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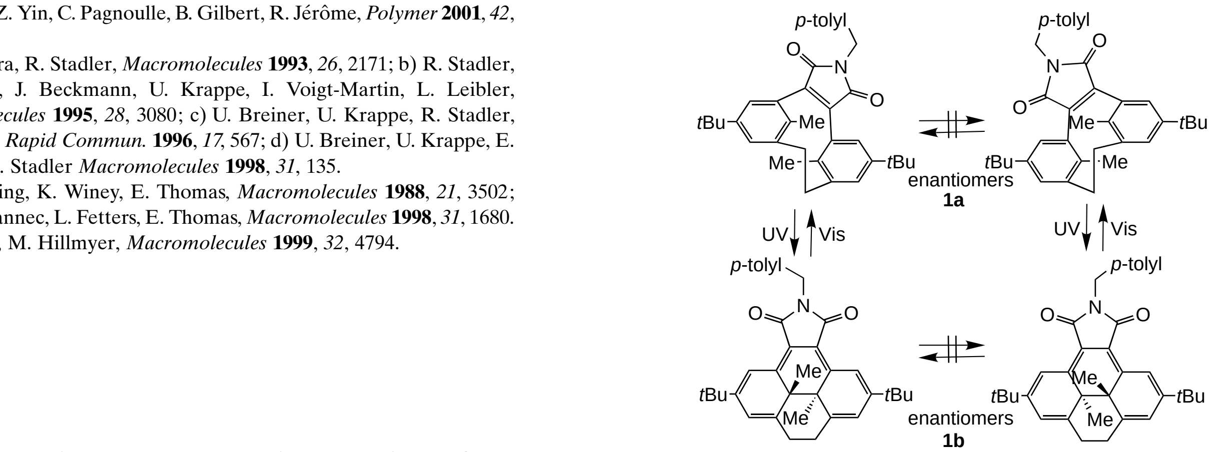
Enantioselective Photochromic Reaction of a [2.2]Metacyclophan-1-ene[**]

Michinori Takeshita[*] and Takehiko Yamato

Photochromic compounds have been extensively studied owing to their potential as photomemory and photoswitching materials.[1] Photochromic compounds reversibly change their absorption spectra (color) upon photoirradiation. However, reading the photomemory by changes in the absorption spectrum causes the destruction of the memory, since photoirradiation results in excitation of photochromic compounds.[1] Therefore, various attempts at nondestructive readout have been reported,[1] for example, by locking one of the photoisomers by the addition of chemical substances[2] or by electrooxidation (gated photochromic reaction).[3] Reading the change in chiral information originated in photochromic reactions is one of the most promising systems, since chiral information can be read without excitation of photochromic compounds.[4, 5] In photocyclization systems, for example, diarylethenes,[5a] fulgides,[5b] and spiropyrans,[5c] the enantiomers of the photochromic compounds undergo diastereoselective photocyclization. In these systems, one should be aware of the diastereoselectivity of the cyclization, since such selectivity is altered by the conditions (e.g. temperature, medium, etc). This fact encouraged us to study enantiomeric photocyclization, that is, a photochromic reaction between two enantiomers in which no racemization takes place.

We chose 1,2-disubstituted [2.2]metacyclophan-1-enes (MCP-1-enes),[6] which we recently reported,[7] as the enantiomeric photocyclization system (Scheme 1). It is well known that ring inversion of the phenyl groups in the *anti* 8,16-dimethyl[2.2]metacyclophane system is forbidden because of the steric hindrance between the inner methyl groups and the opposite phenyl groups.[8] For similar reasons, ring inversion of MCP-1-enes does not occur, and MCP-1-enes are chiral molecules because no mirror symmetry exists in the molecule.



Scheme 1. Enantioselective photochromic reaction of [2.2]MCP-1-ene **1a** and THP **1b**.

Therefore, one can expect that racemization of the enantiomers of MCP-1-enes does not take place. MCP-1-enes show photochromism,[6, 7] and tetrahydropyrenes (THP) formed from MCP-1-enes by UV irradiation are also chiral. It is expected that no racemization occurs, even during the photochromic reaction, and that the photochromic reaction takes place with both enantiomers.

We have designed and synthesized some MCP-1-enes and found that the enantiomers of maleimide-type MCP-1-ene **1a** are easily separated.[9] MCP-1-ene **1a** was synthesized from 1,2-dicyano[2.2]MCP-1-ene[7] in three steps.[10] Figure 1 shows the changes in the absorption spectrum of a solution of **1a** in hexane upon irradiation with 313-nm light. The pale yellow solution of **1a** changed to violet upon UV irradiation, and irradiation with visible light returned the spectrum to its initial form. The violet color shows the formation of THP **1b**.[11] The photostationary state at 313 nm was analyzed with HPLC (silica gel, hexane/AcOEt 10:1, 385 nm (isosbestic point)) and contains 35 % of MCP-1-ene **1a** and 65 % of THP **1b**.

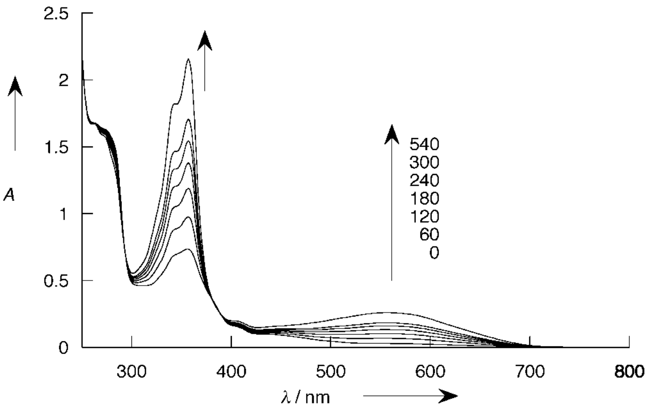


Figure 1. Changes in the absorption spectrum of **1a** (0.16 mM in hexane) upon irradiation with 313-nm light. Numbers indicate the irradiation time (s).

Figure 2 shows a chromatogram of the racemic mixture of **1a** (HPLC on a chiral column).[9] Three peaks were found and these peaks were assigned to one enantiomer of MCP-1-ene

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[**] We are grateful for financial support from The Association for the Progress of New Chemistry (ASPRONC).

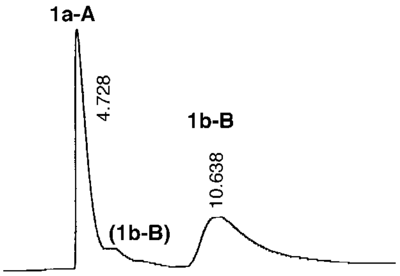

Figure 2. Chromatogram of MCP-1-ene **1a** (HPLC on chiral column).[9]

(**1a-A**), THP **1b-A**, and the other enantiomer of MCP-1-ene (**1a-B**). The enantiomers **1a-A** and **1a-B** were perfectly separated under these conditions. After separation, neither of the enantiomers racemize, even when heated at 200 °C for 1 h under Ar, and no decomposition could be detected by HPLC or by ^{1}H NMR, absorption, and circular dichroism (CD) spectroscopy either.

The CD spectra of solutions of MCP-1-enes **1a-A** and **1a-B** in hexane were measured (Figure 3, 4). The CD spectra of **1a-A** and **1a-B** were symmetrical; **1a-A** and **1a-B** are enantiomers (Figure 3). The CD spectra of the photostationary state of **1-A** and **1-B** at 313 nm were also symmetrical. The CD spectra of **1a-A** were changed upon irradiation with 313-nm light, as shown in Figure 4. As irradiation times became longer, the concentration of **1b-A** (colored form) increased and the CD spectrum changed according to the increase in the concentration. Upon irradiation with visible light, the CD spectra were identical to the initial spectra. HPLC on a chiral column also showed that the enantiomer **1b-A** was converted back cleanly into the initial enantiomer **1a-A** after one photochromic reaction cycle (visible irradiation followed by UV irradiation). These results indicate that the photochromic reaction of the enantiomers of MCP-1-ene **1** are enantioselective and no racemization occurs.

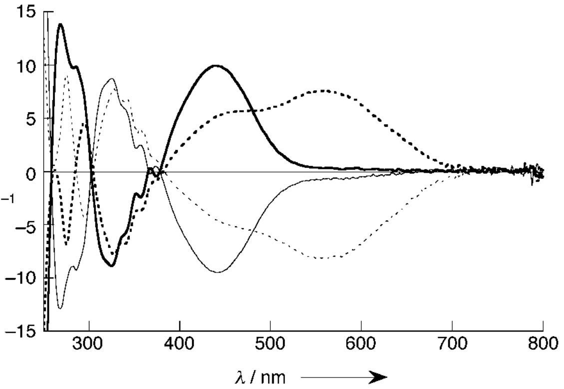

Figure 3. Changes in CD spectrum of **1** in hexane upon irradiation with 313-nm light (plain line: **1a-A**, plain dot line: PSS$_{313}$ of **1-A**, bold line: **1a-B**, bold dot line: PSS$_{313}$ of **1-B**).

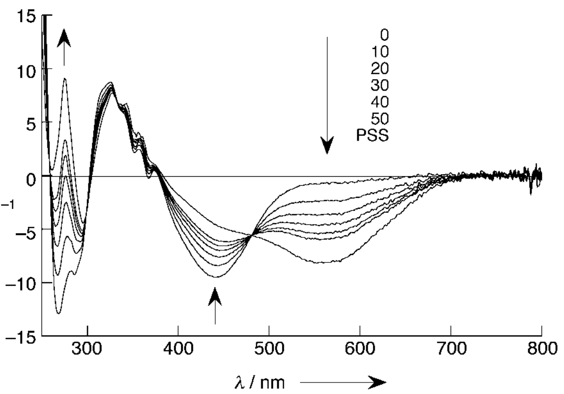

Figure 4. Changes in CD spectrum of **1a-A** in hexane upon irradiation with 313-nm light. Numbers indicate the irradiation time (s), PSS = photostationary state.

This is the first example of a photochromic reaction with two enantiomers. Thus we believe that the nondestructive read-out of photomemory will be possible by the use of this enantiomeric photochromic system.

Received: January 2, 2002
Revised: March 25, 2002 [Z18463]

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[9] DICEL Chiralpak AD-H was used as the chiral prepacked column for HPLC separation (hexane/2-propanol (100:1), 1 mL min^{-1}).

[10] The synthesis of MCP-1-ene **1a** will be reported in the near future; **1a**, pale yellow prisms, m.p. 69.0–71.0 °C; ^{1}H NMR (CDCl$_3$, 25 °C, 300 MHz, TMS): $\delta = 0.62$ (s, 6H), 1.29 (s, 18H), 2.36 (s, 3H), 2.49–2.62 (AA′XX′ multiplet, 2H), 2.89–3.02 (AA′XX′ multiplet, 2H), 4.80 (s, 2H), 7.11 (d, 2H, $J = 2$Hz), 7.19–7.22 (d, 2H, $J = 2$Hz), 7.19–7.22 (AA′BB′ multiplet, 2H), 7.45–7.48 ppm (AA′BB′ multiplet, 2H); HRMS (EI, 70 eV): calcd for $[M^+]$ $C_{36}H_{41}NO_2$, 519.3137; found, 519.3147.

[11] The formation of tetrahydropyrene **1b** was also confirmed: ^{1}H NMR (CDCl$_3$, 25 °C, 300 MHz, TMS): $\delta = 1.11$ (s, 18H), 1.84 (s, 6H), 2.32 (s, 3H), 2.22–2.25 (AA′XX′ multiplet, 2H), 2.62–2.65 (AA′XX′ multiplet, 2H), 4.64 (s, 2H), 5.79 (d, 2H, $J = 2$Hz), 7.04 (d, 2H, $J = 2$Hz), 7.08–7.11 (AA′BB′ multiplet, 2H), 7.29–7.32 ppm (AA′BB′ multiplet, 2H).