First absolute asymmetric synthesis with circularly polarized synchrotron radiation in the vacuum ultraviolet region: direct photoderacemization of (*E*)-cyclooctene

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A newly developed polarizing undulator installed in a storage ring was employed for the first time as a source of circularly polarized synchrotron radiation in the vacuum ultraviolet to effect enantiodifferentiating direct photoisomerization of (*E*)-cyclooctene; the photolysis is taken as a terrestrial mimic or proof of extraterrestrial absolute asymmetric synthesis on interstellar grains by the polarized synchrotron radiation from fast electrons orbiting a neutron star, which is thought to be a distant origin of the homochirality in the biosphere.

Biologically crucial molecules such as amino acids and sugars are chiral and consist exclusively of one of two possible enantiomers. Since the time of Pasteur, the origin of such absolute chiral homogeneity in the biosphere has been of much interest and debate, and a wide variety of biotic/abiotic and terrestrial/extraterrestrial theories have been proposed.[1] Of these proposals, a cosmic scenario involving synchrotron radiation from a neutron star and an interstellar grain was presented recently as a hypothesis in support of the extraterrestrial origin of chiral homogeneity, and has attracted much attention.[2–5] In theory, racemic compounds in the organic mantles of interstellar grains are postulated to suffer enantioselective photodecomposition by elliptically polarized off-angle synchrotron radiation from fast electrons orbiting the neutron star remnants of supernova explosions, the resulting grains containing optically active compounds then drifting to Earth. A recent analysis of the amino acids isolated from the Murchson meteorite supports this theory; a sample of alanine containing a high $^{13}C/^{12}C$ ratio which indicates its extraterrestrial origin, is enriched in the L-isomer by 18% over the antipodal D-isomer.[6]

In the present work, we employed a newly developed polarizing undulator as the only available source of pure, intense, monochromatic, circularly polarized light (CPL) in the vacuum ultraviolet (VUV) region. The helical undulator is an insertion device that is installed in an electron storage ring to produce a crossed and retarded magnetic field.[7–9] With this novel CPL source in the VUV region, we carried out the direct photolysis of racemic (*E*)-cyclooctene (Scheme 1), in which the reversible geometrical and enantiomeric photoisomerizations take place simultaneously. By using this method we can simulate extraterrestrial absolute asymmetric synthesis in VUV and open a new channel to asymmetric photochemistry with circularly polarized synchrotron radiation that is monochromatic and tunable over a very wide range of wavelengths from IR to X-ray.

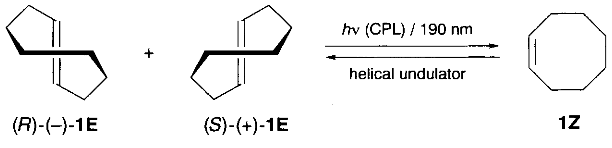
The optical yields reported so far for absolute asymmetric syntheses using CPL are inherently low and often unreliable.[10,11] Hence, the choice of chiral substrate becomes very important; we employed (*E*)-cyclooctene (**1E**) as the most appropriate compound for the following reasons: (i) **1E** undergoes efficient geometrical isomerization in high chemical and quantum yields upon direct irradiation in the VUV regions,[12–14] and (ii) its pure enantiomer shows an extraordinarily high optical rotation $\{[\alpha]_D^{20} -426$ for (*R*)-**1E**$\}$,[15] both of which enable us to detect even minimal optical activities induced by CPL irradiation.

Pentane solutions of racemic **1E** ($[\alpha]_D^{20}\,0.00 \pm 0.05$), sealed under an argon atmosphere in Suprasil cells ($10 \times 10 \times 45$ mm), were irradiated at 25 °C for varying periods of time by left- or right-handed CPL or linearly polarized light (LPL) at 190 nm emitted from the polarizing undulator at a distance of *ca.* 3.5 m. This new device, installed in storage ring NIJI II at the Electrotechnical Laboratory, produces much stronger and purer monochromatic CPL than the previously reported prototype model installed in the storage ring TERAS.[7–9]

Upon irradiation, **1E** was efficiently transformed to the achiral (*Z*)-isomer (**1Z**). The conversion was proportional to the irradiation dose up to 100 mA h or 70%; in these experiments, the concentrations of **1E** and **1Z** in irradiated solutions were determined by gas chromatographic analysis using a 3 m column of 20% polyethylene glycol-300 at 60 °C; error ±3%. As shown in Fig. 1(*a*), the irradiation with l- and r-CPL, as well as LPL, gave essentially the same linear dose–conversion plot, which proves stable operation of the polarizing undulator irrespective of the changed mutual arrangements of crossed magnet pairs.[7–9]

By contrast, the optical rotation (α) of the irradiated solution, measured in a 1 dm microcell with a Perkin Elmer model 243 polarimeter (error in $\alpha \pm 0.001$), was a critical function of the sense of CPL and also of the irradiation dose, which was estimated integrating the storage-ring current over the irradiation period since the ring current decreases gradually as the time elapses. As can be seen from Fig. 1(*b*), irradiation with l- and r-CPL produced substantial optical rotations in *opposite* directions, whereas the LPL irradiation did not give any detectable optical activity in the solution. The specific rotations of the remaining **1E** [filled symbols in Fig. 1(*b*)], calculated from the conversion and the optical rotation, increase with the dose, approaching an apparent plateau upon prolonged irradiation in both runs; the ultimate optical purities of the remaining **1E** are +0.12 and −0.12%, respectively.

These results clearly indicate that (*R*)-(−)- and (*S*)-(+)-**1E** are enantioselectively photoisomerized to achiral **1Z** respectively by l- and r-CPL from the helical undulator, leaving antipodal **1E** in the solution. It is also emphasized that, in contrast to the combination of a conventional light source and polarizing optics



Scheme 1

or the prototype model employed earlier, this helical undulator is a useful wide-range CPL source that is tunable and strong enough to effect various photochemical reactions. Furthermore, the cosmic scenario, involving the off-angle synchrotron radiation and interstellar grains, has been formally verified in this study by using the circularly polarized synchrotron radiation in the VUV region. Future experiments with racemic amino acids and other biomolecules will provide further insights into the crucial role of the cosmic scenario in chemical evolution.

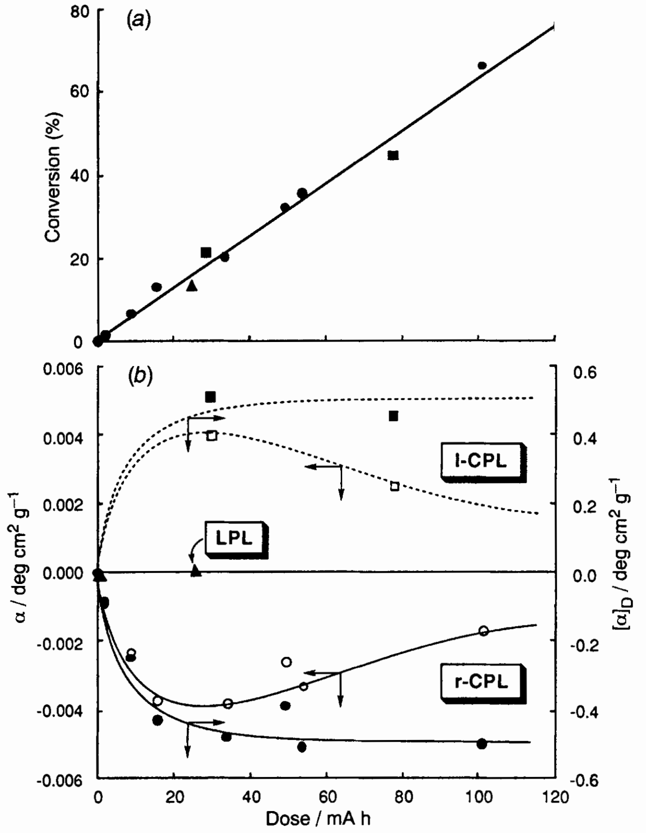


Fig. 1 (*a*) Conversion (%) and (*b*) optical rotation (α; open symbols) of irradiated solution and specific rotation ([α]$_D$; solid symbols) of remaining (*E*)-cyclooctene (**1E**) as function of irradiation dose in direct photolysis of racemic **1E** (0.09 M) in pentane with l-CPL (■), r-CPL (●) and LPL (▲) at 190 nm radiated from a helical undulator

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