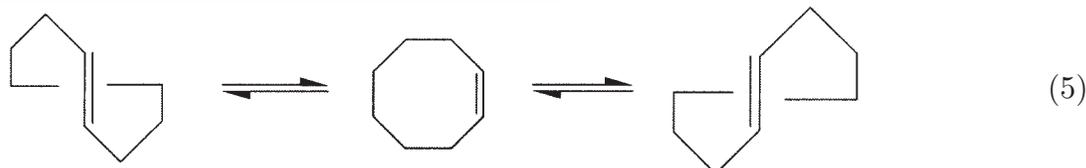
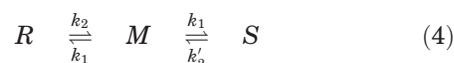
tomers and the ee as a function of time may be used to differentiate one mechanistic pathway from another.

RESULTS AND DISCUSSION

In addition to the three systems described above, there are many others involving enantiomers and CPL—some of which may have synthetic utility—that can be used to probe a photochemical mechanism, or probe the prebiotic origin of optically active molecules. Several of these systems have been worked out here in detail mathematically, and the results are shown in the sections below. Unlike our earlier publication in this area where significant mathematical detail was given,³ only the final results are given here; suitable graphs are also given when appropriate. The interested reader may consult our earlier paper³ to see how the mathematics are developed in detail. In all cases, the photochemical steps were assumed to be 1st order in the substrate, which can usually be attained by manipulation of substrate concentration and/or light intensity.⁶ All of the systems below yield sets of 1st-order simultaneous differential equations whose general solutions can be found in any elementary differential equations book.⁷ In cases where transient species are produced, the steady-state approximation was applied to them.

Photoequilibration of Enantiomers through an Achiral or Meso Compound

The photoequilibration of enantiomers *R* and *S* via an achiral or meso compound (*M*) is well known [see eq. (4) below]. The enantiomers of *trans*-cyclooctene, for example, interconvert photochemically with the achiral *cis* isomer [see eq. (5) below].⁸ The *trans* compound is in fact synthesized by the photolysis of *cis*-cyclooctene in the presence of CuCl.⁹ When *cis*-cyclooctene is photolyzed with CPL from a synchrotron light source, the resulting *trans*-cyclooctene is optically active.¹⁰ The reversible photochemically-induced electrocyclic ring closure of stilbenes (achiral compounds) yields chiral dihydrophenanthrenes with *C*₂ symmetry [see eq. (6) below].¹¹ The photochemistry of suitable stilbenes with CPL and an oxidizing agent such as iodine has been used to make optically active helicenes.¹² Certain fullerenes exist in chiral and achiral forms. C₈₄, for example, exists in many isomeric forms including *R*, *S*, and meso isomers.¹³ The chiral and meso C₈₄ can interconvert, at least theoretically, via the so-called Stone–Wales transformation.¹³



It is informative to begin the analysis of eq. (4) by considering what happens when the reactions are initiated with unpolarized light. Here, $k_2 = k_2' = \epsilon_{R,S} \phi_{R,S} k$, where $\epsilon_{R,S}$ is the extinction coefficient of *R* and *S* and $\phi_{R,S}$ is the quantum yield for *R* and *S* going to *M*, and $k_1 = \epsilon_M \phi_M k$, where ϵ_M is the extinction coefficient of *M* and ϕ_M is the quantum yield of *M* going to *R* and *S*; k is a phenomenological constant common to k_2 , k_2' , and k_1 .⁶ If $[M] = C_0$ and $[R] = [S] = 0$ at $t = 0$, one obtains

$$[M] = \frac{k_2}{2k_1 + k_2} C_0 + \frac{2k_1}{2k_1 + k_2} C_0 e^{-(2k_1 + k_2)t}, \quad (7)$$

$$[R] + [S] = \frac{2k_1}{2k_1 + k_2} C_0 - \frac{2k_1}{2k_1 + k_2} C_0 e^{-(2k_1 + k_2)t}. \quad (8)$$

$[M]$ and $[R] + [S]$ reach their asymptotic values at $t = \infty$, the photostationary state (pss). At the pss we obtain

$$\left(\frac{[M]}{[R] + [S]} \right)_{\text{pss}} = \frac{k_2}{2k_1} = \frac{\epsilon_{R,S} \phi_{R,S}}{2\epsilon_M \phi_M}, \quad (9)$$

which can also be obtained by other methods.¹⁴ Because $\epsilon_{R,S}$ and ϵ_M can be obtained from UV spectroscopy, $\phi_{R,S}/\phi_M$ can be obtained from eq. (9).

If one begins instead with $[R] = [S] = \frac{1}{2} C_0$ and $[M] = 0$ at $t = 0$, the evolution of $[R]$, $[S]$, and $[M]$ will of course be different than described in eqs. (7) and (8), but at the pss, the same concentrations of $[M]$, $[R]$ and $[S]$ are obtained as in the previous case. More interesting results are obtained when one starts with optically active substrate: $[R] = C_0$, $[S] = [M] = 0$

at $t = 0$, for example. Solution of the differential equations yields

$$[M] = \frac{k_2}{2k_1 + k_2} C_0 - \frac{k_2}{2k_1 + k_2} C_0 e^{-(2k_1 + k_2)t}, \quad (10)$$

$$[R] + [S] = \frac{2k_1}{2k_1 + k_2} C_0 + \frac{k_2}{2k_1 + k_2} C_0 e^{-(2k_1 + k_2)t}, \quad (11)$$

$$[R] - [S] = C_0 e^{-k_2 t}. \quad (12)$$

These starting conditions yield a new time-dependent equation [eq. (12)] from which k_2 can be obtained directly.

We have examined the photolysis of (-)-*trans*-cyclooctene in cyclopentane. Both the decay of $[R] - [S]$ and $[R] + [S]$ as a function of time are strictly first order, that is, plots of $\ln \left(\frac{[R] - [S]}{C_0} \right)$ versus t and $\ln \left(\frac{[R] + [S]}{C_0} \right)$ versus t are linear. In this latter case, this is only possible if $k_2 \gg k_1$ or $\varepsilon_{R,S} \phi_{R,S} \gg \varepsilon_M \phi_M$. Details of these experiments will be published elsewhere.¹⁵

We may now consider what happens if the reactions in eq. 4 are initiated with CPL. Here, $k_2 \neq k_2'$, with $k_2 = \varepsilon_R \phi_{R,S} k$ and $k_2' = \varepsilon_S \phi_{R,S} k$. If $[M] = C_0$ and $[R] = [S] = 0$ at $t = 0$, the following equations result:

$$[M] = \frac{k_2 k_2'}{r_2 r_3} C_0 + \frac{(k_2 + r_2)(k_2' + r_2)}{r_2(r_2 - r_3)} C_0 e^{r_2 t} - \frac{(k_2 + r_3)(k_2' + r_3)}{r_3(r_2 - r_3)} C_0 e^{r_3 t}, \quad (13)$$

$$[R] = \frac{k_1 k_2'}{r_2 r_3} C_0 + \frac{k_1(k_2' + r_2)}{r_2(r_2 - r_3)} C_0 e^{r_2 t} - \frac{k_1(k_2' + r_3)}{r_3(r_2 - r_3)} e^{r_3 t}, \quad (14)$$

$$[S] = \frac{k_1 k_2}{r_2 r_3} C_0 + \frac{k_1(k_2 + r_2)}{r_2(r_2 - r_3)} C_0 e^{r_2 t} - \frac{k_1(k_2 + r_3)}{r_3(r_2 - r_3)} C_0 e^{r_3 t}, \quad (15)$$

where

$$r_{+/-} = -\frac{k_2 + k_2'}{2} \left[\left(\frac{2k_1}{k_2 + k_2'} + 1 \right) \pm \frac{k_2 + k_2'}{2} \left[\left(\frac{2k_1}{k_2 + k_2'} \right)^2 + \left(\frac{g}{2} \right)^2 \right]^{1/2} \right], \quad (16)$$

with $r_2 = r_+$ the positive root, and $r_3 = r_-$ the negative root.

Unlike the cases with unpolarized light, the loss of $[M]$ and build up of $[R] + [S]$ are biexponential. At the pss, where $[R] - [S]$ is at its maximum value, we obtain

$$\left(\frac{[M]}{[R]} \right)_{\text{pss}} = \frac{\varepsilon_R \phi_{R,S}}{\varepsilon_M \phi_M}, \quad (17)$$

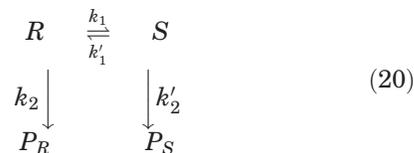
$$\left(\frac{[M]}{[S]} \right)_{\text{pss}} = \frac{\varepsilon_S \phi_{R,S}}{\varepsilon_M \phi_M}, \quad (18)$$

$$\left(\frac{[R]}{[S]} \right)_{\text{pss}} = \frac{\varepsilon_S}{\varepsilon_R}, \quad (19)$$

where ε_M is obtained by UV spectroscopy and ε_R and ε_S from a combination of UV spectroscopy and CD. Because $\phi_{R,S}/\phi_M$ can be determined independently from previously described experiments, one can calculate the pss ratios a priori. The maximum value of ee, which is attained at the pss, equals $-g/2$. Thus, a low ee is expected in these cases because g is normally small. If one initiates the photoreactions with $[R] = [S] = (1/2)C_0$ and $[M] = 0$, the concentrations of the three alkenes evolve differently as a function of time than when one starts with $[M] = C_0$, but identical pss ratios and ee are obtained, as expected.

Interconversion of Enantiomers, Each Leading to a Product

The reaction scheme in which two species interconvert and also react to give products has been solved exactly.¹⁶ Of interest here is that when the interconverting species are enantiomers, each of which reacts photochemically to give a product [see eq. (20) below]. The enantiomers of binaphthyls, helicenes, biphenyls, and sulfoxides are known to interconvert thermally,¹⁷ as do the enantiomers of *trans*-cyclooctene ($k_1 = k_1'$).¹⁸



When the photoreactions in eq. (20) are initiated with unpolarized light ($k_2 = k_2' = \varepsilon_{R,S} \phi_{R,S} k$) and $[R] = C_0$ and $[S] = 0$ at $t = 0$, the following solutions result:

$$[R] + [S] = C_0 e^{-k_2 t}, \quad (21)$$

$$[R] - [S] = C_0 e^{-(2k_1 + k_2)t}, \quad (22)$$

$$ee = e^{-2k_1 t}. \quad (23)$$

Suitable plots give k_1 and k_2 directly. k_1 can also be obtained from the kinetics of racemization of the substrate.

When the photoreactions in eq. (20) are initiated with CPL ($k_2 = \varepsilon_R \phi_{R,S} k$; $k_2' = \varepsilon_S \phi_{R,S} k$), a more complicated time-dependent behavior of the various species results. If $[R] = [S] = (1/2)C_0$ at $t = 0$, we obtain

$$ee = \frac{\frac{g}{2}(-1 + e^{(r_2 - r_1)t})}{\left\{ \left(\frac{2k_1}{k_2 + k_2'} \right) + Q^{1/2} \right\} - \left\{ \left(\frac{2k_1}{k_2 + k_2'} \right) - Q^{1/2} \right\} e^{(r_2 - r_1)t}}, \quad (24)$$

$$r_2 - r_1 = -(k_2 + k_2')Q^{1/2}, \quad (25)$$

where

$$Q = \left[\left(\frac{2k_1}{k_2 + k_2'} \right)^2 + \left(\frac{g}{2} \right)^2 \right]. \quad (26)$$

It is clear from eq. (24) that the g value and the ratio $2k_1/(k_2+k_2')$, dominate the time-dependent enantiomeric excess. For a given value of g and $2k_1/(k_2+k_2')$, ee reaches its maximum value at $t = \infty$. The behavior of eq. (24) is best illustrated in two graphs. In Figure 1, ee is plotted against time, with g kept constant at 0.1 but $2k_1/(k_2+k_2')$ varied. Because of the manner in which ee is defined, it can have positive or negative values between 0 and 1. Here, ee becomes dramatically more negative as $2k_1/(k_2+k_2')$ decreases. Any equilibration of R and S (i.e., $k_1 \neq 0$) will inevitably reduce the absolute value of ee. One still can control the situation to a certain extent because the value of k_1 is temperature dependent. In Figure 2, $2k_1/(k_2+k_2')$ is kept constant at 0.5 with g varied. In this case, ee increases as g increases. Thus, the ee of the system described in eq. (24) is still dominated by g , which (as noted above) is usually small.

A more interesting case develops if the equilibration of R and S is also photochemically induced. The more likely scenario here is that a single excited state of R or S is responsible for both the isomerization to the other enantiomer and the irreversible reaction to a product. If one defines ϕ_1 as the quantum yield for $R \rightarrow S$ and $S \rightarrow R$ and ϕ_2 as the quantum yield for $R \rightarrow P_R$ and $S \rightarrow P_S$, it follows that in eq. (20), $k_1 = k_1' = \phi_1 \varepsilon_{R,S} k$ and $k_2 = k_2' = \phi_2 \varepsilon_{R,S} k$ when unpolarized light is used to initiate the reaction. Thus,

$$\frac{d[R]}{dt} = -(\phi_1 + \phi_2)\varepsilon_{R,S} k[R] + \phi_1 \varepsilon_{R,S} k[S], \quad (27)$$

$$\frac{d[S]}{dt} = \phi_1 \varepsilon_{R,S} k[R] - (\phi_1 + \phi_2)\varepsilon_{R,S} k[S]. \quad (28)$$

If $[R] = R_0$ and $[S] = 0$ at $t = 0$, it follows that

$$[R] + [S] = R_0 e^{-(2\phi_1 + \phi_2)\varepsilon_{R,S} kt} \quad (29)$$

$$[R] - [S] = R_0 e^{-\phi_2 \varepsilon_{R,S} kt} \quad (30)$$

$$ee = e^{-2\phi_1 \varepsilon_{R,S} kt} \quad (31)$$

From suitable plots of eqs. (29) and (30), it is a simple matter to deduce ϕ_1/ϕ_2 , which will be useful in the case described immediately below.

When the photoequilibration and irreversible photoreactions of R and S are initiated with CPL, $k_1 = \phi_1 \varepsilon_R k$, $k_1' = \phi_1 \varepsilon_S k$, $k_2 = \phi_2 \varepsilon_R k$, and $k_2' = \phi_2 \varepsilon_S k$. If at $t = 0$, $[R] = [S] = 1/2 C_0$, the following time-dependent ee of Chirality DOI 10.1002/chir

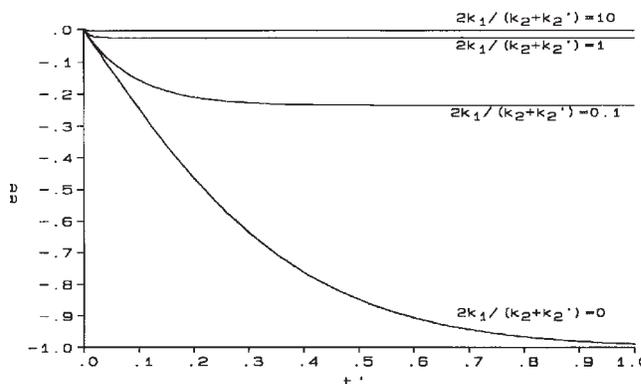


Fig. 1. ee vs. t' in units of $\text{sec}/(k_2 + k_2')$ for the reaction scheme in equation with $g = 0.1$ and $2k_1/(k_2 + k_2')$ varied from 0 to 10.

recovered R/S is obtained:

$$ee = \frac{\frac{g}{2}(2\phi_1 + \phi_2)(-1 + e^{(r_2 - r_1)t})}{(\phi_1 + T^{1/2}) - (\phi_1 - T^{1/2})e^{(r_2 - r_1)t}}, \quad (32)$$

$$r_2 - r_1 = -k(\varepsilon_R + \varepsilon_S)T^{1/2}, \quad (33)$$

$$T = \left[\phi_1^2 + \phi_2(2\phi_1 + \phi_2) \left(\frac{g}{2} \right)^2 \right]. \quad (34)$$

In Figures 3 and 4, where ee is plotted versus time in units of $k(\varepsilon_R + \varepsilon_S)$ ($=100$), eq. (33) is displayed graphically. From Figure 3, where ϕ_1 and ϕ_2 are each kept constant at 0.1 but g is varied, it is clear that ee goes up with g at a given time. Again, a large g value is essential in order to obtain a synthetically useful ee of recovered reactant. From Figure 4, where ϕ_1 and ϕ_2 are varied but the ratio ϕ_1/ϕ_2 and g are held constant, it is apparent that one always obtains the same limiting ee.

Reaction Proceeding through Chiral Intermediates

In our earlier paper we assumed that the intermediate radical or ion pair is achiral. It is more likely, however, that the intermediate is chiral. There are various schemes

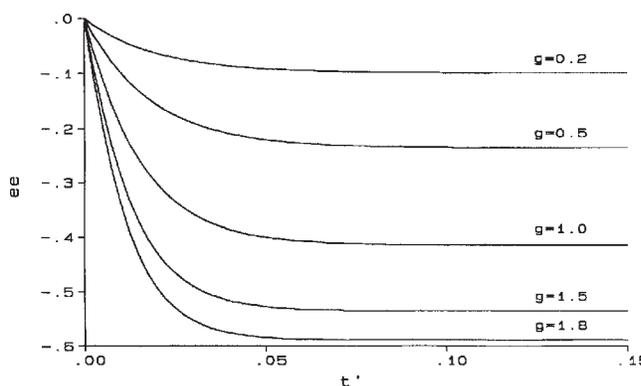


Fig. 2. ee vs. t' in units of $\text{sec}/(k_2 + k_2')$ for the reaction scheme in equation with $2k_1/(k_2 + k_2') = 0.5$ and g varied from 0.2 to 1.8.

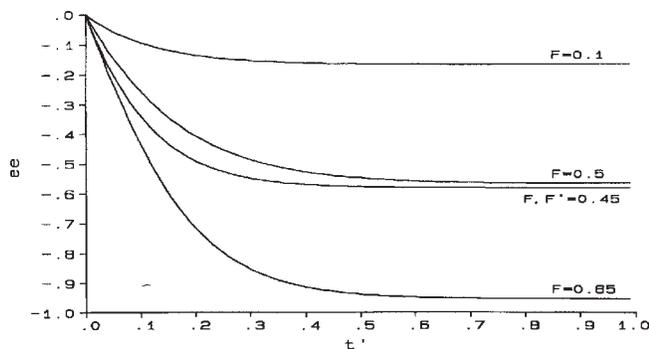


Fig. 5. ee vs. t' in units of $\text{sec}/(k_1 + k'_1)$ for reaction scheme equation 35 with $F' = 0.45$ while F is varied.

but larger at longer times. The effect that viscosity will have on this system is thus hard to predict. Viscosity will influence F because it involves the components of I_R and I_S diffusing into the bulk solvent. Viscosity may not influence F' , however, because this involves the interconversion of R and S without diffusion of their components diffusing into the bulk solution.

CONCLUDING REMARKS

In any asymmetric synthesis initiated with circularly polarized light which involves recovery of reactant, it is clearly desirable to maximize both ee and the amount of recovered reactant. For a reversible reaction, the reactant is not consumed, thus, ee reaches its maximum value at $t = \infty$. Unfortunately, this usually occurs at $ee = -g/2$. For an irreversible reaction this is seemingly impossible, because ee ($= [R - S]/[R + S]$) increases as a function of time while recovered reactant ($[R + S]$) decreases. One plausible way to handle this situation is to maximize the product of these two functions which is, of course, $[R - S]$. The greatest disparity between R and S normally occurs when ee is also equal to $-g/2$. This analysis shows that there is no mathematical way to find an

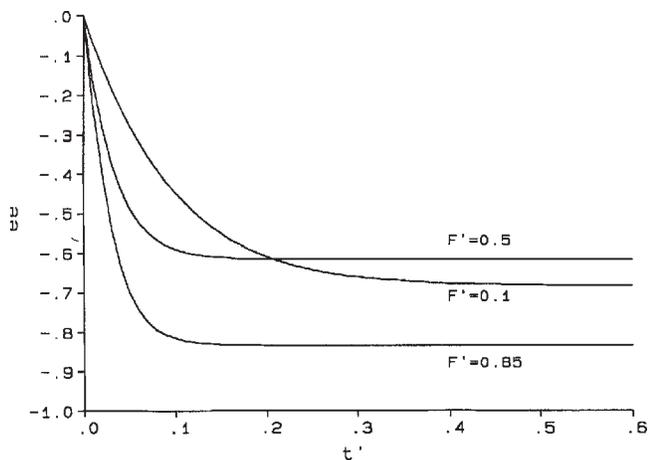


Fig. 6. ee vs. t' in units of $\text{sec}/(k_1 + k'_1)$ for reaction scheme in equation 35 with $g = 1.0$ and $F = 0.1$ held constant while F' is varied.

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acceptable compromise between ee and the recovered reactant and that an empirical approach is likely to be required. For example, it may be acceptable to obtain an ee of -0.90 and a recovery of 5–10% of starting material if alternate synthetic procedures are not available.

More can be done, however. Because g is so dominant in determining the size of ee , it is important to maximize g by careful selection of wavelength. Doubling the value of g will have a pronounced influence on the value of ee . When F values (which are partly viscosity dependent) are involved, it may be worthwhile to study the photoreaction as a function of temperature in a given solvent, because viscosity is temperature dependent, or in several solvents of similar polarity but of varying viscosity. Because quantum yields often appear in the mathematical expressions of ee as a function of time, it may be appropriate to vary the temperature of the photoreaction because quantum yields may also be temperature dependent.

There is also a potentially significant way to improve the ee greatly by considerably increasing the value of g . Shimizu has studied the photochemistry of racemic tartaric acid and several amino acids with very intense circularly polarized light generated from a XeF excimer laser.^{20–23} For example, with tartaric acid, which undergoes a two-photon photochemistry, one enantiomer is consumed while the other is unaffected when left-handed circularly polarized light is used while the opposite is observed when right-handed circularly polarized light is used.^{20–22} Similar behavior is seen with the amino acids.²³ These observations are only possible if the multiphoton g values of the substrates are very large and approaching their maximum values of 2. If Shimizu's observations are general, this will revolutionize asymmetric synthesis with circularly polarized light. Further research in the use of intense circularly polarized light in asymmetric synthesis is warranted.

Even if photochemistry initiated with circularly polarized light never becomes a general tool in asymmetric synthesis, it still may prove useful for proving reaction mechanisms. Different mechanisms will yield different ee -versus-time behaviors. Matching the theory to experiment will then reinforce one mechanistic pathway at the expense of others.

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