Synchronous enantiomeric enrichment of both reactant and product by absolute asymmetric synthesis using circularly polarized light. Part 1.[1] Theoretical and experimental verification of the asymmetric photoisomerization of methyl norbornadiene-2-carboxylate to methyl quadricyclane-1-carboxylate †

Hideo Nishino, Asao Nakamura and Yoshihisa Inoue *

*Inoue Photochirogenesis Project, ERATO, JST, 4-6-3 Kamishinden, Toyonaka, 560-0085, Japan*

We propose a new absolute asymmetric synthesis (NAAS), in which the irradiation with left- or right-handed circularly polarized light (CPL) of a racemic reactant leads to the synchronous enantiomeric enrichment of both reactant and product. NAAS has two subcategories: (a) reversible NAAS (CPL excites both the reactant and the product), (b) irreversible NAAS (only the reactant is excited by CPL). Here in the first paper of this series of papers we consider irreversible NAAS. We have deduced the theoretical equations that determine the relationship between the enantiomeric excesses (ee's) of both reactant and product and the progress of the CPL-induced photoreaction. Using the clear and reversible photoisomerization of chiral methyl norbornadiene-2-carboxylate (**I**) to chiral methyl quadricyclane-1-carboxylate (**II**) by CPL-irradiation in acetonitrile, we experimentally verified the equations. The ee's of both reactant and product are remarkably dependent on the anisotropy factor ($g = \Delta\varepsilon/\varepsilon$) of the reactant. The ee of the reactant increases to 100% if the irradiation is continued to the stage that nearly all of the reactant is consumed. Conversely, the ee of the product gradually decreases from $g/2$ during the initial stages to zero at the final stage of the irradiation. This is the first time that the relationship between the ee of product and the progress of the photoreaction is experimentally examined based upon theoretical considerations.

The asymmetric synthesis of chiral compounds has become important in modern chemistry, as optically pure compounds are among other things, biologically active, playing vital roles in pharmacological and agrochemical processes. Many attempts have been made to obtain optically active materials using circularly polarized light since le Bel[2] and van't Hoff[3] recognized the potential usefulness of left- and right-handed circularly polarized light (*l*- and *r*-CPL) in the late 19th century. Using CPL to obtain optically active materials is a type of "absolute asymmetric synthesis," wherein asymmetric induction is brought about through preferential excitation of one of the enantiomers in a racemic mixture using *l*- or *r*-CPL irradiation. The degree of preferential excitation is determined by the anisotropy factor, also known as the *g* factor, which was defined by Kuhn[4,5] as the normalized difference in molar extinction coefficients between optical isomers toward *l*- or *r*-CPL at a given wavelength, eqn. (1), where ε_R and ε_S are the molar extinction

$$g = |\varepsilon_R - \varepsilon_S|/\varepsilon \qquad (1)$$

coefficients of each enantiomer towards *l*- or *r*-CPL, $\varepsilon = (\varepsilon_R + \varepsilon_S)/2$ and $0 \leq g < 2$.[4–9]

Absolute asymmetric syntheses (AAS) have been classified into three categories according to the manner of enantio-differentiation, these being (a) asymmetric photodestruction, (b) photochemical deracemization, and (c) photochemical asymmetric fixation.[7–10] In asymmetric photodestruction, each enantiomer in a racemic reactant is destroyed photochemically according to the degree of preferential excitation by *l*- and *r*-CPL at a given wavelength, Scheme 1. Here the enantiomer
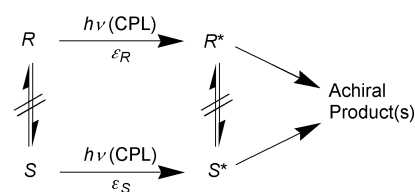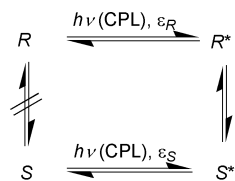

Scheme 1 Asymmetric photodestruction.

which is less able to absorb the *l*- or *r*-CPL undergoes lower photodestuction, thus increasing the ee of this reactant, as the antipode is preferentially destroyed to achiral product(s). In this type of AAS, the photochemical process is irreversible, and the enantiomers do not interconvert. There have been many reports concerning asymmetric photodestruction,[7] typical examples being the photodestructions of camphor and *trans*-bicyclo[4.3.0]nonan-8-one.[11]

Kagan provides us with a theoretical examination of the evolution of the ee by photodestruction of a racemic sample using *l*- or *r*-CPL.[6,12] If the photodestruction product is also chiral, the evolution of the optical purity of both the reactant and the decomposition product is expected to proceed simultaneously. However, a theoretical and experimental study of this scenario has not been performed.[6,12]

In photochemical deracemization processes,[7–9,12] by definition the combined enantiomer concentration does not change during the photoreaction and the process is photochemically reversible. The shift of the photochemical equilibrium between the enantiomers occurs through CPL-induced enantioselective excitation, as shown in Scheme 2. This is a photoresolution process, and does not produce a new product. There are some reports concerning photochemical deracemization processes of, for example, transition metal complexes,[13,14] and to the best of our knowledge there are only a few descriptions of

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Scheme 2 Asymmetric photoderacemization.

organic compounds which undergo exclusive photoderacemization.[10,15–17] Indeed, the enantiomeric isomerization of many organic compounds is often accompanied by side reactions.[18]

The photochemical process of asymmetric fixation is very similar to asymmetric destruction as shown in Scheme 3. Here, a
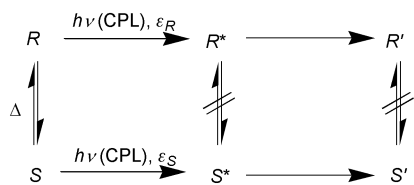


Scheme 3 Photochemical asymmetric fixation.

thermal racemization of the reactants occurs, and an enantioselective photoreaction, induced by *l*- or *r*-CPL, then leads to optically active products.[7] When the thermal racemization of the reactant is absent, this becomes an asymmetric photodestruction process. The *R/S* ratio of the product is equal to the ratio of the molar extinction coefficients, $\varepsilon_R/\varepsilon_S$. There are a few examples of photochemical asymmetric fixation, with the oxidative photocyclization of 1-(2-benzo[*c*]phenanthryl)-2-phenylethylene to hexahelicene, *via* dihydrohexahelicene, and the photocyclization/hydrogen migration of *N*-methyl-*N*-arylenamines to *N*-methyldihydroindoles in this category of AAS.[19,20]

In this paper, we propose a new absolute asymmetric synthesis (NAAS) induced by CPL as shown in Scheme 4, in which
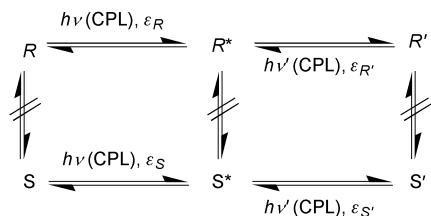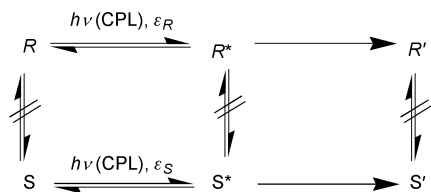
Scheme 4 Reversible (a) and irreversible (b) new absolute asymmetric synthesis (NAAS), where both reactant and product are chiral.

the reactant is chiral and the product is also chiral. The reactant and the product are photochemically interconvertible, and the enantiomers do not racemize either photochemically or thermally at ambient temperature. The product is not the stereoisomer of the reactant. This renders the NAAS different from all previously described absolute asymmetric syntheses. It is predicted that enantiomeric enrichment will occur in both the reactant and the product.

A closer inspection reveals that there are two subcategories of NAAS, as follows; in class (a) a photochemical equilibrium between the reactant and the product(s) is established, because the reaction mixture is irradiated with CPL which is able to excite both of the components of the reaction (see Scheme 4b). In class (b), the reactant is excited by the CPL, but the product is not, thus as it cannot absorb the incident light it is rendered an irreversible process.

Burnham and Schuster have proposed in a recent paper a new AAS using the reversible photodestruction of 1,1′-binaphthylpyran.‡[21] The crucial difference between this AAS and the AAS proposed in this paper is whether or not the enantiomers racemize photochemically. In Schuster's AAS the enantiomers of the reactant racemize photochemically, but in our case the enantiomers do not racemize either photochemically or thermally at ambient temperature. The theoretical equations reported in the present paper are not applicable to Schuster's AAS.

Norbornadienes and quadricyclanes have been widely investigated, because the photoisomerization of norbornadiene to quadricyclane has a potential application as a solar energy storage system.[22–25] Quadricyclane is a highly strained cyclopropane–cyclobutane-fused compound, which can be prepared photochemically *via* an intramolecular [2 + 2] cycloaddition of excited norbornadiene. The reverse reaction is also possible with photolysis or thermolysis of quadricyclane leading to the recovery of norbornadiene.[22,26–28] The interconversions of some norbornadiene and quadricyclane derivatives are reported not to be accompanied by side reactions, and quadricyclanes are thermally stable at ambient temperature.[22,27] The asymmetric introduction of substituents renders the norbornadiene–quadricyclane system chiral, and thus, photoisomerization between chiral norbornadiene and quadricyclane using CPL irradiation should behave as an example of our proposed NAAS.

Curiously it has rarely been recognised that norbornadienes and quadricyclanes will have chiral properties when appropriately substituted, and the chiroptical properties of only a few chiral norbornadiene derivatives have been reported.[29,30] To the best of our knowledge, no optical resolution of chiral quadricyclane derivatives has to-date been reported. Moreover, no systematic investigations have been performed on the photochemical conversion between such chiral norbornadienes and quadricyclanes, and thus, the stereochemical consequences of such a photocyclization are not yet known.

In this study, the theoretical equations are formulated for the relationship between the reactant and product ee's and the conversion in the class (b) NASS, *i.e.* the one-way photoisomerization of a norbornadiene derivative to the corresponding quadricyclane. Thus, the chiroptical properties of methyl norbornadiene-2-carboxylate (**I**) and methyl quadricyclane-1-carboxylate (**II**) are reported, as are the stereochemical consequences of the photocylization of **I** to **II**. This is followed by details of the CPL induced isomerization of **I** to **II** (Scheme 5),
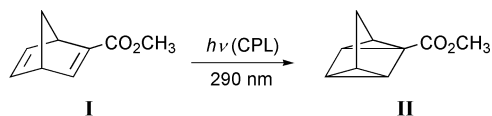
Scheme 5 Photoisomerization of **I** to **II**.

and discussion concerning the relationship between the ee of **I** and the conversion, and as well as the relationship between the ee of **II** and the conversion. This is the first report in which the focus is on the theoretical formulation of the relationship between the ee of the product and the conversion.

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‡ The IUPAC name for 1,1′-binaphthylpyran is 4*H*-benzo[*f*]naphtho-[2,1-*c*]chromene.

Results and discussion

Theoretical treatment

The relationship between the ee of the reactant and the conversion. The relationship between the ee of the remaining reactant, y, and the extent of the reaction, x, is described by the following equations [eqn. (2)–eqn. (4)], which were originally introduced

$$x = 1 - \frac{1}{2}\left\{\left(\frac{1+y}{1-y}\right)^{\frac{1}{2}+\frac{1}{g}} + \left(\frac{1+y}{1-y}\right)^{-\frac{1}{2}+\frac{1}{g}}\right\} \qquad (2)$$

$$x = 1 - (c_R + c_S)/(c_{R0} + c_{S0}) \qquad (3)$$

$$y = (c_R - c_S)/(c_R + c_S) \qquad (4)$$

by Kagan *et al.* for asymmetric destruction,[6,12] where c_R and c_S are the concentrations of (R)- and (S)- isomers of the reactant, respectively, c_{R0} and c_{S0} are the initial concentrations of the reactant isomers, and g is the anisotropic factor of the remaining reactant defined by eqn. (1).

The sign of g is naturally dependent on the helical sense of the CPL employed for excitation. Eqn. (2) is described for the excitation by r-CPL. If one uses l-CPL for excitation, g should be replaced by $-g$.

Eqn. (2) is based on the assumption that the consumption rate for each enantiomer of the reactant is proportional to ε for the CPL excitation. This assumption can be justified, if the absorbance of the solution is so low that the % absorption for the solution is nearly proportional to the concentration. (See Appendix 1 for details.)

Fig. 1a shows the dependence of the ee of the reactant on the conversion x upon CPL irradiation. The ee curves were calculated for reactants with various g factors using eqn. (3). In all cases, the ee of the reactant approaches 100% during the final stages of the reaction. Thus, **I** irradiated with l- or r-CPL at 290 nm, should ultimately obtain 100% ee of $(+)$- and $(-)$-**I**, respectively.

Relationship between the ee of product and the conversion. The ee for the product, y', is expressed in terms of y and x in eqns. (5) and (6), if the photocyclization is not accompanied by

$$y' = \frac{c_{R'} - c_{S'}}{c_{R'} + c_{S'}} = \frac{(c_{R0} - c_R) - (c_{S0} - c_S)}{(c_{R0} - c_R) + (c_{S0} - c_S)}$$
$$= \frac{(c_R - c_S)}{(c_{R0} + c_{S0}) - (c_R + c_S)} = -\frac{(c_R - c_S)/(c_R + c_S)}{(c_{R0} + c_{S0})/(c_R + c_S) - 1}$$
$$= -\frac{y}{1/(1-x) - 1} \qquad (5)$$

$$y' = -\frac{y(1-x)}{x} \qquad (6)$$

racemization or side reactions, where the notation R' and S' is used for the products of R and S in terms of reactant.

Fig. 1b shows the dependence of the product's ee on the conversion upon irradiation. The ee values were calculated for various reactants with differing g factors, putting them into eqn. (6), using the values of x and y which were calculated with eqn. (2). This simulation demonstrates that the ee of the product is $g/2$ during the initial stages of the reaction, ultimately approaching zero over the final stages. This is also
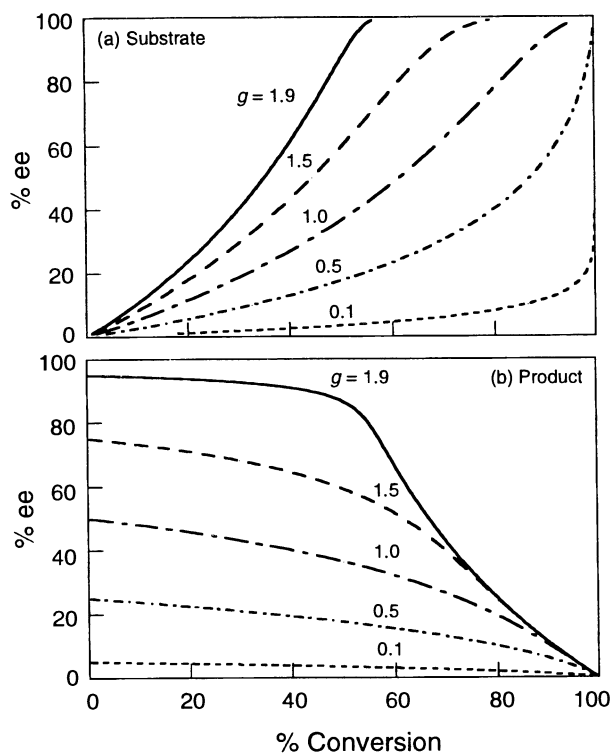

Fig. 1 (a) Simulated relationship between the ee of the remaining reactant and the conversion according to the reactant's g factor at the CPL irradiation wavelength. (b) Simulated relationship between the ee of the product and the conversion according to the reactant g factor at the CPL irradiation wavelength.

verified by the limiting value of y' as $x \to 0$ [eqn. (7)]. (See Appendix 2 for details.)

$$\lim_{x \to 0} y' = -\lim_{x \to 0} \frac{dy}{dx} = \frac{g}{2} \qquad (7)$$

Kagan *et al.* expected that the ee of the product should be $g/2$ during the initial stages of the CPL induced photodestruction.[6] However, the dependence of y' on x has not been described in the literature.

Fig. 1b also shows that, when the g factor is larger, the ee of the product falls sharply at the 50% conversion point, whereas a smaller g factor results in a decrease in ee only at the very final stage of the reaction, albeit that the initial ee is lower for smaller g factors.

Experimental verification

Chiroptical properties of I and II. The chiroptical properties of **I** and **II**, *i.e.* the CD and UV spectra and the g factor derived from these spectra, are shown in Fig. 2. All of the UV and CD spectra were measured in acetonitrile. Specific rotations ($[a]_D^{20}$) were also measured: $(-)$-**I**, -41.55 (c 0.0624 in acetonitrile), $(+)$-**II**, 322 (c 0.00375 in acetonitrile). §

Fig. 2a shows two absorption maxima at 229.5 nm and around 265 nm in the UV spectrum of $(\pm)$-**I**, although norbornadiene and methyl acrylate, which may be regarded as model compounds for **I**, do not have any absorption bands beyond 250 nm.[31,32] $(+)$-**I** and $(-)$-**I** show bisigned CD spectra over the 200–340 nm region (Fig. 2c). The g factors for $(+)$-**I** and $(-)$-**I** also exhibit two extrema in this region (Fig. 2e), indicating that the broad absorption in this region is composed of two bands.

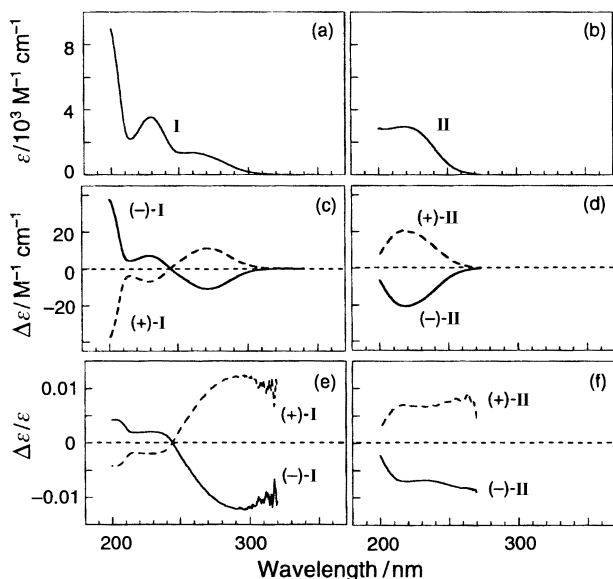§ $[a]_D$ Values are given in units of 10^{-1} deg cm^2 g^{-1}.

Fig. 2 Chiroptical properties of (+)- and (−)-**I** and (+)- and (−)-**II** in acetonitrile. These CD data are corrected to 100% enantiomeric excess using the results from chiral HPLC analysis.
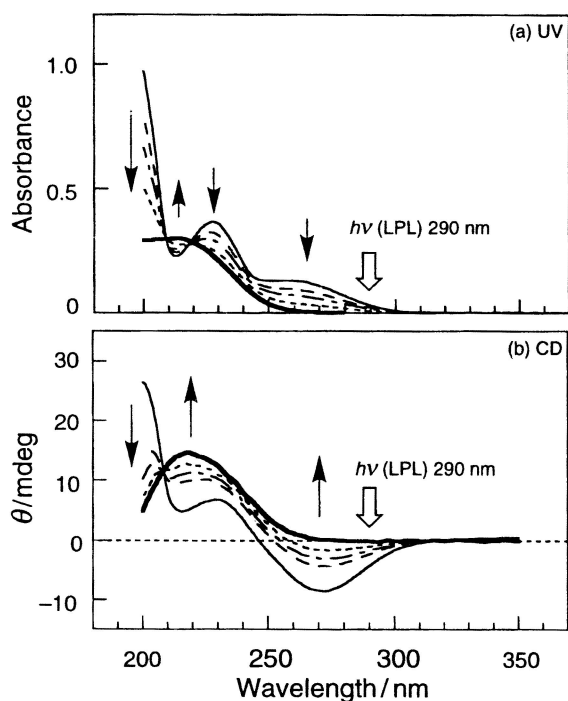

Fig. 3 Stereochemical consequences of photocyclization from (−)-**I** to (+)-**II** in acetonitrile. (a) Changes in the UV spectra when (−)-**I** (0.102 mM) was irradiated with LPL for 0 min (solid line), 3 min (broken line), 68 min (short and long broken line), 146 min (short broken line) at 290 nm. (b) Changes in the CD spectra when (−)-**I** (0.0236 mM) was irradiated with LPL for 0 min (solid line), 70 min (broken line), 105 min (short and long broken line), 165 min (short broken line) at 290 nm. The bold solid lines represent the UV and CD spectra of enantiopure (+)-**II**.

In contrast, the UV spectrum of (±)-**II** exhibits only one absorption maximum at 220 nm, which tails off until 270 nm. These spectral features are consistent with those of methyl cyclopropanecarboxylate (**MCP**), which do not show absorptions above 270 nm. The CD spectra of (+)-**II** and (−)-**II** also show a maximum at 217.5 nm, as shown in Fig. 1d, and it appears that the UV and CD absorptions are composed of a single band. Hence, the anisotropy factor shows an almost flat profile over the wavelength region.
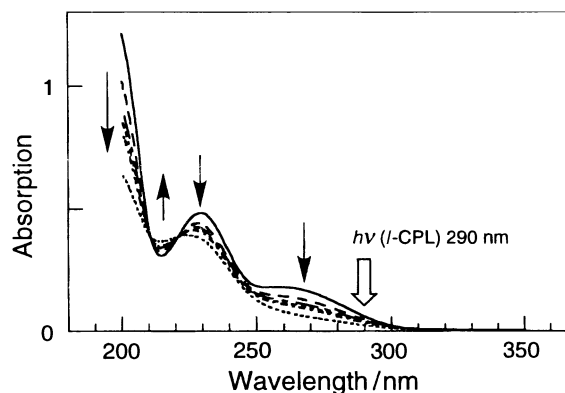
Fig. 4 UV spectral changes of the acetonitrile solution of racemic **I** (0.261 mM) irradiated with *l*-CPL for 0 min (solid line), 60 min (broken line), 90 min (short and long broken line), 105 min (short broken line), 200 min (short and dot line), 340 min (dot line) at 290 nm.
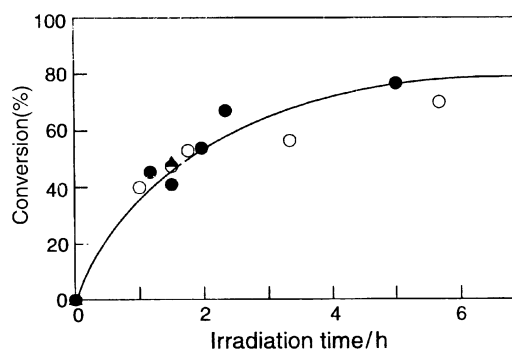

Fig. 5 Relationship between the % conversion and the irradiation time upon irradiation of the solutions of racemic **I** with *l*-CPL (○), *r*-CPL (●) and LPL (▲) at 290 nm.

The stereochemical consequence of photocyclization. The stereochemical consequences of photocyclization of **I** to **II** were examined for (−)-**I** using UV and CD spectroscopy, by irradiating with LPL at 290 nm, a wavelength at which **II** does not absorb.

Fig. 3a shows the evolution of the UV spectrum of an acetonitrile solution of (−)-**I** upon irradiation at 290 nm. The absorption bands for (−)-**I** at 228 and 256 nm slowly disappear and a new band appears at 215 nm, which is similar in shape to the UV spectrum of **II**. Two isosbestic points were observed at 209 and 218 nm during this irradiation.

Changes in the CD spectra of (−)-**I** upon irradiation at 290 nm are shown in Fig. 3b. Here, the CD extrema of (−)-**I** at 229 and 271.5 nm gradually diminished and a new extreme appeared at 215 nm, accompanied by an isosbestic point at 207 nm.

The changes in the CD and UV spectra are consistent with the complete photocyclization of (−)-**I** to (+)-**II** carried out at a wavelength where the product does not absorb the exciting light.

Asymmetric photoisomerization of racemic I with CPL. As demonstrated in Fig. 3a, a NAAS was carried out when (±)-**I** was irradiated at 290 nm with *l*-CPL (Fig. 4). The absorption band at 260 nm weakened in intensity, and two isosbestic points were observed in the UV spectra at 209 and 218 nm. Similar changes in the UV spectra were also observed when (±)-**I** was irradiated with *r*-CPL or linearly polarised light (LPL) at 290 nm.

Fig. 5 shows the relationship between the conversion and the irradiation time for (±)-**I**, irradiated with *l*- or *r*-CPL or LPL at 290 nm. The conversions were determined by the intensities of the UV absorption at 280 nm where only **I** absorbs light. Because all of the points fall on the same time–conversion
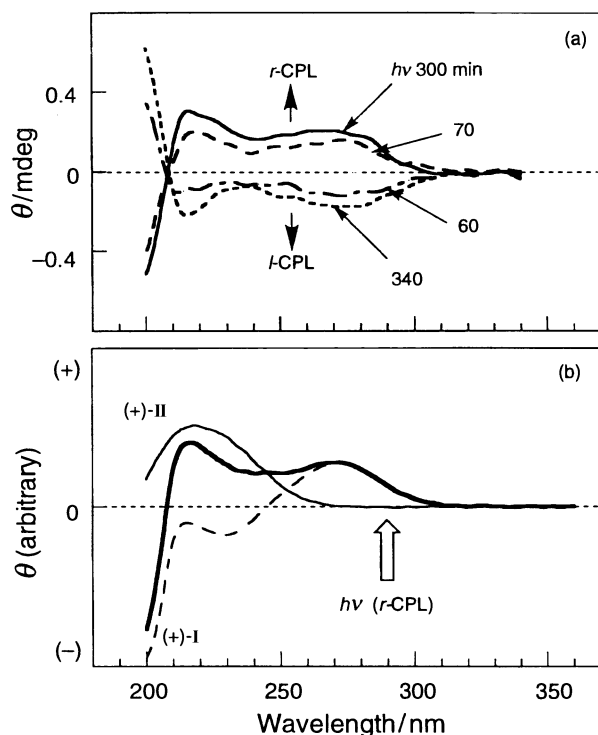
Fig. 6 (a) Typical CD spectral changes upon irradiation at 290 nm of the acetonitrile solutions of racemic **I** with *l*- and *r*-CPL. (b) The ultimate CD spectrum obtained upon *r*-CPL irradiation for 290 min was simulated by the sum (bold line) of the CD spectra of (+)-**I** (dashed line) and (+)-**II** (solid line).

Fig. 7 Development of the circular dichroism at (a) 280 nm and (b) 245 nm upon irradiation at 290 nm of racemic **I** in acetonitrile with *l*-CPL (○), *r*-CPL (●) and LPL (▲).

curve, it is likely that the intensities of the incident CPL and LPL were essentially identical.

The changes in the CD spectrum that arose when **I** was irradiated with *l*- and *r*-CPL at 290 nm are shown in Fig. 6a. The two peaks observed at 215 and 270 nm became more intense during the course of the irradiation. A simulated CD spectrum for the irradiation of (±)-**I** is given in Fig. 6b. It is predicted that (−)-**I** is preferentially excited with *r*-CPL at 290 nm, resulting in enrichment of (+)-**I**.

After measuring the CD spectra, the reaction mixtures were analyzed by GC, using a biphenyl added as an internal standard. The UV spectra and GC analysis showed that the total concentration of **I** and **II** was conserved after CPL irradiation, and no byproduct was detected, thus the photoisomerization of **I** to **II** in acetonitrile proceeds without any side reactions. The presence of isosbestic points in the UV spectra also supports a quantitative conversion.

It is well known that the photocyclization is a unimolecular reaction,[33] and thus the decrease in the concentration of **I** is always equal to the increase in the concentration of **II**. When a solution of **I** is irradiated with *r*-CPL at 290 nm, the CD spectra should be mixture of the CD spectrum of (+)-**I** and the CD spectrum of (+)-**II** at a ratio of 1 : 1. The spectra shown in Fig. 6b, which were generated based on this assumption, perfectly coincide with the experimentally obtained spectra (Fig. 6a).

The CD band at 280 nm, which is shown in Fig. 6a, reflects the enantiomeric enrichment of **I** when **I** is irradiated with CPL at 290 nm, where Δε of (+)- and (−)-**II** is zero, and the band at 220 nm reflects the simultaneous enantiomeric enrichment of **II** when **I** is irradiated with CPL at 290 nm. However, the enantiomeric enrichment of **II** was estimated from the CD extinction at 245 nm because the magnitude of the Δε of (+)- and (−)-**I** is zero at this wavelength.

Fig. 7 shows the relationship between the ellipticity at 280 nm and the irradiation time. The ellipticity at 280 nm first increases, and then levels out. However, the concentration of **I** changes during the irradiation. The concentration of **I** decreases
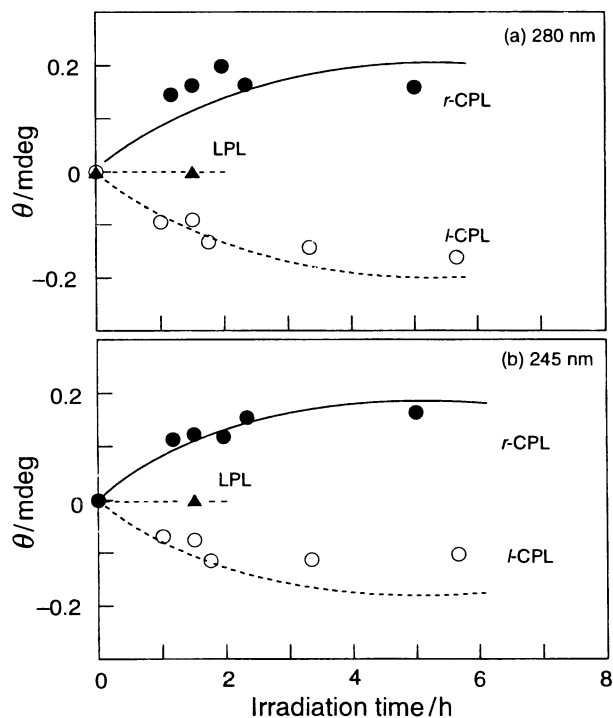
throughout the irradiation, as shown in Fig. 4. Therefore, we have to use the ee instead of the ellipticity for evaluating the development of the enantiomeric enrichment.

Here, we define the ee of the reactant **I** and the product **II** when the enantiomeric enrichment occurs by CPL irradiation. We have to do this because absolute configuration of the enantiomers of **I** and **II** has not yet been determined. We correlate (−)-**I** with (*R*)-**I**, (+)-**I** with (*S*)-**I**, (+)-**II** with (*R*)-**II**, (−)-**II** with (*S*)-**II**. Therefore we define the ee of **I** and **II** as given in eqns. (8) and (9), respectively.

$$(\text{ee of } \mathbf{I}) = \frac{[(-)\text{-}\mathbf{I}] - [(+)\text{-}\mathbf{I}]}{[(-)\text{-}\mathbf{I}] + [(+)\text{-}\mathbf{I}]} \qquad (8)$$

$$(\text{ee of } \mathbf{II}) = \frac{[(+)\text{-}\mathbf{II}] - [(-)\text{-}\mathbf{II}]}{[(+)\text{-}\mathbf{II}] + [(-)\text{-}\mathbf{II}]} \qquad (9)$$

The ee's of **I** and **II** were calculated using the values of the ellipticity and absorbance obtained from CD and UV measurements. The concentration of **I** was obtained by using the value of the absorbance at 280 nm, where **II** has no absorbance. The concentration of **II** was obtained by assuming no side reactions for the isomerization, eqn. (10), where $[\mathbf{I}]_0$ is the initial concentration of **I**.

$$[\mathbf{II}] = [\mathbf{I}]_0 - [\mathbf{I}] \qquad (10)$$

The optical purities (op's) are obtained using eqns. (11) and (12), where θ's are the ellipticity (mdeg) of the solution.

$$(\text{op of } \mathbf{I}) = \{\theta_{280}/33(\Delta\varepsilon_{280} \text{ of } (-)\text{-}\mathbf{I})\}/[\mathbf{I}] \qquad (11)$$

$$(\text{op of } \mathbf{II}) = \{\theta_{245}/33(\Delta\varepsilon_{245} \text{ of } (+)\text{-}\mathbf{II})\}/[\mathbf{II}] \qquad (12)$$

Throughout this study, the ee is assumed to be equal to the op. For the ee of **I** the values of the ellipticity at 280 nm were used, because Δε of (+)- and (−)-**II** is zero at this wavelength. For the ee of **II** the value of θ at 245 nm was used, because Δε of (+)- and (−)-**I** is zero at this wavelength.
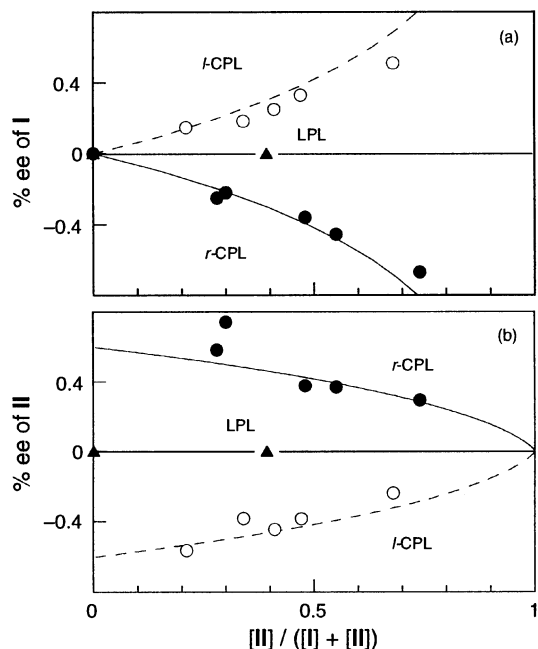
Fig. 8 Theoretical (solid and broken lines) and experimental (plots) relationship between the % ee of (a) reactant (**I**) and (b) product (**II**) and the conversion.

The ee for **I** was plotted against the conversion in Fig. 8a, which shows that the ee of **I** increases with the conversion. The ee for **II** was plotted against the conversion in Fig. 8b. Upon CPL irradiation, as shown in Fig. 7b, the ellipticity at 245 nm first increased and then remained constant, and as shown in Fig. 4, the concentration of **II** increases during this period. This means that the enantiomeric enrichment of **II** decreases according to the CPL irradiation as shown in Fig. 8b.

The solid and dashed lines in Fig. 8a are calculated by putting the observed g value at 290 nm ($g = 0.012$) into eqn. 2, and the curve shows good agreement with experimental data. Thus, ($\pm$)-**I** irradiated with l- and r-CPL at 290 nm results in the enrichment of ($+$)- and ($-$)-**I**, respectively, and the behavior of the ee at 280 nm obeys eqn. (2).

Upon deriving eqn. (2), Kagan assumed that the rate constants of the asymmetric photoreaction (photodestruction) are proportional to the molar extinction coefficients, ε_R and ε_S, respectively.[6,12,34] This can be justified if the concentration of the solution is so low that the % absorption is approximately proportional to the concentration. So, in our experiment, absorbance of solutions at 290 nm was always kept less than 0.1.

The solid and dashed lines in Fig. 8b depict eqn. (6), and also show a good agreement with experimental data. The ee of product **II**, gradually decreases, approaching zero at the final stage of the photoisomerization. The theoretical curve in Fig. 8b also shows that the ee of the product (**II**) is initially $g/2$, *i.e.* 0.6%, and this is also verified by experiment. The ee of the product can be predicted accurately with eqns. (2) and (6).

Therefore, our work presents the first report which demonstrates, with experimental evidence, that a class (b) NAAS actually exists, and that the ee of the chiral product is initially $g/2$, further explaining in detail the relationship between the ee of product and the progress of the photoreaction.

Conclusions

In this study, we have described an NAAS, the photoisomerization of racemic reactant (**I**) into the chiral product (**II**). Kagan's equation for the ee of the reactant, which was originally formulated to describe the photodestruction of racemic

reactants to achiral products, has also been shown to be valid for the photoisomerization of racemic mixtures. Our study has also provided a method which can be used for the analysis of the product ee, and eqns. (2) and (6) derived from Kagan's equation are also useful for making this analysis.

The chiroptical properties of **I** and **II** were examined in acetonitrile. ($-$)-**I** isomerizes to ($+$)-**II** when it is irradiated with LPL at a non-absorbing wavelength of **II** (290 nm), and ($+$)-**I** isomerizes to ($-$)-**II** under the same conditions. The photoisomerization proceeds without any side reactions. When **I** is irradiated with r-CPL at 290 nm, the enantiomeric enrichment of ($+$)-**I** and ($+$)-**II** occurs, and the reverse relationship is observed for irradiation with l-CPL at 290 nm. This reaction obeys eqn. (2), and thus the enantiomeric enrichment of the reactant **I** by CPL irradiation will increase to 100% ee at nearly 100% conversion. Conversely, the enantiomeric enrichment of the product **II** gradually decreases and approaches zero at the final stage. The relationship between the ee of the product and the conversion is remarkably dependent on the g factor of the reactant. The initial ee of the product is $g/2$ (here: 0.6%) in agreement with eqn. (7). These results suggest that we can obtain a reactant and product ee of around 40% at a conversion of 50% if starting material with a g factor of unity is used.

Experimental

General

^{1}H-NMR spectra were recorded on a 400 MHz NMR spectrometer (JEOL EX-400). All chemical shifts (δ) are reported in ppm from a TMS internal standard (0.00 ppm) and coupling constant (J) values are reported in Hz. UV spectra were measured with a JASCO V-560 spectrometer. CD spectra were measured with a JASCO J-720WI or a JASCO J-725 spectrometer. The optical rotations were measured with a Perkin Elmer 341 polarimeter with a thermostated 10 cm cell. Molar circular dichroism ($\Delta\varepsilon$) and specific rotation ($[a]_D^{20}$§) of each enantiomer of **I** and **II** reported were corrected for the enantiomeric excesses (ee's) of the isolated enantiomers following chiral HPLC analysis. In the present paper, the notations of ($+$) or ($-$) refer to the sign of the optical rotations that were measured at the sodium D-line (589.3 nm).

Photolyses were carried out in UV spectroscopic grade acetonitrile (Merck) without any further purification. The photolyzed solutions were analyzed with CD and UV spectrometers, as well as gas chromatography (Shimadzu, GC14-A) over a CBP-1 column (Shimadzu).

Materials

Methyl norbornadiene-2-carboxylate (I, methyl bicyclo[2.2.1]-hepta-2,5-diene-2-carboxylate). **I** was synthesized according to the procedure of Fienemann and Hoffmann.[35] Anhydrous aluminum trichloride (22.4 g, 0.17 mol) was added to a 300 mL round-bottomed flask fitted with a reflux condenser and a thermometer, and then 200 mL of dry benzene was added to the vessel suspended in an ice bath. Methyl prop-2-ynoate (28.0 g, 0.33 mol) was then added, resulting in a yellow coloration. Finally, cyclopentadiene (22.1g, 0.33 mol) was added in a dropwise fashion within 30 min with stirring, and the reaction mixture was stirred for additional 1 h. Then, the solution was poured into aqueous sodium hydrogen carbonate solution. Ether (200 mL) was then added to the mixture, and the mixture was washed several times with water (300 mL). The ether solution was dried over magnesium sulfate. After the ether was evaporated from the solution, the crude product was purified by chromatography on a column of silica gel eluted with toluene: yield 40.8 g (82.3%), bp 43.5–44.0 °C/1 Torr (Found: C, 71.96; H, 6.72. Calc. for $C_9H_{10}O_2$: C, 71.98; H, 6.71%); δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 7.65 (1 H, d, $J = 2.9$ Hz, 3-H), 6.91 (1 H, dd, $J = 4.4, 3.4$ Hz, 6-H), 6.73 (1 H, dd, $J = 4.4, 3.4$ Hz, 5-H), 3.90

(1 H, br s, 1-H), 3.73 (3 H, s, COMe), 3.71 (1 H, br s, 4-H), 2.15 (1 H, d, $J = 6.4$ Hz, 7-H), 2.12 (1 H, d, $J = 6.4$ Hz, 7-H).

Methyl quadricyclane-1-carboxylate (II, methyl tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane-1-carboxylate). II was synthesized according to the procedure of Kaupp and Prinzbach.[36] **I** (3.00 g, 0.020 mol) in acetonitrile (160 mL) was photolyzed through a Pyrex filter under a nitrogen atmosphere. The product was purified by column chromatography (toluene) on silica gel, and was distilled under vacuum: yield 2.43 g (81%), bp 40–41 °C/2 Torr (Found: C, 71.92; H, 6.75. Calc. for $C_9H_{10}O_2$: C, 71.98; H, 6.71%); δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 3.67 (3 H, s, COMe), 2.42 (1 H, ddd, $J = 2.4, 1.5, 1.5$ Hz, 5-H), 2.27 (1 H, dd, $J = 4.8, 1.5$ Hz, 2-H), 2.17 (1 H, ddd, $J = 11.7, 1.5, 1.5$ Hz, 3-H), 2.09 (1 H, ddd, $J = 11.7, 1.5, 1.5$ Hz, 3-H), 2.00 (1 H, ddd, $J = 2.4, 2.4, 1.5$ Hz, 4-H), 1.67 (1 H, ddd, $J = 5.8, 4.8, 2.4$ Hz, 7-H), 1.58 (1 H, ddd, $J = 5.8, 2.4, 2.4$ Hz, 6-H).

Methyl cyclopropanecarboxylate (MCP). MCP was distilled at atmospheric pressure (bp 118–119 °C).

Optical resolution

Each enantiomer was isolated using HPLC (Japan Analytical Industry, LC-908) with the following chiral columns: **I** was resolved using a Chiracel OD column (Daicel, 20.0 × 250 mm) eluted with propan-2-ol–hexane (1 : 100) as eluent; **II** was resolved using a Chiralpack AS column (Daicel, 4.6 × 250 mm) with propan-2-ol–hexane (1 : 200) as eluent.

The % ee's of the resolved enantiomers were estimated by using HPLC (JASCO, Gulliver PU-980, 860-CO, UV-970) with the following conditions; for (+)- and (−)-**I**, Chiracel OD (Daicel, 4.6 × 250 mm) with propan-2-ol–hexane (1 : 200) as eluent, and for (+)- and (−)-**II**, Chiralpack AS (Daicel, 4.6 × 250 mm) with propan-2-ol–hexane (1 : 200) as eluent (% ee: (−)-**I**, 99.4%; (+)-**I**, 97.6%; (−)-**II**, 97.3%; (+)-**II**, 98.9%).

Photolysis

A solution of **I** (0.26 mM) was put in a rectangular cell (10 × 10 × 40 mm) made of Suprasil quartz, and the cell was sealed under an argon atmosphere. The solutions were irradiated at 290 nm with *l*- and *r*-CPL generated with a CPL source made in-house in collaboration with JASCO. A 500 W xenon arc lamp (Ushio) was used as the light source, which was placed in front of an elliptical mirror. After the light beam was made parallel by two mirrors, it was made monochromatic with a grating monochromator (JASCO, CT-10) and then collimated with a fused silica lens. The light beam was linearly polarized with a polarizer (Melles Griot, 03PTA403), and was circularly polarized with a Soleil-Babinet's compensator (Shimadzu, 691-02013-02). The degree of circular polarization was estimated to be 92%, using a combination of an analyzer (Melles Griot, 03PTA403) and a silicon photodiode (Hamamatsu Photonics, S1336-8BQ). The full width at half-maximum (FWHM) of CPL and LPL was 15 nm at 290 nm. The sample cell was located in the cell holder.

Appendix 1

If the concentration of the solution is so low that the % absorption for the solution is approximately proportional to the concentration, the rates of the decrease of the enantiomers of the reactant *via* the irradiation of *r*-CPL are as given in eqns. (13) and (14),[37] where c_R and c_S are the concentrations of the (R)- and (S)-isomers respectively, I_{ex} is the incident photon flux expressed as einstein cm^{-2} s^{-1},¶ S is the area of the cross section

¶ 1 einstein = 1 mole of light (6.023 × 10^{23} quanta).

$$\left(\frac{dc_R}{dt}\right)^r = -I_{ex}\frac{S}{V}(1 - 10^{-A})\frac{\varepsilon^r_R c_R l}{A}\Phi$$
$$= -2.303\, I_{ex}\frac{Sl}{V}\,\Phi\varepsilon^r_R c_R = -k^r_R c_R \tag{13}$$

$$\left(\frac{dc_S}{dt}\right)^r = -I_{ex}\frac{S}{V}(1 - 10^{-A})\frac{\varepsilon^r_S c_S l}{A}\Phi$$
$$= -2.303\, I_{ex}\frac{Sl}{V}\,\Phi\varepsilon^r_S c_S = -k^r_S c_S \tag{14}$$

of the incident light beam (cm^2), V is the volume of the solution (dm^3), A is the absorbance of the reaction mixture in the reaction cuvette, ε^r_R and ε^r_S represent the molar extinction coefficients when (R)- and (S)-isomers are excited by the irradiation of *r*-CPL, respectively, l is the path length of the reaction cuvette, Φ is the quantum yield of the reaction, k^r_R and k^r_S represent the rate constants when (R)- and (S)-isomers are excited by the irradiation of *r*-CPL respectively and t is the reaction time. If the incident light beam covers all the surface of the cuvette, the value of the term, Sl/V, becomes 1000.[37]

Thus the rate constants for the reaction become proportional to the molar extinction coefficients.

Appendix 2

In eqn. (7) the limit value of y' was given as in eqn. (15).

$$\lim_{x \to 0} y' = -\frac{\lim\limits_{x \to 0}\dfrac{d}{dx}\{y(1-x)\}}{\lim\limits_{x \to 0}\dfrac{d}{dx}x} = -\lim_{x \to 0}\left\{\frac{dy}{dx}(1-x) - y\right\}$$
$$= -\lim_{x \to 0}\frac{dy}{dx} \tag{15}$$

Eqn. (4) can be reduced into the form shown in eqn. (16), by differentiating this equation we obtain eqn. (17). Finally dy/dx can be expressed as in eqn. (18). If x reaches 0, y reaches 0 to give eqn. (19).

$$x = 1 - \frac{1}{1+y}\left(\frac{1+y}{1-y}\right)^{\frac{1}{g}+\frac{1}{2}} \tag{16}$$

$$\frac{dx}{dy} = \left(\frac{1+y}{1-y}\right)^{\frac{1}{g}+\frac{1}{2}}\frac{\left(\dfrac{2}{g}+y\right)}{(1+y)(1-y^2)} = \frac{(x-1)\left(\dfrac{2}{g}+y\right)}{1-y^2} \tag{17}$$

$$\frac{dy}{dx} = \frac{1-y^2}{(x-1)\left(y+\dfrac{2}{g}\right)} \tag{18}$$

$$-\lim_{x \to 0}\frac{dy}{dx} = \frac{g}{2} \tag{19}$$

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