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Is Circularly Polarized Light an Effective Reagent For Asymmetric Synthesis?

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Abstract: Photoreactions initiated with circularly polarized light (CPL), which exists in left-handed and right-handed forms and is easy to prepare, has had limited success in asymmetric synthesis although they may model the pre-biotic origin of optically active molecules on the earth. Other approaches including multiphoton excitation with CPL may prove more successful in asymmetric synthesis.

Keywords: Circularly polarized light, asymmetric synthesis, multiphoton excitation.

INTRODUCTION

One of the great triumphs of modern organic synthesis is the ability to carry out most non-photochemical reactions involving stereogenic centers with high enantiomeric excesses. One of the recent Nobel Prizes in Chemistry was awarded to three pioneers in this field [1]. Photochemical reactions have proven more problematic in this regard because many of them proceed through achiral intermediates. Nonetheless, successes are known and are becoming more common. If the substrate, for example, is optically active, the photoproduct may be partially [2] or completely [3] optically pure. Photolysis of substrates in chiral environments, such as zeolites containing optically active amines [4], often yields optically active products. The photochemistry of optically active crystals has led perhaps to the greatest success in asymmetric synthesis [5]. Surprisingly, the use of left- and right-handed circularly polarized light, which is chiral and easy to prepare, in asymmetric photochemistry has had sustained interest, but limited success. What is circularly polarized light? Why is there intense interest in it? Why has it not typically been useful in asymmetric photochemistry? Are there any prospects that it can be used successfully in the future? These are the questions which will be addressed in this article. Recent research from our laboratory will highlight the article.

CIRCULARLY POLARIZED LIGHT [6]

In 1938, Niels Bohr introduced the concept of *complementarity* in order to explain certain inconsistencies in the new quantum theory. *Complementarity* asserts that a "complete" understanding of nature may require mutually exclusive (complementary) but necessary physical descriptions. Central to the idea of *complementarity* was the so-called wave-particle duality theory of light. In order to explain diffraction and interference of light it was then necessary to consider light to be a wave. On the contrary, the experimental discoveries of the photoelectric effect and Compton scattering along with observations of light interactions at very low light levels required a particle description of light. The currently accepted theory of light combines these two wave-particle concepts into a single "quantized electromagnetic field theory", i.e., Quantum Electrodynamics or QED. This theory is so complete that the QED is often referred to as Q.E.D. (*Quod erat demonstrandum*). A very readable and enlightening description of this theory is found in the Alix G. Mautner Memorial Lectures by Richard Feynman [7]. Thus, we will describe light as particles (photons) having no rest mass and always traveling at the speed of c in vacua and whose probabilities of observation are predicted by the quantum mechanical wave equation. However, in order to discuss polarization we will often revert to the wave description as a convenient mental crutch.

The massless photon has unit intrinsic spin and its spatial exchange properties are described as obeying Bose-Einstein (even spin) statistics. Photons moving in a straight line at the speed c carry a spin angular momentum $\pm\hbar$ depending upon the projection of the intrinsic spin upon the direction of propagation. Thus a single photon can be thought of as having "right-" or "left-" handed helicity and can alternately be called right- or left-circularly polarized light (CPL). Unpolarized light, which is often called natural light, can be viewed as an equal (racemic) admixture of these circularly polarized photons. Linearly polarized light (LPL) consists of an electromagnetic wave in which the E vector is confined to a spatially fixed plane, the plane of vibration. The wave vector changes direction randomly and rapidly for unpolarized light. Linearly polarized light results when there is a definite phase relationship between left- and right-circularly polarized beams. When LPL passes through a sample of resolved enantiomers, one component of the CPL may exhibit a greater speed than the other component because the real part of the refractive indicies, n_L and n_R, of the left- and right-CPL can be different. This difference gives rise to optical activity (rotation of the polarization of the LPL). The angle of rotation of LPL light with wavelength λ passing through a length l of sample is equal to $(n_L - n_R)\pi l/\lambda$. The rotation of the plane of polarization of the light can be either clockwise (dextrorotary, +) or counterclockwise (levorotary, -) with respect to a viewer looking at the light source. The imaginary parts of the refractive index describe the absorption of light and the absorption of right- and left-CPL may be different for an enantiomer and its mirror image. This gives rise to circular dichroism, a difference in

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the absorption of RCPL and LCPL as a function of the photon energy. Thus the passage of LPL through an optically active material may result in both optical rotation and the production of a partial imbalance of RCPL and LCPL (i.e., elliptically polarized light). The energy absorbed by the molecule may be re-radiated to a lower energy state of the molecule or the excitation may induce a distinct change in its molecular structure. The molecule may dissociate or revert to another isomeric form including a possible inversion into its mirror image. It is these changes that address the question in the title of this article "Is circularly polarized light an effective reagent for asymmetric synthesis?". The Holy Grail in this field is the efficient photoconversion of one enantiomer into its mirror image with minimal destruction of either enantiomer of the starting racemic mixture.

There are many experimental tools for the preparation of circularly polarized light. We will briefly summarize the standard methods used in many studies involving circular dichroism. In doing so we will rely upon the wave theory of light to describe these methods. A quarter-wave plate consists of a thin sheet of material in which the speed of light of one component of linearly polarized light possesses a different speed than its perpendicular component. If the plane of polarization of LPL is aligned 45° with respect to the optical axis, one component can be retarded or advanced relative to the other. If the thickness of the sheet is chosen to advance (retard) one wave by a relative distance of one-quarter wavelength of the light RCPL (LCPL) can be produced. Using this method a specific quarter wave plate (i.e., thickness) is required for each wavelength. The Soliel-Babinett compensator alleviates this problem by providing two sliding wedges whose thickness can be adjusted to give one-quarter wavelength retardation for any desired wavelength. Finally, the most useful device consists of a single Fresnel rhomb in which the plane of polarization of linearly polarized light is adjusted to + 45° with respect to the optical axis of the Fresnel Rhomb to produce RCPL. Rotation of the plane of polarization of the incident LPL to -45° results in LCPL. This method will produce CPL for a wide range of wavelengths. The only disadvantage is that the propagation direction of the CPL is displaced from that of the incident light after passing through the Fresnel Rhomb.

HOMOCHIRALITY

All living things have one very interesting and fundamental property in common, and that is, they are made up predominantly of single enantiomers of sugars, amino acids, and other molecules. When molecules have the same relative configuration, they are said to be homochiral. Because the pre-biotic world was almost certainly made up of achiral and racemic molecules, it is an interesting question of how the preponderance of one enantiomer over the other came about on the earth. This, in fact, is one of the great unanswered questions in all of science. Not surprisingly, there has been intense interest in this topic and a plethora of often poorly tested suggestions have been offered on how this may have occurred [8-10]. This is not the place to discuss this issue in detail. Suffice it to say that photoreactions initiated with circularly polarized light represent a plausible mechanism for the origin of specific homochirality [11,12]. There are two issues which must be resolved before this suggestion is viable: (1) Where did circularly polarized light originate in the pre-biotic world [13]? and (2) Do photoreactions initiated with circularly polarized light afford resolved optically active products?

PHOTOREACTIONS INITIATED WITH CIRCULARLY POLARIZED LIGHT

Kagan was the first to show theoretically the difficulties one may encounter in carrying out asymmetric synthesis using photoreactions initiated with circularly polarized light [14,15]. Because of what will be described later, it is important for the reader to understand what these difficulties are. Consider the hypothetical case of a racemate R/S undergoing a photochemical reaction with left-handed circularly polarized light. Because the enantiomers have slightly different extinction coefficients (ε_R and ε_S), one enantiomer of the racemate will react faster than the other, thus leaving the substrate enriched in the less reactive stereoisomer. It can be easily shown that the enantiomeric excess of recovered substrate goes to 100% as the amount of substrate goes to nearly zero. This is obviously an undesirable situation. A similar analysis also applies to any chiral product produced in the reaction. The feature of the system that matters most is the anisotropic g value which is defined as $g/2 = (\varepsilon_R - \varepsilon_S)/(\varepsilon_R + \varepsilon_S)$, with g having values between 0 and 2. To obtain the optimum resolution one wants a large g value. This is rarely the case because the numerator in the expression is almost always small and the denominator may be large.

$$R \xrightarrow{\varepsilon_R} P$$

$$S \xrightarrow{\varepsilon_S} P'$$

Imagine now a system in which the enantiomers interconvert photochemically using circularly polarized light. Because R and S have different extinction coefficients, there will be an imbalance in the amounts of the enantiomers once the photostationary state has been attained. Although R and S are not consumed in the process, which is desirable, the results are still not satisfactory since the enantiomeric excess of recovered substrate will be small because, as in the previous case, the g value is usually very small.

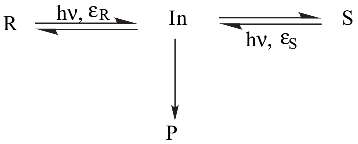
$$R \underset{\varepsilon_S}{\overset{\varepsilon_R}{\rightleftharpoons}} S$$

There have probably been no more than four or five score of photoreactions initiated with circularly polarized light reported in the literature. Almost without exception the enantiomeric excess of photoproduct or recovered reactant has been low for the reasons detailed above. A few examples illustrate this clearly. Kagan, for example, has shown that photodegradation of camphor with circularly polarized light to 99% completion yields recovered camphor that is 20% optically pure [14]. Bonner [16] and Inoue [17] have both investigated the photodegradation of amino acids and have obtained low enantiomeric excess of recovered substrate. Photoequilibration of *cis*- and *trans*-cyclooctene with circularly polarized light yields the chiral *trans*-cyclooctene with very low optical purity [18]. Photodegradation or photoequilibration of ketones in general affords low enantiomeric excesses of substrate and/or product [19-22]. Michl and coworkers have photolyzed 1-azidoadamantane with circularly polarized light in a low temperature matrix and obtained a chiral cyclic imine having 2% optical purity [23].

Although the above results clearly point out the difficulties of carrying out asymmetric synthesis with circularly polarized light, there have been some attempts to amplify the low enatiomeric excesses [9]. Of particular note are the experiments of Soai and coworkers where slightly enriched (1%) amino acids have been used to dramatically amplify the optical purity of products deriving from reactions of aldehydes with diethylzinc; added valine, for example, afforded an alcohol product which was 51% optically pure [24].

REACTIONS PROCEEDING THROUGH RADICAL PAIRS AND ION PAIRS

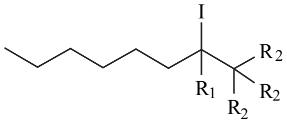
It is desirable to have a reaction with the features of the irreversible and reversible systems described above, i.e. high enantiomeric excess of the irreversible system and no loss of substrate of the reversible system, and hopefully possessing few of their undesirable features, i.e. loss of substrate of the irreversible system and low enantiomeric excess of the reversible system. A plausible scheme where this may occur is illustrated below. Here the R and S enantiomers equilibrate through an achiral intermediate (In) such as a radical or ion pair and the intermediate in turn reacts to give product(s). We may define F as the fraction of the intermediate which goes on to product. If the components of the intermediate diffuse apart and into the bulk solvent, F should depend on the viscosity of the medium. Furthermore, the enantiomeric excess of recovered substrate should depend on F and thus viscosity. We have modeled this reaction scheme mathematically and indeed the enantiomeric excess depends on F, as well as time and the anisotropic g value [25].



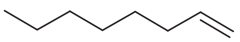
The relationship between F and the viscosity was explored by examining the photochemistry of racemic, optically active, and deuterated 2-iodooctane under four conditions: in the gas phase, and in liquid mixtures with cyclopentane, methanol, and 2-methyl-2-propanol [26]. The gas phase has no viscosity while cyclopentane and methanol have similar viscosities at room temperature but vastly different polarities; and 2-methyl-2-propanol is non-polar, but considerably more viscous. Photochemistry in the gas phase and liquid phases, cyclopentane, and 2-methyl-2-propanol, proceeded exclusively through radical pairs and afforded octane, 1-octene, *cis*- and *trans*-2-octene, meso- and racemic 7,8-dimethyltetradecane, the dimers of the 2-octyl radical, HI and I_2, the dimer of I•. In methanol, on the other hand, between 50% and 80% of the reaction proceeded through an ion-pair intermediate and afforded, in addition to the products already mentioned, predominantly 2- and 3-methoxyoctane. Some 2-octyl carbene is formed in methanol but not in the other phases.

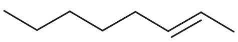
A simple mechanism accounts for these results. Photoexcitation of racemic 2-iodooctane through an n to σ^* transition around 270 nm results in rapid homolysis of the carbon-2 iodine bond to produce, at least in fluid solution, a radical pair. The radical pair can revert back to either enantiomer of the reactant, react internally to make the octenes and HI, or its components, the 2-octyl radical and iodine atom, or diffuse apart into the bulk solution where octane, 7,8-dimethyl-tetradecane, and I_2 are produced. In the very polar medium methanol, the radical pair can also undergo electron transfer to form an ion pair consisting of the 2-octyl cation and iodide which can revert back to reactant, react internally to make the octenes and HI, and diffuse apart to yield 2-methoxyoctane via reaction of the carbocation with methanol. The 3-methoxyoctane product arises through reaction of the 3-octyl cation, formed by 1,2-hydride shift of the 2-octyl cation, with methanol.

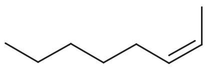
The F values were determined by comparing the rate of disappearance to the rate of racemization of the optically active substrate. As seen in (Table **1**), the magnitude of F does not correlate with the viscosity of the medium. This is a consequence of the fact that the two components in the radical/ion pair can react internally to form products (octenes and HI) and diffuse apart to form products such as the dimers, 7,8-dimethyltetradecane and I_2. Interestingly, the yields of the dimers do appear to correlate with viscosity (Table **1**).

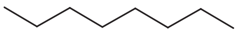


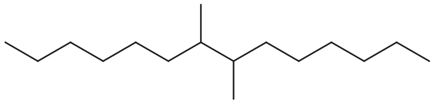
1a $R_1 = R_2 = H$
1b $R_1 = D, R_2 = H$
1c $R_1 = H, R_2 = D$



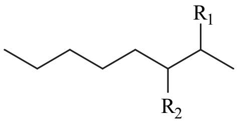








meso and dl



$R_1 = OCH_3, R_2 = H$
$R_1 = H, R_2 = OCH_3$

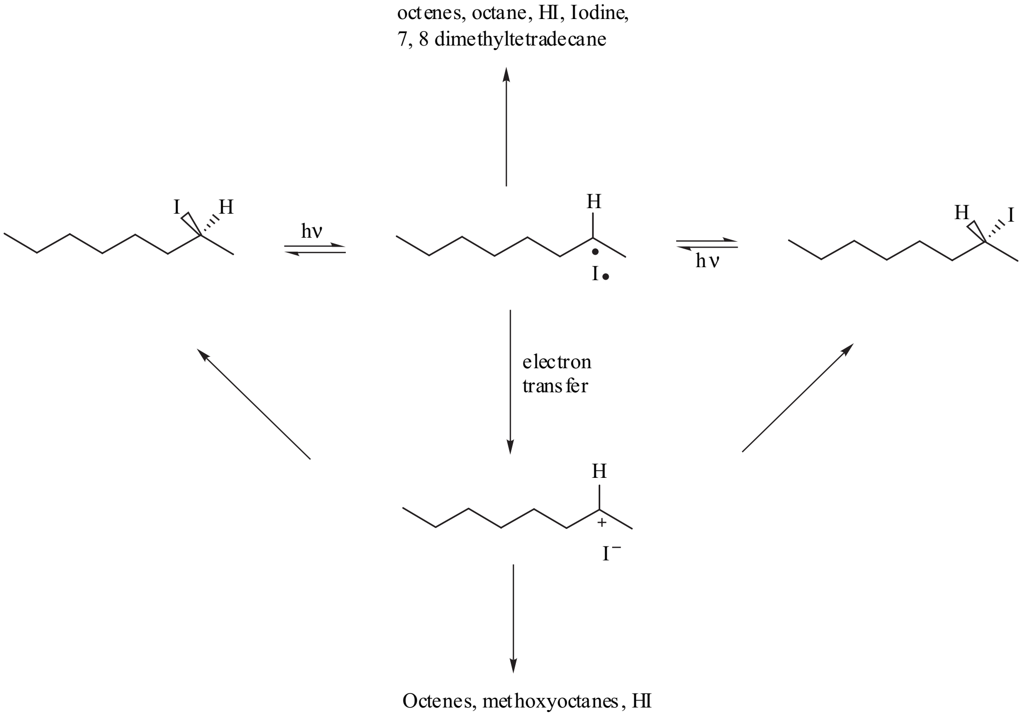


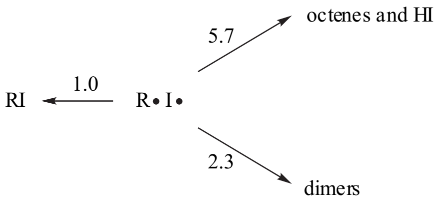
Table 1. Comparison of Viscosity to F and Yields of Dimers

Phase	Viscosity/cp (25%)	F	% yield	
			7, 8-dimethyltetradecane	I_2
Gas	0	1	63	76
Cyclopentane	0.416	>0.80	18	45
Methanol	0.551	0.60	3	3
2-methyl-2-propanol	4.438	0.74	0	2

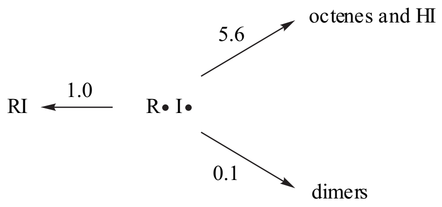
It is possible to compare the F values of cyclopentane and 2-methyl-2-propanol with the corresponding yields of dimers and arrive at the relative reactivity of three reactions which the radical pair can undergo: reform the 2-iodooctane, react internally to form octenes and HI, and reaction externally via diffusion to form dimers [27]. This was not attempted for the gas phase because a genuine radical pair does not exist there and methanol where both radical and ion pairs are involved in product formation. The relative reactivities are shown below and are quite informative. The two pathways of internal reaction, i.e. to reform 2-iodooctane and to yield octenes and HI, have the same relative reactivities (1:5.7 for cyclopentane and 1:5.6 for 2-methyl-2-propanol) but quite different external reactivities (26% of the reaction of the radical pair in cyclopentane is external but only 1.5% in 2-methyl-2-propanol) which is a reflection of the quite different viscosities of the two media.

At least with the limited data in hand, the value of F depends on the phase in which the reaction is carried out, but does not correlate with the viscosity of the phase. Work currently in progress will determine F values for 2-iodooctane in the same phases described above but at different temperatures and new liquid phases. The behavior of other substrates such as mandelic acid which also reacts

CYCLOPENTANE



2-METHYL-2-PROPANOL

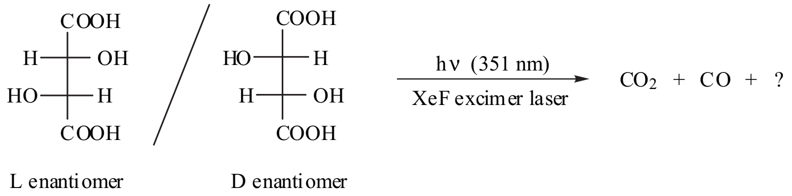


photochemically through radical pairs, but with far different F values, is also being explored.

MULTIPHOTON PHOTOCHEMISTRY WITH CIRCULARLY POLARIZED LIGHT

It is still not clear if one can alter F values enough through a change of phase in order to have a significant effect on the enantiomeric excesses of recovered substrate. Fortunately, there is another very promising approach to using circularly polarized light in asymmetry synthesis. This hinges upon the exciting results of Shimizu on the multiphoton photochemistry of racemic tartaric acid [28-30] and several amino acids [31] with circularly polarized light. The idea will be illustrated with tartaric acid.

When racemic tartaric acid in water is photolyzed with intense 351-nm light from a XeF excimer laser, the substrate undergoes a two photon-induced decomposition to make carbon dioxide, carbon monoxide and other low molecular weight compounds. Tartaric acid does not exhibit a one-photon absorption band at 351 nm. When tartaric acid absorbs two 351-nm photons, this is equivalent to absorption of one 175.5 nm photon where the molecule does absorb. Although the selection rules for the absorption of two-photons are different from that of one-photon, there are available two-photon allowed electronic states in the region of 175.5 nm. From the data presented in Shimizu's papers one can conclude that, when right-handed circularly polarized light is used, the L enantiomer decomposes at a faster rate than does the D enantiomer, thus yielding a significant enhancement of the D enantiomer as the reaction proceeds. When left-handed circularly polarized light is used, the opposite is seen, i.e. the D enantiomer decomposes much faster than the L. One may surmise that the two-photon anisotropic g value for tartaric acid at 351 nm must be close to its maximal value of 2. Similar results were observed by Shimizu in the multiphoton photochemistry of several amino acids in water [31]. If other substrates have large g values under multiphoton conditions, this will result in a viable way of using photochemistry in asymmetric synthesis.



With Shimizu's results in mind, we examined the photochemistry of 2-iodooctane in methanol using 266-nm photons from a pulsed frequency quadrupled Nd-YAG laser [32]. The results are strikingly different than the one-photon results described earlier (Table **2**). First, none of the ionic products, 2- and 3-methoxyoctane, which dominated the one-photon photochemistry, were observed here. Second, no octane, 7,8-dimethytetradecane, and I_2, the products from the 2-octyl radical and iodine atom reacting in bulk solution, are formed. Third, none of the observed products, 1- and *cis*- and *trans*-2-octene, arose from the 2-octyl carbene. Fourth, F = 1 in contrast to its value of 0.60 observed under one-photon conditions. These results can be understood when it was determined from the power dependence that three photons are required to make the reaction occur.

One can formulate a simple mechanism to rationalize these results. After absorption of the first photon, 2-iodooctane undergoes homolysis in the picosecond time regime to make the 2-octyl radical/iodine atom radical pair. Because the intense 266-nm pulse of light is about 6 nanoseconds in duration, the 2-octyl radical can undergo a two-photon excitation to produce what we chose to call an excited state radical pair from which the observed products are generated.

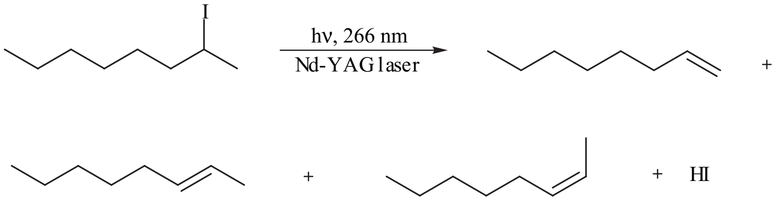


Table 2. Photolysis of 2-Iodooctane in Methanol

	1-Photon	Multiphoton
% Ionic	50-80%	0%
2-Octylcarbene	Yes	No
Dimers	Yes	No
F	0.60	1.0
Power Dependence	1	3

$$\text{RI (R = 2-octyl)} \xrightarrow[\text{Nd-YAG laser}]{h\nu,\ 266\ \text{nm}} \text{RI}^*$$

$$\text{RI}^* \longrightarrow \text{R}\bullet\ \text{I}\bullet$$

$$\text{R}\bullet\ \text{I}\bullet \xrightarrow[\text{two photons}]{h\nu} [\text{R}\bullet\text{I}\bullet]^*$$

$$[\text{R}\bullet\text{I}\bullet]^* \longrightarrow \text{Products}$$

When the experiment was repeated with 266-nm circularly polarized light, the recovered 2-iodooctane was unfortunately optically inactive. Superficially this may be construed to negate the generality of Shimizu's results. This is not the case, however. Unlike the examples of Shimizu where the substrates were photolyzed at wavelengths where the substrates had no absorption bands, this example involved multiphoton absorption through the compound's n to σ^* band. It is the first photon which dictates how the enantiomeric excess of recovered substrate will evolve. Because 2-iodooctane has a very small g value at 266 nm, a low enantiomeric excess is to be expected. What is needed is to photolyze 2-iodooctane at wavelengths where it does not absorb. These experiments are currently being carried out.

The application of multiphoton circular dichroism offers many potential advantages to the photoproduction of enantiomeric excesses. Circular dichroism effects are generally larger at higher energies where absorption cross-sections are larger. These larger cross-sections make it difficult to penetrate the medium as well as to transmit through the containment vessel. Two- and three-photon excitation processes can overcome these limitations. In addition the absorption of two photons offers access to new parity forbidden transitions not allowed under one-photon absorption. Also, circular dichroism in bound-bound transitions is a result of the magnetic dipole interaction whereas circular dichroism in bound-free transitions (ionization) involves the stronger dipole transitions. The field of multiphoton optical activity, optical rotary dispersion (MPORD) and circular dichroism (MPCD), is essentially in its infancy. Intensity dependent ORD was first predicted in 1968 by Atkins and Barron [33]. Unfortunately, there have been only two experimental reports of MPORD. In 1987, Gedanken and Tamir [34] observed a decrease in the optical rotation with increasing laser power for 10% aqueous solutions of (+)- and (-)-camphorsulfonic acid in the region of 460 nm which, from the power dependence, they ascribe to a three-photon process. Ten years later, Cameron and Tabisz [35] reported a two-photon optical rotation for uridine and sucrose which also show a decrease in optical rotation with increasing laser power for a focused 308 nm excimer laser. Hache *et al.* [36] have reported experimental evidence of a third-order nonlinear circular dichroism in liquid ruthenium(II)tris(bipyridyl). They observe a maximum in the CD at ~ 475 nm of 1.25×10^{-2}. They define a parameter K which is a measure of the magnitude of the MPCD. Interestingly, they find K to be a minimum at the maximum in the CD. Naguleswaran *et al.* [37] as well as Hache *et al.* [36] show that for this case, the pure electric-dipole mechanism can give larger contributions than the standard electric-dipole-magnetic dipole interaction mechanism. Circular dichroism involving bound-continium transitions (e.g., ionization) can be large as predicted by Ritchie [37] in 1976. The CD for the angular distributions (CDAD) of the outgoing electrons is derived purely from an electric dipole interaction and asymmetries as large as 10 to 80% have been reported [38,39]. Finally, but perhaps most importantly, single-photon ionization CD of nanoparticles consisting of chiral molecules has been reported [40] to be as large as 10%. All of these studies provide considerable hope that multiphoton excitation techniques may provide new and more efficient routes to asymmetric resolution.

Before concluding, we briefly refer to recent theoretical ideas concerning possible new routes toward asymmetric synthesis. Fujimura *et al.* [41] have proposed the selective preparation of enantiomers by means of optimal, elliptically polarized, infrared laser pulses. In this study of laser-driven molecular dynamics, the torsional motion of the hydrogen atom in H_2POSH along the path from one enantiomer to its mirror image is considered. Preparation of 100% pure enantiomer from a 50:50 racemic mixture was obtained. A second study considered the separation of enantiomers using ultraviolet laser pulses in H_2POSH [42]. The calculations showed that it would be possible to prepare pure enantiomers from an initial racemate using five *linearly* polarized pulses in the sub-picosecond time period. In another area of research, the basic theories of "coherent control" [43] have also been applied to asymmetric resolution by Brumer *et al.* [44] to consider phase-selective transfer of a racemic mixture into the pure R or S enantiomeric form. In a separate study these authors [45] also showed that preferential production of a chiral photofragment can occur even though the parent molecule is not chiral. To our knowledge, there has been no experimental verification of these exciting possibilities.

MAGNETOCHIRAL PHOTOCHEMISTRY

A static magnetic field does not provide a chiral environment in which to carry out reactions. The combination of a magnetic field and unpolarized light colinear with the field, however, does [8]. A photoreaction carried out under such circumstances has been shown to result in optically active products.

The enantiomers of $K_3Cr(oxalate)_3$, octahydral complexes of Cr(III), equilibrate both thermally and photochemically [46]. When racemic $K_3Cr(oxalate)_3$ in water is subjected to circularly polarized light a partial resolution of the compound results [46]. When the photoreaction is carried out with unpolarized light colinear to a strong magnetic field in which the aqueous solution resides, the substrate becomes slightly optically active [47]. The real significance of this result is not its applicability in asymmetric synthesis, which seems nil, but a possible mechanism for the origin of homochirality in the pre-biotic world [48]. However, it is generally believed that the Earth's magnetic field is too small to have produced an enantiomeric advantage factor sufficient to influence the production of homochirality of biological molecules. Magnetic fields in extraterrestrial environs however could be considered.

CONCLUSIONS

Photoreactions initiated with circularly polarized light will generally yield optically active recovered reactants and products, but with very low optical purity. It may be possible to control the optical purity of products formed in reactions involving radical and ion pairs by manipulation of solvent viscosity. The most promising approach, however, involves multiphoton photochemistry using circularly polarized light. Hopefully, other innovative approaches will be developed as well.

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