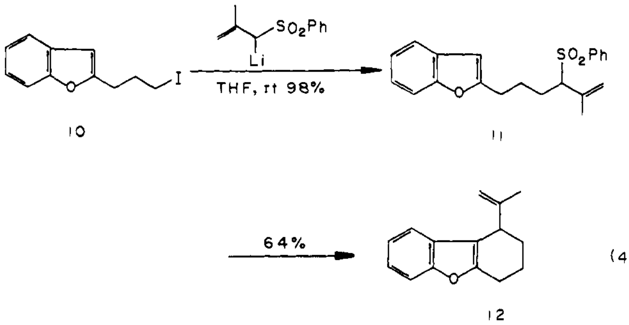
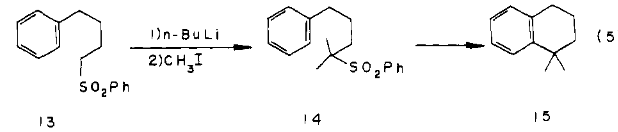
straightforward alkylation of the iodide, itself prepared from 2-lithiated benzofuran (eq 4). Exposure of **11**[5] to aluminum chloride (3 equiv, CH_2Cl_2, -78 °C, 1.5 h) gave **12**[5] in 64% yield. Thus, relatively simple allyl groups provide sufficient activation to facilitate cyclization.

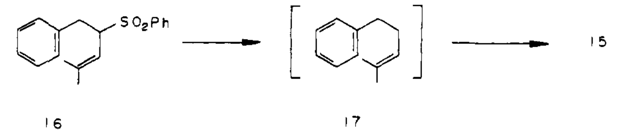


Since a tertiary carbonium ion is about as stable as a simple allyl cation, tertiary sulfones are also candidates as substrates. Treating **14** with 2 equiv of aluminum chloride (CH_2Cl_2; -78 to 0 °C, 1 h) gave the cyclic product **15**[5] in 70-80% yield (eq 5).



This example also illustrates the umpolung provided by the sulfone since carbanion chemistry introduces the two methyl groups.

The question of an endo vs. exo type of cyclization was briefly examined. Aluminum chloride induced reaction of **16** led to a complex mixture of products. On the other hand, 2 equiv of ethylaluminum dichloride (CH_2Cl_2, -78 °C, 15 min) led to **15** in 44-51% yields—a net reductive cyclization. The failure of the allyl cation derived from **16** to cyclize may derive from geometrical constraints of the cisoid isomer or from preferential formation of the transoid cation which is geometrically precluded from cyclizing. However, if it is reduced by hydride delivery from the ethyl group of the Lewis acid to the less substituted carbon to form **17**, then acid-type cyclization would be expected to produce **15** as observed.



The surprising facility of these Lewis acid catalyzed cyclization reactions extends the prospects for application of sulfones in synthesis. Clearly, aromatic nucleophiles are only one type of many that can be envisioned. Sulfones appear to be chemical chameleons; they become either nucleophiles or electrophiles depending upon their environment.[10]

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our program.

Registry No. 1, 92643-23-7; **2**, 92643-24-8; **3**, 92643-25-9; **4a**, 589-10-6; **4b**, 85262-44-8; **5**, 15874-80-3; **6a**, 92643-26-0; **6b**, 92643-27-1; **7a**, 92643-28-2; **7b**, 92643-29-3; **8**, 92643-30-6; **9**, 92643-31-7; **10**, 92643-32-8; **11**, 92643-33-9; **12**, 92643-34-0; **13**, 92643-35-1; **14**, 92643-36-2; **15**, 1985-59-7; **16**, 92643-37-3; $Ph(CH_2)_3Br$, 637-59-2; $AlCl_3$, 7446-70-0; $Mo(CO)_6$, 13939-06-5; 2-[[5-methyl-3-(phenylsulfonyl)hex-4-en-1-yl]-oxy]naphthalene, 92643-38-4; 1-(2-methyl-1-propenyl)-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran, 92643-39-5; 9,9-dimethyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[9,1-*bc*]pyran, 92643-40-8; 2-[6-methyl-4-(phenylsulfonyl)hept-5-en-1-yl]-1-methylpyrrole, 92643-41-9; 1-methyl-4-(2-methyl-1-propenyl)-4,5,6,7-tetrahydro-1*H*-indole, 92643-42-0; 1-[5-methyl-3-(phenylsulfonyl)hex-4-en-1-yl]naphthalene, 92643-43-1.

Supplementary Material Available: Spectral data for **1-3**, **6a,b**, **7a,b**, **11**, **12**, **14**, **15**, and the starting material and products of eq 2 (3 pages). Ordering information is given on any current masthead page.

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Enantiomeric Enrichment of *cis*-Bicyclo[3.2.0]hept-3,6-dien-2-one with Circularly Polarized Light via the Photointerconversion of the Enantiomers

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Photochemical induction of optical activity with circularly polarized light (CPL)[1] is known to occur via either (i) the preferential photodecomposition of one enantiomer of a racemate,[2a-d,g] (ii) asymmetric photosynthesis,[1b,2a,e] or, finally, (iii) the photointerconversion of the enantiomers of a racemate.[2f] However, while the first two modes of inducing optical activity are well established for organic compounds,[1b,2a-e,g] mode iii, despite its fundamental importance, is confined to a few bidentate complexes of transition metals.[2f]

Actually, a variety of optically active organic substrates, such as biaryls,[3a] ketones,[3b] diketones,[3c] thiones,[3d] carboxybenzyl esters,[3e] [2.2]paracyclophanes[3f] and pyramidally blocked oxaziridines[3g] and sulfoxides[3h] have been photoracemized with achiral light. This, however, does not necessarily imply that CPL irradiation would induce optical activity in the corresponding racemates via the

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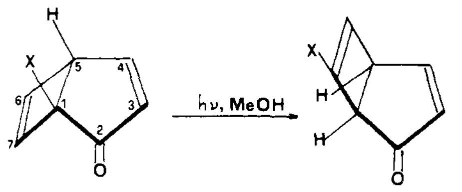
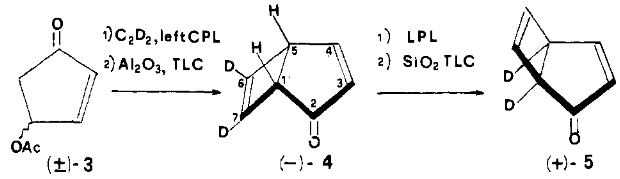
Scheme I



(−)(1S,5R)-**1a**, X = OMe
(−)(1S,5R)-**1b**, X = NHCOMe
(−)(1S,5S)-**1c**, X = H

(+)(1R,5R)-**2a**, X = OMe
(+)(1R,5R)-**2b**, X = NHCOMe
(+)(1R,5R)-**1c**, X = H

Scheme II



(±)-**3** (−)-**4** (+)-**5**

photointerconversion of the enantiomers. For this to occur, the Kuhn's g factor ($\Delta\epsilon/\epsilon$) must have a high value at the irradiation wavelength, while intermolecular transfer of energy must be at a minimum.[4]

It is therefore interesting to report here the first case of induced optical activity in an organic racemate by CPL via the photointerconversion of enantiomers. The choice of the substrate was dictated by the observation that either (−)-**1a** or (−)-**1b**,[5] on irradiation with ultraviolet, linearly polarized light (LPL), give (+)-**2a**[2a] or (+)-**2b**,[2c] respectively, with inversion of configuration at the angular carbons C(1) and C(5)[6] (Scheme I). Therefore, photointerconversion of enantiomers can be expected with the unsubstituted analogue **1c**, and this might lead to optical activation of racemic **1c** under CPL irradiation.

In fact this proved to be the case. The irradiation of (±)-**1c**[7] with left CPL,[2a] followed by TLC purification, led to (−)-**1c**.[5] However, instead of achieving the photostationary state expected for a clean photointerconversion of the **1c** enantiomers,[1b] the optical activity of **1c** increased continuously with irradiation time while the concentration of **1c** decreased. Though this is, qualitatively, the typical trend of a process of preferential photodestruction of one enantiomer, we prove below that there is a concomitant photointerconversion of the enantiomers.

The relative importance of these two processes was assessed as follows. The 6,7-$^2H_2$ analogue of (−)-**1c**, (−)-**4**, was prepared according to Scheme II. A methanolic 0.03 M solution of (−)-**4**, of OP 1.2%, was irradiated with laser LPL (351- and 363-nm lines, jointly, 0.3 W) until there was an 18% disappearance of **4**. Evaporation of the solution, and TLC, led to a 1:9 mixture of **4** and **5** according to NMR[9] and an optically inactive byproduct.

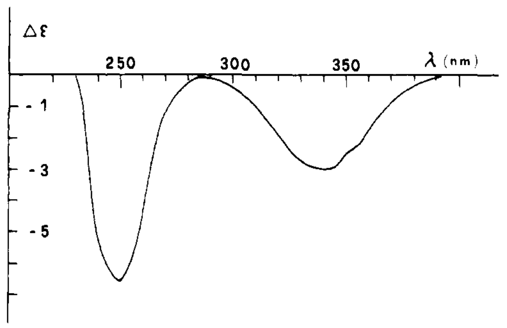


Figure 1. Circular dichroism spectrum of the (−)-**1c** antipode in MeOH (mol^{-1} L cm^{-1}).

The 1:9 mixture was lower in optical activity than the starting (−)-**4**, by 22%. Here, the 22% loss of optical activity is attributable to an 11% inversion of configuration at the angular carbons,[6,10] corresponding to the formation of 11% of (+)-**5** during the LPL irradiation of (−)-**4** (Scheme II).

From the extent both of the inversion of configuration and of the disappearance of **4**, the ratio r of the quantum yields for the photointerconversion (Φ_{interc}) and the photodestruction (Φ_{destruc}) of **4** can be calculated as

$$r = \Phi_{\text{interc}}/\Phi_{\text{destruct}} = 11/18 = 0.61$$

Now, making use of all data obtained above in the CPL experiment for **1c**, we can evaluate the dichroism, $\Delta\epsilon$, for enantiomerically pure (−)-**1c**, by eq 1.[11] Here $\delta\epsilon$ and ϵ are the dichroism

$$\Delta\epsilon \simeq \left(\frac{1}{2r+1}\,2\epsilon\left|\frac{\delta\epsilon}{\ln x}\right|\right)^{1/2} \qquad (1)$$

and the molar extinction coefficient, respectively, at the mean wavelength of irradiation (355 nm), while x is the fraction of residual **1c** after CPL irradiation. The CD spectrum of (−)-**1c** is shown in Figure 1.

It is worth emphasizing that the CPL photointerconversion of the **1c** antipodes leads to (−)-**1c** with optical purity (ca. 1.5%) higher than that expected (ca. 0.67%) from preferential photodestruction alone. This allowed us to extend the CD measurements to the $\pi \rightarrow \pi^*$ spectral region, which gives a deeper insight into the chiral properties of a compound (**1c**) that would be troublesome to obtain in optically active form by other methods.

The present results, and the widespread occurrence of photoracemizations with achiral light,[3] suggest that optical activation of organic racemates via the interconversion of the enantiomers by CPL can be more easily achieved than heretofore thought. This should stimulate further work in this area, particularly as we have shown here that concomitant, preferential photodestruction of one enantiomer, which is expected to be the rule, may prove useful for CD studies.

Acknowledgment. We thank M.P.I., Roma, for a grant within the Progetti di Interesse Nazionale, and the Istituto di Chimica Quantistica and the Centro per le Macromolecole Stereoordinate, C.N.R., Pisa, for instrumental facilities.

Registry No. (±)-**1c**, 92419-38-0; (+)-**1c**, 92469-49-3; (−)-**1c**, 92419-39-1; (−)-**4**, 92346-78-6; (+)-**5**, 92346-79-7.

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(5) Unless otherwise stated, in this work the sign of the optical rotation (sodium line) simply stands for the enantiomer in excess.

(6) This rests on the assignment of absolute configurations by the octant rule.[2a,c] The configuration inversions can be rationalized within, for example, Chapman's dipolar or ketene mechanisms (Chapman, O. L.; Lassila, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 2449–2450). In any case, formal C(1)–C(2) and C(5)–C(4) bond breaking and C(7)–C(2) and C(6)–C(4) bond formation must have occurred.

(7) A 0.03 M solution of **3** in acetonitrile, at 0 °C, saturated with acetylene, was irradiated with the 351- and 363-nm emissions, jointly, of a Spectraphysics 171-19 Ar ion CW laser. The product (±)-**1c** was purified by TLC on deactivated alumina (60% yield).

(8) Data of **4**: ^{1}H NMR (CDCl$_3$, 100 MHz) $\delta_{\text{Me}_4\text{Si}}$ 7.65 (dd, J = 5.6, 2.9 Hz, 1 H, H-C(4)), 6.10 (d, J = 5.6 Hz, 1 H, H-C(3)), 4.00 (dd, J = 2.9, 2.0 Hz, H-C(5)), 3.50 (br d, J = 2.0 Hz, 1 H, H-C(1)); UV $\lambda_{\text{max}}^{\text{MeOH}}$ 330 (ϵ 90); CD $\lambda_{\text{max}}^{\text{MeOH}}$ 343 ($\delta\epsilon$ −0.037, OP ≃ 1.2%); EI MS, m/z (%) 108 (36, M$^+$), 80 (100, M$^+$ − CO). **4** showed loss of CO from M$^+$, while no appreciable peak for the loss of ethylene could be detected.

(9) In addition to the ^{1}H NMR signals described above for **4**, we observed two doublets at $\delta_{\text{Me}_4\text{Si}}$ 6.49 and 6.29, J = 2.25 Hz, integrating as 1:9 with respect to the sum of signals for H-C(3) and H-C(4). In accordance with the spectrum observed for **1c**, these two doublets can be attributed to H-C(6) and H-C(7) of **5**. At the FT ^{1}H NMR sensitivity level, we could not observe other signals, such as for deuterium labeling at other carbons.

(10) The pattern of deuterium labeling on going from (−)-**4** to (+)-**5** (Scheme II) is in accordance with the mechanisms in ref 6. Implicitly, we are treating (−)-**4** and (+)-**5** as if they were true enantiomers, which is clearly allowed.

(11) Relationship 1 has been derived from the kinetic equations governing both the CPL photodestruction and the photointerconversion processes of the **1c** antipodes, for small degrees of photodestruction.[2a]