Photoresolution of an Axially Chiral Bicyclo[3.2.1]octan-3-one: Phototriggers for a Liquid Crystal-Based Optical Switch

Yifan Zhang and Gary B. Schuster*,†

Department of Chemistry, University of Illinois, Roger Adams Laboratory, Urbana, Illinois 61801

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The axially chiral ketones 8-(phenylmethylene)bicyclo[3.2.1]octan-3-one (**1**) and 3-(phenylmethylene)-bicyclo[3.2.1]octan-8-one (**2**) were prepared and investigated for suitability as a chiroptical trigger in a liquid crystal-based optical switch. Irradiation of optically active ketone **1** with unpolarized light leads to its efficient photoracemization. Its irradiation with circularly polarized light leads to partial photoresolution with an enantiomeric excess sufficient for it to function as a chiroptical trigger. However, **1** is not sufficiently soluble in ZLI-1167, a nematic liquid crystalline material, to induce a measurable pitch. Ketone **2** is unstable to irradiation and is not suitable for use as a chiroptical trigger.

Introduction

Magnetic materials currently dominate the technology for erasable direct read after write memory devices.[1] Materials which can be reversibly written and read by light will have some advantages over current magnetic devices.[2] Development of such devices requires compounds that can be switched between two distinct forms by light and are sensed by light without their destruction. The most advanced materials for light-triggered applications are based upon reversible magneto-optical phase transitions of inorganic compounds.[3] Organic photochromic compounds have been considered as alternative candidates for such light-controlled devices. We recently reported results from investigation of a set of chiral ketones capable of being partially resolved with circularly polarized light.[4] These compounds are potential triggers for the reversible switching of liquid crystalline materials.

When dissolved in a nematic liquid crystal (the switch), irradiation of an appropriate trigger with circularly polarized light can induce an enantiomeric excess (photoresolution) in the trigger which will convert the liquid crystal to a cholesteric (twisted nematic) form. This process can be reversed by irradiation of the trigger with unpolarized light, which regenerates the racemate and reforms the nematic liquid crystal. The difference between the nematic and cholesteric forms of the liquid crystal can be sensed with light at a wavelength not absorbed by the trigger, which provides a means for the nondestructive readout of the switch and solves one of the most difficult problems associated with photochromic materials as memory devices.[7,8]

Photoresolution of the trigger molecule with circularly polarized light requires that three key parameters be satisfied. First, irradiation should cause only the interconversion of enantiomers without any photodestruction. Second the circular dichroism (CD) spectra of the enantiomers must be sufficiently strong. That is, irradiation of the racemic mixture of enantiomers must lead to a photostationary state (pss) with a sufficiently large enantiomeric excess ($[\gamma]_{PSS}$). This quantity depends on $\Delta\epsilon$ and ϵ, according to eq 1, where g_λ is the Kuhn anisotropy factor.[9] Third, the quantum efficiency for photoracemization (Φ_{rac}) must be large.

$$[\gamma]_{PSS} = (\Delta\epsilon/2\epsilon) = g_\lambda/2 \quad (1)$$

The primary challenge in finding suitable triggers has been discovery of compounds with sufficiently large $[\gamma]_{PSS}$. Previous systems investigated often have very small g_λ, which generally makes photoresolution undetectable.[6] Our strategy to solve this problem and to increase g_λ is to incorporate a ketone chromophore as the absorbing unit in a trigger molecule. Since the $n\pi^*$ transition of the ketone group is forbidden, it has a small extinction coefficient and, potentially, a large g_λ. Further, twisted ketones often show exceptionally large $\Delta\epsilon$ values.[11] Finally, we note that frequently to obtain a large $\Delta\epsilon$, the ketone must be incorporated in a relatively rigid skeleton which prevents conformational averaging of CD spectra with opposite signs.[12] On this basis we have focused our investigation of potential triggers on chiral bicyclic ketones.

Clearly, a further requirement for discovery of a suitable chiroptical trigger is that the compounds investigated undergo a reversible light-initiated reaction that causes interconversion of enantiomers. To satisfy this requirement, we are investigating enantiomers of axially

† Current address: School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332.

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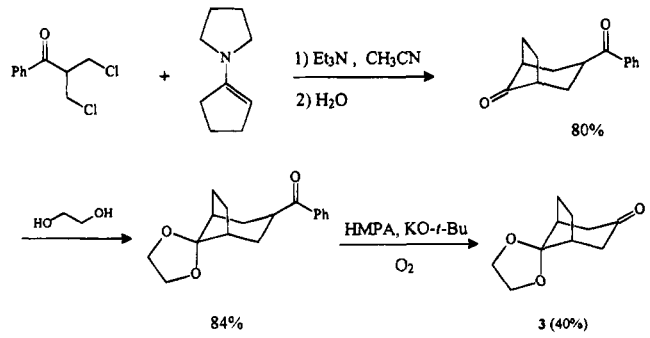
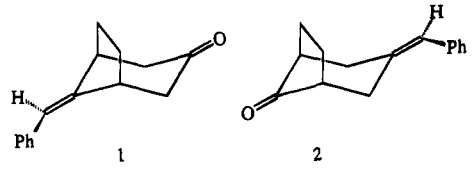
Scheme 1



chiral compounds that are interconverted by rotation about a carbon–carbon double bond. This isomerization reaction generally occurs rapidly from the triplet state of the olefin. Critically, the triplet energy of aryl-substituted olefins[13] is below that of simple ketones,[14] while the order of their excited singlet state energies is the opposite. Consequently, light of suitable wavelength will be absorbed by the ketone (and advantage taken of its large g_λ), and intramolecular, exothermic triplet–triplet energy transfer, which follows a typically rapid intersystem crossing in ketones, will yield the isomerizing olefin triplet. Further, the destructive Norrish I reaction of cyclic ketones[15,16] may be circumvented in these cases by rapid transfer of energy from the ketone to the aryl olefin. Synthetic difficulties in the bicyclo[3.3.1]nonane series of ketones[17] led us to consider 8-(phenylmethylene)-bicyclo[3.2.1]octan-3-one (**1**) and 3-(phenylmethylene)-bicyclo[3.2.1]octan-8-one (**2**) as potential triggers for a liquid crystal based chiroptical switch.

Potential Chiroptical Triggers



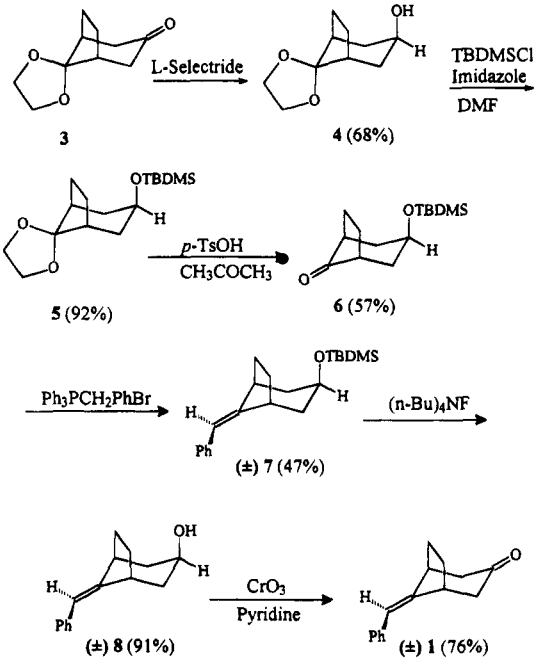
1 2

Results and Discussion

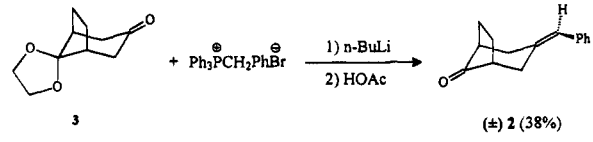
(1) Synthesis. The syntheses of bicyclic ketones **1** and **2** follow readily from bicyclo[3.2.1]octan-3,8-dione 8-ethylene ketal (**3**) as a key intermediate. Details for the preparation of **3** are reported in the Experimental Section; its synthesis was modeled after the previously reported procedure[18,19] that is outlined in Scheme 1.

Racemic ketone **2** was synthesized according to the route shown in eq 2. The reaction of ketal **3** with 2 equiv of benzyltriphenylphosphonium bromide, followed by acidic deprotection of the ketone, gives **2** in 38% overall yield. Unfortunately, our attempts to prepare optically

Scheme 2. Synthesis of Racemic 1



active **2** by the Hanessian chiral olefination route[20] were unsuccessful. Apparently, steric hindrance by the dimethylene bridge slows addition to the carbonyl group at position C-3 enough to prevent the addition.



(2)

Ketone **1** was prepared from ketal **3** according to the route shown in Scheme 2. The bicyclic ketal **3** was reduced selectively by L-selectride to give alcohol **4** in 68% yield. The alcohol was protected with TBDMSCl to give **5** in 92% yield. Removal of the ethylene ketal group in acetone solution with a catalytic amount of *p*-toluenesulfonic acid gives ketone **6** in 57% yield. Wittig olefination of **6** followed by removal of the protecting TBDMS group with fluoride gives racemic alcohol **8**. Finally, oxidation of **8** gives racemic ketone **1**.

The synthesis of (−)-8-(phenylmethylene)bicyclo[3.2.1]-octan-3-one proceeds first by Hanessian olefination of **6** in 56% yield. Subsequent removal of the TBDMS protecting group gives (−)-**8** in 98% yield. Oxidation of **8** with chromium trioxide gives (−)-**1** in 80% yield. These reactions are outlined in Scheme 3. The enantiomers of ketone **1** were analyzed by chiral HPLC on a WHELK-01 column. The enantiomeric excess of (−)-**1** prepared as described is 60%.

(2) Photochemical Properties of Ketones 1 and 2. Irradiation of a suitable chiroptical phototrigger must lead to racemization (resolution) with no competing irreversible chemical reactions. Irradiation of a N_2-saturated, 8×10^{-3} M cyclohexane solution of ketone **2** at 313 nm leads to its consumption. Analysis of this reaction by GC/MS reveals formation of two isomeric products. Also, ^{1}H NMR spectroscopic analysis of the

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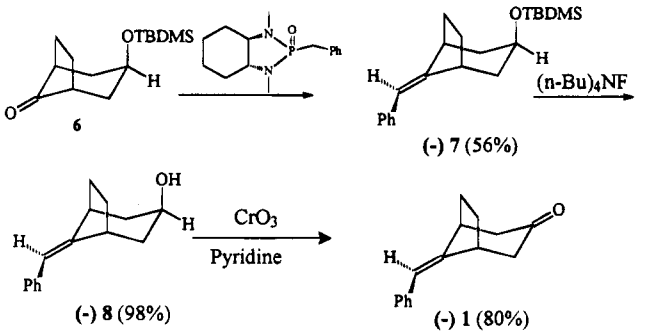
Scheme 3. Synthesis of Optically Active 1



reaction mixture reveals two new absorptions at δ 9.63 and 9.72 that are characteristic of aldehydes. The quantum yield for photodestruction of **2** was measured to be 0.054 using 2-hexanone as an actinometer.[21]

Although the products from the photolysis of **2** are not fully characterized,[22] it seems certain that the dominant photochemical reaction follows the well known Norrish I route of α-cleavage followed by hydrogen atom transfer to form aldehydes. Because of this decomposition, **2** is not be a suitable trigger for a chiroptical switch. In contrast to the light-induced destruction of **2**, ketone **1** is photostable. In particular, a ca. 8×10^{-3} M, N_2-saturated cyclohexane solution of **1** irradiated at 313 nm shows no significant decomposition after 105 h according to analysis by ^{1}H NMR spectroscopy and GC/MS.

The different behavior of **1** and **2** is attributed to structural features. The carbonyl group of **2** is contained in a five-membered ring, and α-cleavage generates a secondary radical. It is in just such cases where the Norrish I reaction is reported to be exceptionally rapid (ca. 10^{10} s^{-1}).[23] In contrast, the carbonyl group of **1** is contained in a six-membered ring, and α-cleavage will generate a primary radical. Evidently, intersystem crossing of the ketone and triplet energy transfer to the styryl group (see later) is faster than bond cleavage. The photochemical stability of **1** makes it a suitable candidate for a trigger in a chiroptical liquid crystal switch.

A second key requirement for the discovery of a suitable trigger for a chiroptical switch is efficient photoracemization. The quantum yield for photoracemization (Φ_{rac}) of (−)-**1** was determined by monitoring its loss of optical activity during irradiation at 313 nm in a N_2-saturated cyclohexane solution. The Φ_{rac} for **1** was found to be 0.14 using 2-hexanone as an actinometer.[21] Since the theoretical maximum value of Φ_{rac} is 0.5, the photoracemization of **1** is about 30% efficient. This is suitable for **1** to function as a chiroptical trigger.

(3) Spectroscopic Properties of Ketones 1 and 2. The UV-absorption spectra of ketones **1** and **2** are shown in Figures 1 and 2, respectively. Critically, both compounds show absorption bands at 313 nm, a wavelength characteristic of simple ketone absorptions and one at which the styrene chromophore absorbs weakly, if at all. Further, the extinction coefficient for absorption at 313 nm (ϵ_{313}) for ketone **1** is 14.5 M^{-1} cm^{-1}. Recall that simple ketones were selected for investigation as potential

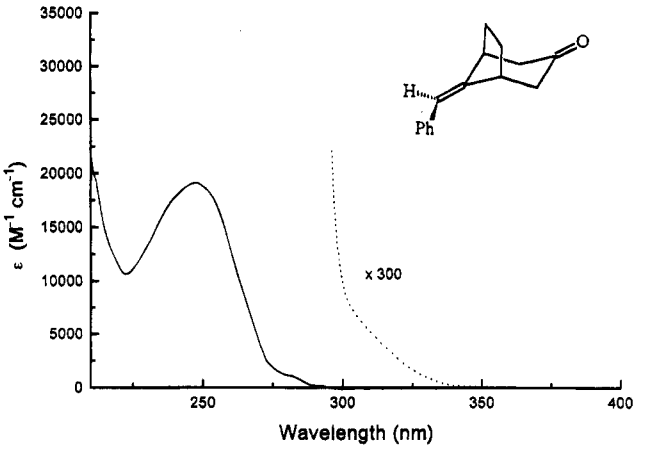


Figure 1. UV absorption spectrum of ketone **1** in cyclohexane solution.

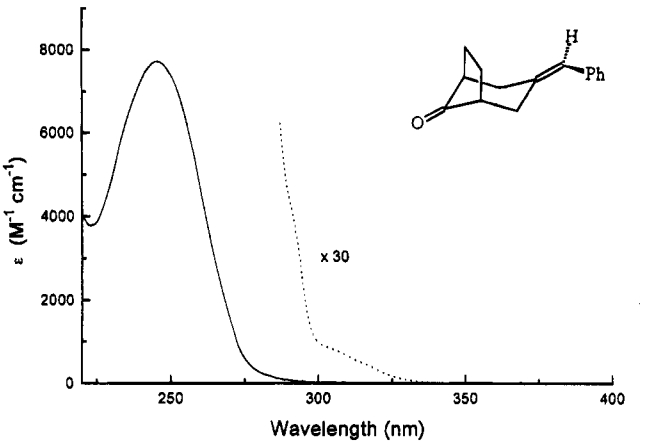


Figure 2. UV absorption spectrum of ketone **2** in cyclohexane solution.

chiroptical triggers because a small extinction coefficient will contribute to a large $[\gamma]_{PSS}$. Finally, from a practical point of view, it is important to note that 313 nm light is readily available from mercury lamps.

The CD spectra of (−)-**1** in cyclohexane solution at 6.59×10^{-4} and 6.59×10^{-3} M are shown in Figure 3 parts a and b, respectively. For **1**, $\Delta\epsilon_{313} = 0.728$ M^{-1} cm^{-1}. From the absorption and CD spectra of **1**, and calculation according to eq 1, $g_{313} = 0.0502$. Thus, irradiation of **1** at 313 nm with circularly polarized light will result in $[\gamma]_{PSS} = 2.5\%$ according to eq 1. This is the largest enantiomeric excess we have observed for a bichromophoric compound, and it is sufficient for development of this compound as a chiroptical trigger.

(4) Photoresolution of 1. Irradiation of **1** at 313 nm leads to excitation of the ketone group, subsequent intersystem crossing to the ketone triplet and energy transfer will form the styryl triplet state and cause interconversion of the enantiomers of **1** by rotation about the double bond. Consequently, the irradiation of racemic **1** with circularly polarized light (CPL) will result in the partial resolution of the ketone. A solution of racemic **1**, 8×10^{-3} M in cyclohexane, was irradiated with CPL through a 305 nm cutoff filter. The photoresolution was monitored by measuring the CD spectrum of the solution. At the start, of course, there is no detectable CD spectrum. After a few hours of irradiation, a spectrum becomes apparent, and after 47 h the spectrum shown in Figure 4 was recorded. Comparison of Figures 3 and

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(22) The absorption spectra of the products and starting ketone overlap so that the reaction can be taken only to low conversion before the products themselves are destroyed and a complex mixture results.

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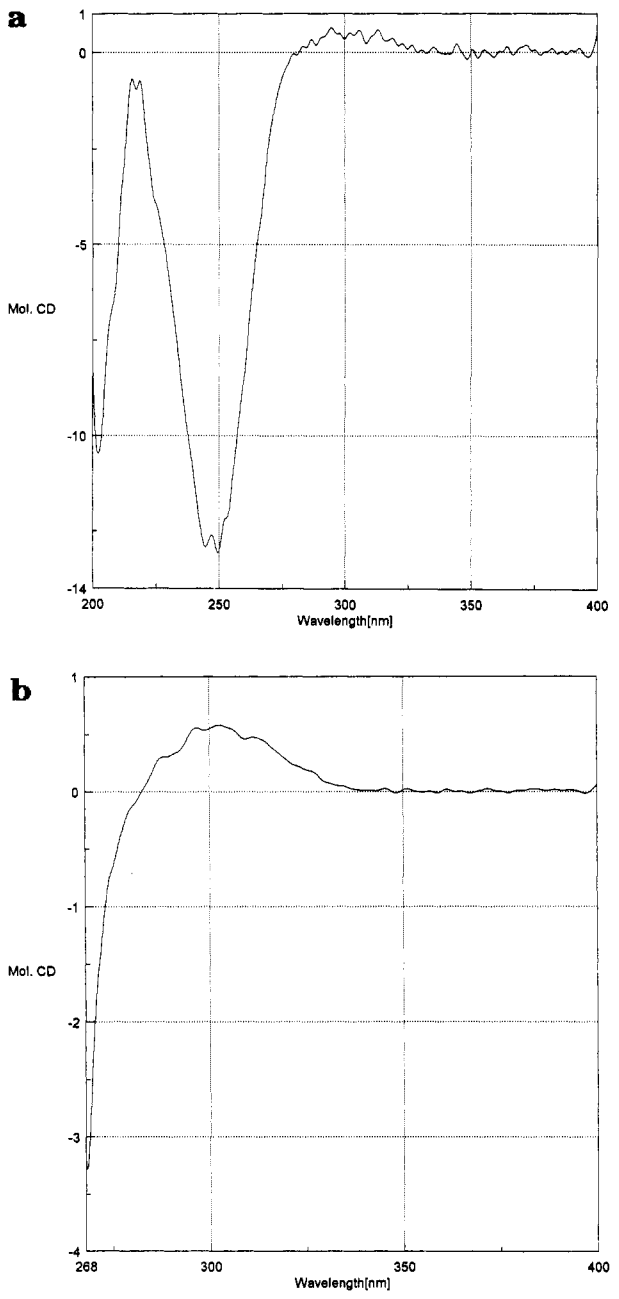

Figure 3. (a) Circular dichroism spectrum of (−)-**1** in cyclohexane solution at 6.59×10^{-4} M in a 0.1 cm pathlength cell. (b) Circular dichroism spectrum of (−)-**1** in cyclohexane solution at 6.59×10^{-3} M in a 0.1 cm pathlength cell.

4 reveals an enantiomeric excess of 1.6% in the irradiated solution. Clearly, the photoresolution of **1** is a success, and this compound can function as a chiroptical trigger.

(5) Properties of 1 in Liquid Crystalline Media. When an optically active compound is dissolved in a nematic liquid crystal, a helical pitch (p) develops according to eq 3 where β_M is a material parameter dependent on the specific additive and liquid crystalline material, and C is the concentration of the additive.

$$(p)^{-1} = [\gamma]\beta_M C \qquad (3)$$

ZLI-1167, a saturated hydrocarbon, is one of the few commercially available liquid crystalline materials that is transparent at 313 nm and has a nematic phase near room temperature. Ketone **1** shows poor solubility in

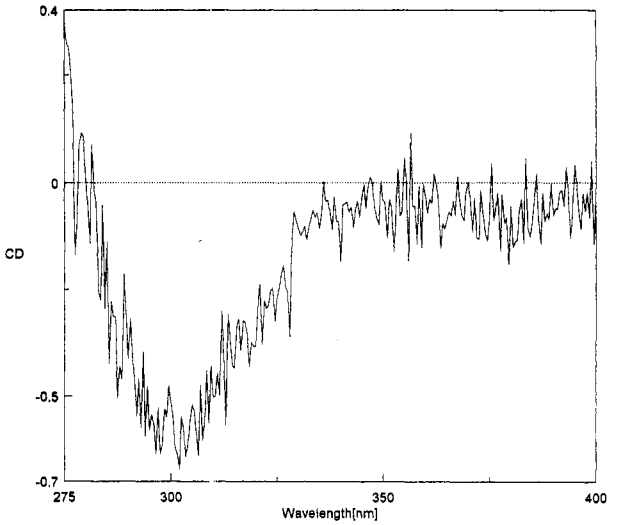

Figure 4. Circular dichroism spectrum recorded after irradiation of racemic **1** with circularly polarized light. The spectrum is recorded after 47 h of irradiation and is a 8.15×10^{-3} M cyclohexane solution in a 0.1 cm pathlength cell.

ZLI-1167. Unfortunately, it has not been possible to measure β_M by use of the droplet[24] or Grandjean–Cano methods for **1** in ZLI-1167.[25] Thus, **1** itself in ZLI-1167 is not suitable for use as a chiroptical trigger.

Conclusion

The work reported herein verifies the suitability of our strategy for the discovery of appropriate chiroptical triggers for liquid crystalline switches. Linking a ketone chromophore to a styryl rotating unit in a relatively rigid, bicyclic framework provides a $[\gamma]_{PSS}$ sufficiently large to trigger the reversible conversion of nematic and cholesteric liquid crystals. This solves the most difficult problem faced in the discovery of chiroptical triggers. Moreover, by appropriate control of structural features, it is clear that such compounds possess suitable thermal and photochemical stability to function as triggers. Unfortunately, ketone **1** is not sufficiently soluble in ZLI-1167 to function itself as a trigger. However, it is well-known that the solubility of liquid crystal dopants can be modified by incorporation of suitable substitutents. Future work will be focused on the discovery of analogs of **1** that maintain its chemical and chiroptical properties but have greater solubility in liquid crystalline materials such as ZLI-1167.

Experimental Section

General. Analytical spectroscopy and chromatography were performed generally as previously described.[4] Analyses of optical purity by HPLC were carried out with a WHELK-01 column (25 cm × 4.6 mm i.d., Regis Chemical Co.). Microscopic analyses were performed with a Fisher Micromaster polarizing microscope equipped with a Mettler FP 82 hot stage. All solvents and reagents obtained from commercial sources were used without further purification, unless other-

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wise noted. Cyclohexane was of spectrophotometric grade (Burdick & Jackson). Melting points were measured on a Büchi apparatus and are uncorrected. Elemental analysis were performed by the University of Illinois Microanalysis Service Laboratory.

(3a*R*,7a*R*)-2-Benzylhexa[3a,4,5,6,7,7a-hexahydro-1, 3-dimethyl-1,3,2-benzodiazaphosphole-2-Oxide (Hanessian Reagent, see Scheme 3, HR-I).[20] Under a N_2 atmosphere, a solution of diethyl benzylphosphonate (5 g, 21.9 mmol) in trimethylsilyl bromide (7.77 g, 50.7 mmol) was stirred at room temperature for 1 h. The volatile products were removed under reduced pressure, and the residue was dissolved in dry CH_2Cl_2 (40 mL) and treated with 18 drops of DMF, followed by adding oxalyl chloride (6.7 mL, 76 mmol). The mixture was stirred at room temperature overnight. Evaporation of the volatile products gave a crude product, which was recrystallized from hexane to afford 2.2 g (48%) of a yellow solid: ^{1}H NMR ($CDCl_3$) δ 3.93 (d, J = 17.5 Hz, 2H), 7.35–7.40 (m, 5H). This material was used directly for next step reaction.

Under a N_2 atmosphere, a solution of benzyl phosphonyl dichloride (2.16 g, 10.3 mmol) in benzene (30 mL) was added dropwise to a mixture of (−)-*trans*-N,N′-dimethyl-1,2-diaminocyclohexane (1.11 g, 7.82 mmol) and Et_3N (2.8 mL, 20.1 mmol) in benzene (30 mL) at 0 °C. After the addition, the reaction mixture was warmed to room temperature, stirred for 24 h, and then filtered. The precipitate was washed with EtOAc (50 mL), and the combined filtrate was dried ($MgSO_4$) and concentrated. Purification by column chromatography (silica gel, 9:1, ethyl acetate/methanol) gave 1.87 g (86%) of HR-I as a white solid: mp 100–103 °C; $[\alpha]_D$ = −107.4 (*c* 1.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.82–1.32 (m, 4H), 1.67–2.00 (m, 5H), 2.39 (d, J = 10.8 Hz, 3H), 2.57 (d, J = 10.2 Hz, 3H), 2.60–2.70 (m, 1H), 3.00–3.20 (m, 1H), 3.25–3.40 (m, 1H), 7.15–7.35 (m, 5H).

3-Benzoylbicyclo[3.2.1]octan-8-one. This compound was prepared according to the procedure of Stetter and co-workers.[18] Recrystallization from MeOH gave 2.75 g (80%) of the octanone: ^{1}H NMR ($CDCl_3$) δ 1.86 (bs, 5H), 2.10–2.30 (m, 2H), 2.40–2.60 (m, 2H), 2.60–2.80 (m, 2H), 3.30–3.60 (m, 1H), 7.40–7.60 (m, 3H), 7.70–7.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.40, 37.54, 37.89, 43.17, 128.42, 128.69, 132.61, 136.22, 203.07, 222.47; GC/MS *m*/*z* (relative intensity) 228 (M^+, 25), 210 (15), 200 (3), 146 (27), 105 (100), 77 (51), 55 (27).

3-*exo*-Benzoylbicyclo[3.2.1]octan-8-one 8-Ethylene Ketal.[18] According to the procedure given,[18] a mixture of ethylene glycol (4.44 g, 71.6 mmol), 3-benzoylbicyclo[3.2.1]octan-8-one (16.3 g, 71.6 mmol), and a catalytic amount of *p*-toluenesulfonic acid gave 16.4 g (84%) of ketal: ^{1}H NMR ($CDCl_3$) δ 1.50–1.80 (m, 4H), 1.90–2.10 (m, 4H), 2.10–2.30 (m, 2H), 3.50–3.70 (m, 1H), 3.95 (s, 4H), 7.40–7.60 (m, 3H), 7.90–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.36, 32.36, 37.02, 38.98, 63.80, 64.87, 116.06, 128.26, 128.58, 132.71, 136.57, 202.98; GC/MS *m*/*z* (relative intensity) 272 (M^+, 18), 218 (10), 167 (9), 140 (4), 105 (21), 99 (100), 77 (21), 55 (32).

Bicyclo[3.2.1]octan-3,8-dione 8-Ethylene Ketal (3). This compound was prepared by modification of the procedure described by Momose and co-workers.[19] To a mixture of 3-benzoylbicyclo[3.2.1]octan-8-one 8-ethylene ketal (2.07 g, 7.61 mmol), potassium *tert*-butoxide (95%, 1.23 g, 10.4 mmol), and *tert*-butyl alcohol (25 mL) was added hexamethylphosphoric triamide (25 mL). The resulting mixture was saturated with O_2 while stirring at 55 °C. After the reaction was complete, determined by GC, water was added, and the mixture was extracted with benzene. The extract was washed with water and evaporated to give a crude product, which on Kugelrohr distillation and column chromatography (silica gel, 4:1, hexane/ethyl acetate) afforded 580 mg (40%) of **3** as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 140–1.60 (m, 2H), 1.90–2.30 (m, 6H), 2.70–2.90 (m, 2H), 3.99 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 25.93, 39.25, 46.82, 64.34, 65.17, 115.78, 211.60; GC/MS *m*/*z* (relative intensity) 182 (M^+, 97), 154 (59), 139 (24), 125 (99), 99 (100), 55 (90). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.66; H, 7.62.

(±)-3-(Phenylmethylene)bicyclo[3.2.1]octan-8-one (2). Under a N_2 atmosphere, n-BuLi (1.18 mL, 1.6 M in hexane, 1.89 mmol) was added dropwise to a stirred suspension of benzyltriphenylphosphonium bromide (866 mg, 2 mmol) in dry THF (20 mL) at room temperature. After stirring for 30 min, a solution of **3** (182 mg, 1 mmol) in dry THF (5 mL) was added. The mixture was heated at reflux for 58 h and then quenched with H_2O. The mixture was extracted with Et_2O, washed with H_2O, dried ($MgSO_4$), and concentrated under vacuum to afford the crude product. Purification by column chromatography (silica gel, 10:1, hexane/ethyl acetate) gave 150 mg (60%) of (±)-3-(phenylmethylene)bicyclo[3.2.1]octan-8-one 8-ethylene ketal which was characterized by ^{1}H NMR spectroscopy, GC, and GC/MS. This material was treated with 80% acetic acid (5 mL) at 100 °C for 6 h. The resulting solution was quenched with saturated $NaHCO_3$ and extracted with Et_2O. The organic layer was washed with H_2O, dried ($MgSO_4$), and concentrated under vacuum. The residue was subjected to column chromatography (silica gel, 10:1, hexane/ethyl acetate) to give 78 mg (38%) of **2** as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.40–3.20 (m, 10H), 6.59 (s, 1H), 7.10–7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.96, 39.19, 44.24, 44.88, 47.21, 126.64, 128.15, 129.04, 130.03, 134.51, 137.39, 221.67; MS *m*/*z* (relative intensity) 212 (M^+, 99), 184 (3), 155 (11), 141 (25), 129 (100), 91 (33); UV (C_6H_{12}) λ_{max} 223 (log ϵ 3.58), 246 (3.89), 260 (3.67), 280 (2.73), 300 (1.51). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.89; H, 7.64.

3-Hydroxybicyclo[3.2.1]octan-8-one 8-Ethylene Ketal (4). Under a N_2 atmosphere, a solution of **3** (1.5 g, 8.24 mmol) in dry THF (10 mL) was cooled to −78 °C, and L-Selectride (11.0 mL, 1.0 M in THF, 11.0 mmol) was added dropwise. The reaction mixture was stirred at −78 °C for 9 h, and then hydrogen peroxide (8 mL, 30%) was added. The solution was warmed to room temperature, and 5% HCl (aq) was added until the solution was slightly acidic. The reaction mixture was poured into Et_2O, and the organic layer was washed with saturated $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated under vacuum to afford a crude product. Purification by column chromatography (silica gel, 4:1, hexane/ethyl acetate) gives 1.03 g (68%) of **4** as a white solid: mp, 101–104 °C; ^{1}H NMR ($CDCl_3$) δ 1.22 (m, 1H), 1.60–2.00 (m, 8H), 2.10–2.30 (m, 2H), 3.92 (bs, 4H), 3.90–4.10 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.16, 38.28, 38.34, 63.73, 64.74, 65.33, 116.51; GC/MS *m*/*z* (relative intensity) 184 (M^+, 24), 167 (9), 125 (9), 113 (100), 99 (71), 55 (47). Anal. Calcd for $C_{10}H_{16}O$: C, 65.19; H, 8.75. Found: C, 65.13; H, 8.98.

3-*endo*-[(*tert*-Butyldimethylsilyl)oxy]bicyclo[3.2.1]octan-8-one 8-Ethylene Ketal (5). A solution of **4** (2.56 g, 13.9 mmol), imidazole (2.01 g, 29.5 mmol), and *tert*-butyldimethylsilyl chloride (3.51 g, 22.6 mmol) in anhydrous DMF (30 mL) was stirred for 48 h. The reaction mixture was taken up in H_2O and extracted with Et_2O, and the organic layer was washed with H_2O again, dried ($MgSO_4$), and concentrated under vacuum to afford a crude product. Purification by column chromatography (silica gel, 8:1, hexane/ethyl acetate) gave 3.81 g (92%) of **5** as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.88 (s, 9H), 1.60–2.20 (m, 10H), 3.91 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −5.04, 17.82, 24.90, 25.77, 38.43, 38.53, 63.65, 64.67, 65.45, 116.85; GC/MS *m*/*z* (relative intensity) 298 (M^+, 23), 241 (100), 197 (20), 167 (30), 123 (43), 99 (32), 75 (89).

3-*endo*-[(*tert*-Butyldimethylsilyl)oxy]bicyclo[3.2.1]octan-8-one (6). A solution of **5** (1.52 g, 5.1 mmol) and *p*-toluenesulfonic acid (59 mg, 0.34 mmol) in dry acetone (200 mL) was heated at reflux for 66 h. After cooling to room temperature, 5% $NaHCO_3$ was added to neutralize the acid. The acetone was evaporated under vacuum, and the residue was diluted with Et_2O. The organic layer was washed with H_2O, dried ($MgSO_4$), and concentrated under vacuum. Purification by column chromatography (silica gel, 8:1, hexane/Et_2O) gives 740 mg (57%) of **6** as a white solid: mp, 87–89 °C; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6H), 0.92 (s, 9H), 2.10–2.50 (m, 10H), 3.99 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −5.04, 17.83, 22.42, 25.73, 44.05, 45.48, 65.67, 223.12; GC/MS *m*/*z* (relative intensity) 254 (M^+, 5), 197 (97), 151 (6), 105 (14), 75 (100).

(±)-3-*endo*-[(*tert*-Butyldimethylsilyl)oxy]-8-(phenylmethylene)bicyclo[3.2.1]octane (7). Under a N_2 atmosphere, n-BuLi (0.49 mL, 1.23 M in hexane, 0.6 mmol) was

added dropwise to a stirred suspension of benzyltriphenylphosphonium bromide (287 mg, 0.66 mmol) in dry THF (10 mL) at room temperature. After stirring for 30 min, a solution of **6** (150 mg, 0.59 mmol) in dry THF (4 mL) was added. The mixture was heated at reflux for 22 h, quenched with H_2O, and extracted with Et_2O. The organic layer was washed with H_2O, dried ($MgSO_4$), and concentrated under vacuum to afford a crude product. Purification by column chromatography (silica gel, hexane) gave 92 mg (47%) of **7** as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.05 (s, 6H), 0.93 (s, 9H), 1.60–2.40 (m, 7H), 2.58 (m, 1H), 3.12 (m, 1H), 4.04 (m, 1H), 6.20 (s, 1H), 7.10–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −5.01, 17.89, 25.80, 25.99, 27.95, 35.74, 43.49, 43.85, 45.06, 66.92, 114.60, 125.73, 128.14, 128.16, 138.61, 154.69; GC/MS *m/z* (relative intensity) 328 (M^+, 92), 271 (83), 195 (40), 155 (17), 115 (15), 91 (31), 75 (100).

(±)-3-*endo*-8-(Phenylmethylene)bicyclo[3.2.1]octan-3-ol (8). To a solution of **7** (316 mg, 0.96 mmol) in dry THF (7 mL) was added a solution of tetrabutylammonium fluoride (3 mL, 1.0 M in THF, 3 mmol) at room temperature. The mixture was heated at reflux for 6 h, water was added, and the mixture was extracted with Et_2O. The organic layer was washed with H_2O again, dried ($MgSO_4$), and concentrated under vacuum. Purification by column chromatography (silica gel, 4:1, hexane/ethyl acetate) gave 187 mg (91%) of **8** as a white solid: mp, 103–105 °C; ^1H NMR ($CDCl_3$) δ 1.60–2.40 (m, 8H), 2.62 (m, 1H), 3.15 (m, 1H), 4.15 (m, 1H), 6.22 (s, 1H), 7.10-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.31, 28.20, 35.38, 43.12, 43.36, 44.73, 66.69, 115.25, 125.87, 128.16, 138.37, 153.46; MS *m/z* (relative intensity) 214 (M^+, 42), 196 (24), 168 (38), 155 (57), 129 (48), 117 (74), 105 (16), 91 (100), 77 (28), 69 (47). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.85; H, 8.54.

(±)-8-(Phenylmethylene)bicyclo[3.2.1]octan-3-one (1). Under a N_2 atmosphere, chromium trioxide (490 mg, 4.9 mmol) was added to a solution of dry pyridine (775 mg, 9.81 mmol) in dry CH_2Cl_2 (13 mL) at room temperature. The reddish solution was stirred for another 15 min, and then a solution of **8** (173 mg, 0.808 mmol) in dry CH_2Cl_2 (3 mL) was added. A tarry, black deposit separated immediately. After stirring an additional 15 min at room temperature, the solution was decanted from the residue, which was washed with Et_2O and CH_2Cl_2. The combined organic layers were washed with 5% NaOH, 5% HCl, 5% $NaHCO_3$ and brine and dried ($MgSO_4$). Purification by column chromatography (silica gel, 4:1, hexane/ethyl acetate) gives 130 mg (76%) of (−)-**7** as a white solid: mp 71–74 °C; ^1H NMR ($CDCl_3$) δ 1.60–2.00 (m, 4H), 2.40–3.00 (m, 5H), 3.30–3.50 (m, 1H), 6.47 (s, 1H), 7.20–7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 27.18, 29.03, 35.41, 42.99, 51.13, 52.26, 119.03, 126.63, 128.22, 128.40, 137.55, 149.44, 211.31; GC/MS *m/z* (relative intensity) 212 (M^+, 100), 170 (37), 156 (15), 142 (33), 128 (34), 115 (27), 91 (28), 77 (17); UV (C_6H_{12}) λ_{max} 247 (log ϵ 4.28), 280 (2.95), 313 (1.16). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.55; H, 7.46.

(−)-3-*endo*-[(*tert*-Butyldimethylsilyl)oxy]-8-(phenylmethylene)bicyclo[3.2.1]octane [(−)-7]. Under a N_2 atmosphere, HR-I (153 mg, 0.55 mmol) was added to dry THF (5 mL) at room temperature. The mixture was cooled to −78 °C and stirred for 30 min. Next, a solution of **6** (129 mg, 0.5 mmol) in dry THF (3 mL) was added, and the mixture was stirred for 5 h. The mixture was warmed to room temperature, and glacial acetic acid (0.4 mL) was added. The reaction was kept at room temperature for 1.5 h and then diluted with Et_2O, washed with 5% $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated. Purification by column chromatography (silica gel, hexane) gave 92 mg (56%) of (−)-**7** as a colorless liquid: $[\alpha]_D$ = −152 (*c* 0.26, C_6H_{12}); ^1H NMR was the same as (±)-**7**; GC/MS *m/z* (relative intensity) 328 (M^+, 76), 271 (68), 195 (29), 167 (17), 115 (16), 91 (33), 75 (100).

(−)-3-*endo*-8-(Phenylmethylene)bicyclo[3.2.1]octan-3-ol [(−)-8]. Removal of the silyl protecting group from (−)-**7** (350 mg, 1.06 mmol) was accomplished as described above for (±)-**7** with tetrabutylammonium fluoride (3.2 mL, 1.0 M in THF, 3.2 mmol) giving 223 mg (98%) of (−)-**8** as a white solid: mp, 100–103 °C; $[\alpha]_D$ = -188 (*c* 0.28, C_6H_{12}); ^1H NMR and GC/MS were identical with (±)-**8**.

(−)-3-*endo*-8-(Phenylmethylene)bicyclo[3.2.1]octan-3-one (1). Following the procedure described for the racemic alcohol, 202 mg, (0.94 mmol) of (−)-**8**, chromium trioxide (620 mg, 6.2 mmol), and pyridine (963 mg, 12.2 mmol) were used to afford 161 mg (80%) of a white solid: mp, 64–67 °C; $[\alpha]_D$ = −167 (*c* 0.27, C_6H_{12}); ^1H NMR δ 1.60–2.00 (m, 4H), 2.40–3.00 (m, 5H), 3.37 (m, 1H), 6.47 (s, 1H), 7.20–7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 27.16, 29.01, 35.39, 42.97, 51.10, 52.24, 119.01, 126.61, 128.19, 128.37, 137.53, 149.42, 211.24; GC/MS *m/z* (relative intensity) 212 (M^+, 100), 170 (37), 156 (17), 142 (44), 128 (51), 115 (42), 91 (40), 77 (26); CD (C_6H_{12}) λ_{ext} 249 ($\Delta\epsilon$ −12.99), 265 (-4.99), 295 (0.519), 306 (0.527), 313 (0.437). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.57; H, 7.62.

Photolysis of Compounds 1 and 2. The irradiation was performed at 25 °C with a high pressure 1000 W Hg–Xe arc lamp fitted with a 313 nm interference filter. The solutions were purged with N_2 for 30 min prior to irradiation and were stirred magnetically during irradiation to maintain homogeneity. The reactions were monitored by GC and GC/MS.

Quantum Yield Determination. For the compounds **1** and **2**, quantum yields were measured using 2-hexanone as an actinometer.[26] The 2-hexanone solution (ca. 1.0 M in pentane) with decane as the internal standard was irradiated at 313 nm for different times at room temperature, and the photolyses were monitored by GC.

Photoresolution of Compound 1. Circularly polarized light (CPL) was produced from the high pressure 1000 W Hg–Xe arc lamp. The beam passed through a 305 nm cutoff filter, a focusing lens, a linear polarizer, and finally a Fresnel rhomb. The circular polarization was confirmed with $Cr(acac)_3$.[27] CPL irradiation of (±)-**1** in cyclohexane was performed at 25 °C and the photoresolution was monitored by circular dichroism (CD).

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