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Chiroptical Studies of Labile or Difficult-to-Resolve Molecules Generated by Chiral Laser Photochemistry. 2.[1] Products and Steric Course of the Phototransformation of the Racemate

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Abstract: This paper deals with a complex photoresolution of a racemate with circularly polarized light (CPL) which involves the phototransformation of the racemate into a chiral, labile compound. We show here how to obtain both the dichroism for the pure enantiomers and their absolute configuration, besides defining the stereochemical course for the phototransformation. This is exemplified by the irradiation of racemic 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**1**) with ultraviolet, left CPL which led to a mixture containing both the photoresolved (−)(1*S*,5*R*)-**1**, with 0.3% optical purity and $\Delta\epsilon_{max}(365) = -2.4$, and the labile product of the phototransformation of the racemate, (−)(1*S*,5*S*)-7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one ((−)(1*S*,5*S*)-**2**), with 1.6% optical purity and $\Delta\epsilon_{max}(350) = -2.0$. Acidification of this mixture led to chemically and optically stable methyl (−)(1*R*)-4-oxo-2-cyclopentene-1-acetate ((−)(1*R*)-**7**), with 1.6% optical purity, $\Delta\epsilon_{max}(320) = -0.39$, by selective hydrolysis of **2**. The absolute configuration for **2** was assigned by correlation with the product of catalytic reduction of (−)(1*R*)-**7**, i.e., methyl (+)-3-oxocyclopentane-1-acetate, whose absolute configuration, (1*R*), is independently known. The above results show that the **1** → **2** phototransformation is attained by complete inversion of configuration at the bridgeheads. The Kronig–Kramers theorem helped to elucidate the chiroptical properties for compounds **1**, **2**, and **7**.

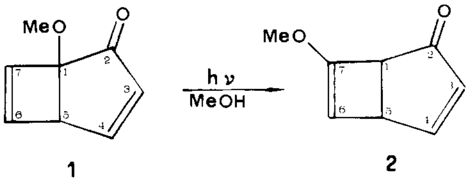
I. Introduction

The potential of chiroptical data to afford more insight into chiral molecules is widely recognized. However, either labile or difficult-to-resolve molecules are not easily amenable to chiroptical studies, and little has been done until quite recently in the direction of overcoming such problems in order to arrive at the dichroism for pure enantiomers.

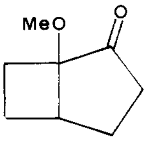
Progress in this direction has come from our recent application of the partial photoresolution of racemates with circularly polarized light (CPL)[1] which bears some connection with previous work.[3] The method[1] consists in partially resolving a racemate with CPL and measuring both the differential CPL absorption of the mixture and the reaction extent. Simple mathematics then allow us to obtain the dichroism for the pure enantiomer from data for the enantiomer present in excess in the mixture.[1]

We have exemplified this approach with the case of racemic 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**1**),[1] the photoresolution of which involves formation of isomeric 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**2**).[4] Chiroptical data for (−)-**1** were deduced through data relative to both (−)-1-methoxybicyclo[3.2.0]heptan-2-one ((−)-**3**) and the hydrogenated mixture of **1** and **2** from which **3** was separated. The octant rule[5] allowed us to assign the absolute configuration for (−)-**3** and, consequently, of (−)-**1**.

Further stereochemical problems are now posed by such complex photoresolution processes. One problem is, in fact, to obtain chiroptical data for the product of the phototransformation, and another problem is to clarify the stereochemical course of the phototransformation itself. These two problems are solved here for the case of the photoresolution of (±)-**1** with CPL.



1 **2**



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II. Results and Discussion

A. Phototransformation of the Racemate Viewed with Two-Dimensional Formulas. It has already been shown that either C(4)- or C(6)-alkyl-substituted bicyclics of type **1** undergo photoisomerization into alkyl-substituted, type-**2** bicyclics by formal C(1)–C(2) and C(5)–C(4) bond rupture followed by C(7)–C(2) and C(6)–C(4) bond re-formation from the fragments.[4a]

We have now proven that this formal bond-rupture, bond-formation process does not require the presence of alkyl substituents at the ring carbons of **1**, but also occurs with deuterium-labeled bicyclics of type **1**, such as **5** (Scheme I). In fact, irradiation of a well-stirred methanolic 0.031 M solution of **4**[6] (25 mL) with linearly polarized light (LPL), obtained from a laser source (350 and 363 nm, jointly, 0.5 W), and ^{1}H NMR examination of the mixture at time intervals, showed the following series of events. Thus, during the first hour of irradiation, the resonances for both the ring protons (δ 7.03 and 6.90) and the methoxy group (δ 3.90) of **4** decreased, while the resonances for **5** (singlets for H(4), H(6), and OCH_3 at respectively δ 7.43, 6.60, and 3.40) emerged, thereafter increasing steadily. After 100 min of irradiation, since a large percentage (ca. 80%) of the strongly light-absorbing **4** had been transformed, thus allowing **5** to compete effectively with **4** for light absorption, the signals for **6** (a doublet

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[1] Previous communication in this series: Cavazza, M.; Zandomeneghi, M.; Festa, C.; Lupi, E.; Sammuri, M.; Pietra, F. *Tetrahedron Lett.* **1982**, *23*, 1387–1390.

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[3] Balavoine, G.; Moradpour, A.; Kagan, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 5152–5158. Buchardt, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 179–185, and references therein.

[4] (a) Dauben, W. G.; Koch, K.; Smith, S. L.; Chapman, O. L. *J. Am. Chem. Soc.* **1963**, *85*, 2616–2621. (b) Chapman, O. L.; Lassila, J. D. *Ibid.* **1968**, *90*, 2449–2450.

[5] Moffitt, W.; Woodward, R. B.; Moscowitz, A.; Klyne, W.; Djerassi, C. *J. Am. Chem. Soc.* **1961**, *83*, 4013–4018. Djerassi, C.; Records, R.; Bunnenberg, E.; Mislow, K. *Ibid.* **1962**, *84*, 870–872.

[6] Pietra, F.; Giocasta, M.; Del Cima, F. *Tetrahedron Lett.* **1969**, 5097–5100.

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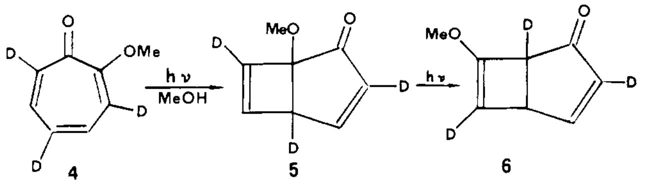
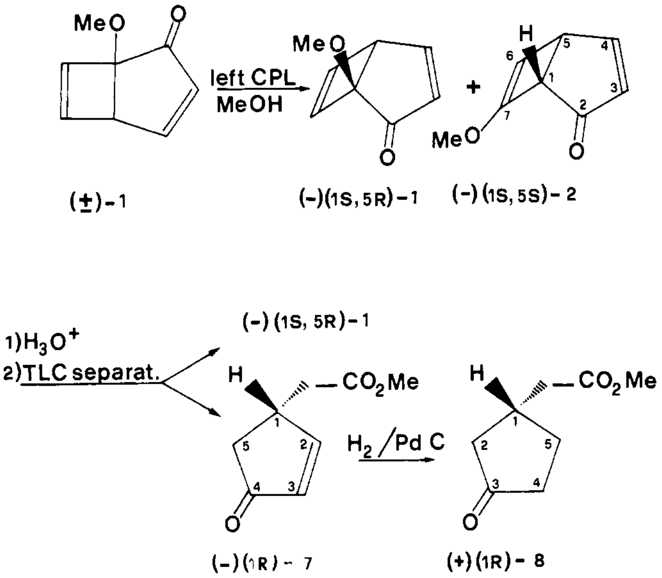
Scheme I



Scheme II. Irradiation of (±)-1 with Circularly Polarized Light (CPL) and Analysis of the Reaction Mixture[a]



[a] Structural formulas or configuration notations represent the absolute configuration for the enantiomer in excess, while the sign of the optical rotation is given at 436 nm.

at δ 7.50, $J_{4,5}$ = 2.0 Hz, for H(4) and a singlet at δ 3.55 for OCH_3, which obscures the doublet for H(5)) began to emerge. No other resonances, besides those for **4**, **5**, and **6**, could be detected.

B. Chiroptical Data for the Product of Phototransformation of the Racemate. Having established, at the level of planar formulas, the course of the **1** → **2** rearrangement (Scheme I), we turned to the problem of the spatial arrangement of the atoms in the product of the phototransformation (**2**). We were already aware that chiral irradiation of (±)-**1** produces a mixture of optically active **1** and **2**, and that optically active **2** could hardly be separated unaltered from the mixture.[1] We were therefore faced with the problem of transforming optically active **2** into a stable derivative which could be separated from the mixture and the absolute configuration of which could be correlated to that of **2**. In analogy with the case of optically active **1**,[1] we first tried to hydrogenate catalytically, at the olefinic bonds, a mixture of **1** and **2** and to separate the product of the hydrogenation of **2** from the isomeric **3**. However, both preparative GC and preparative HPLC gave unsatisfactory results. On further scrutiny, we found that a mixture of **1** and **2**, on slight acidification, rapidly gave a mixture of methyl 4-oxo-2-cyclopentene-1-acetate (**7**) and unchanged **1**, which could easily be determined in the mixture by ^{1}H NMR spectroscopy and could also be separated from one another by preparative TLC (Scheme II).

Formation of **7** from **2** must be interpreted in terms of an acid-catalyzed hydrolysis of **2** as an enol ether, via water attach at C(7) followed by reverse aldol reaction with C(1)–C(7) bond breaking.[7] Consequently, as the stereochemistry at C(5) of **2** is retained, (1*R*)-**7**, (1*S*,5*S*)-**2**, and (1*R*)-**8** must have the same absolute configuration at respectively C(1), C(5), and C(1). So, as **2** is cis-fused, (1*S*,5*S*)-**2** is directly correlated to (1*R*)-**8**.

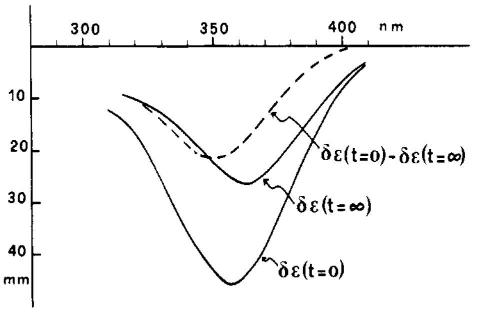


Figure 1. CD spectra (elongation in mm) related to the processes of Scheme II: $\delta\epsilon(t=0)$, a 15:85 mixture of (−)-**1** and (−)-**2** obtained from CPL irradiation of (±)-**1** before acidification of the mixture; $\delta\epsilon(t=\infty)$, residual (−)-**1** plus formed (−)-**7** after 1.5 h for acidification of the mixture at $t = 0$; $\delta\epsilon(t=0) - \delta\epsilon(t=\infty)$, obtained by subtracting spectrum $\delta\epsilon(t=\infty)$ from spectrum $\delta\epsilon(t=0)$; it represents the CD spectrum of (−)-**2** contributed, in the 320–300-nm region, by that of (−)-**7** (**2** shows maximum dichroism − 2.0 at 350 nm).

We can anticipate that the easy route **2** → **7** → **8** will prove more useful, for our purposes, than the difficult one from **2** to the product of hydrogenation of **2**. This is because the absolute configuration for **8** is already independently known.

We could now start with the chiral photochemistry by irradiating a well-stirred solution of (±)-**1** (0.150 g) in methanol (15 mL) with left CPL (350 and 363 nm, jointly, 0.3 W) during 20 min. This led to a 15% conversion of **1** into **2**, as measured by ^{1}H NMR spectroscopy. The resulting optically active mixture showed α_{436} −0.050°. A portion of this mixture, 5 mL, was added to five drops of 0.75 M sulfuric acid, whereby α_{436} steadily increased for 60 min from −0.050 to −0.030°, thereafter remaining constant.

The residual mixture from the chiral irradiation, 10 mL, was distilled at reduced pressure to recover 0.0565 g of a mixture of optically active **1** and **2** which was dissolved in 3 mL of methanol to give the CD spectrum shown in Figure 1 (t = 0). On addition of two drops of 0.75 M sulfuric acid to this mixture, the dichroic spectrum began both to decrease in intensity and to shift toward the visible, until, after 1.5 h, it ended to what is shown in Figure 1 ($t = \infty$).

These results show that acid hydrolysis of the mixture of chiral irradiation of (±)-**1**, owing to the disappearance of optically active **2** and its replacement by optically active **7** (Scheme II), is attained by both a 40% decrease of α_{436} and a decrease in intensity, besides a red shift of 10 nm, of the dichroism (Figure 1). We will show later that (−)-**7** gives only a negligible contribution to $\delta\epsilon$[8] at $t = \infty$, because $\Delta\epsilon$[8] for **7** is centered at about 320 nm and is of little value.[9] Therefore, looking at Figure 1, the dichroism for (−)-**1** is represented by the curve $\delta\epsilon(t=\infty)$, while the dichroism for (−)-**2** is given by the curve $\delta\epsilon(t=0) - \delta\epsilon(t=\infty)$. As regards the optical rotations, that due to (−)-**1** is, substantially, given by $\alpha_{436}(t=\infty)$ while that due to (−)-**2** is given by $\alpha_{436}(t=0) - \alpha_{436}(t=\infty)$. This means that (−)-**1** contributes by about 60% to the optical rotation of the mixture of (−)-**1** and (−)-**2** produced during the above chiral irradiation of (±)-**1**.

Let us now digress briefly about the origin, in terms of dichroic bands, of the optical activities measured here. In order to evaluate the relative contributions of (−)-**1** and (−)-**2** to α_{436} from the n → π* bands, we make use of the $\delta\epsilon^1 = \delta\epsilon(t=\infty)$ and $\delta\epsilon^2 = \delta\epsilon(t=0) - \delta\epsilon(t=\infty)$ curves through the Kronig–Kramers transforms[10]

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[7] In our hands, the **2** → **7** reaction proved to be a thermal, acid-catalyzed reaction. We noticed, however, that irradiation of **1** according to Scheme II does directly produce some **7** if the reactor glass walls have not been previously neutralized, for example, by the shaking with a bicarbonate solution. Therefore, formation of **7** during previous irradiations[4a] must have arisen from hydrolysis of **2** catalyzed by some acid, for example, just acidic glass walls of the reactor employed.

[8] $\Delta\epsilon$ is the circular dichroism of a compound at 100% optical purity, while $\delta\epsilon = \Delta\epsilon$(OP). Moreover, configuration notations represent the absolute configuration for the enantiomer in excess.

[9] We have proved that (−)-**7** neither decomposes nor racemizes under the acidic conditions used for generating it from (−)-**2**. The same is true for optically active **1**.

[10] Moscowitz, A. *Tetrahedron* **1961**, *13*, 48–54. Carver, J. P., Sheckter, E.; Blout, E. R. *J. Am. Chem. Soc.* **1966**, *88*, 2550–2572.

$$[\Phi]_\lambda = \frac{2}{\pi}3298 \int_{n \rightarrow \pi^*} \frac{\delta\epsilon(\lambda')\lambda'}{\lambda^2 - \lambda'^2}\,d\lambda' \qquad (1)$$

Numerical calculations give the molar rotation $[\Phi]^{20}{}_{436} = -2.3$ deg·Liters cm^{-1}·mol^{-1} for (−)-**1** and $[\Phi]^{20}{}_{436} = -9.4$ for (−)-**2**. By comparing these values with the observed ones, −4.2 for (−)-**1** and −21 for (−)-**2**, we see that the dichroism of the $n \rightarrow \pi^*$ transition accounts for only about half of the observed rotation at 436 nm for both compounds. The relatively important contribution of other, more energetic, transitions to α_{436} led us to search for the $\pi \rightarrow \pi^*$ CD band in the 200–250-nm spectral region. However, no such dichroic band could be detected, which implies that the dissymmetry factor, $g = \delta\epsilon/\epsilon$, must be of little value.

Coming back to the central problem, since we know both the percentage of **1** transformed during the chiral irradiation and the differential circular absorbance $\delta A(355)$ of (−)-**1** (from the curve $\delta\epsilon(t{=}\infty)$ in Figure 1), we can evaluate from eq 2 the dichroism for optically pure (−)-**1**.

$$\Delta\epsilon^1(355) = (2\epsilon^1(355)\delta A(355)/\chi\delta c^1)^{1/2} \qquad (2)$$

Equation 2 has been derived from the differential equations governing the rate of disappearance of the enantiomers during the irradiation of a racemate with CPL.[1] Here, 355 is the mean laser-light wavelength, χ is the optical path length, ϵ^1 is the molar extinction coefficient of **1** and δc^1 is the variation of the concentration of **1** during the irradiation. We thus obtain $\Delta\epsilon^1 = -2.28$ at 355 nm and −2.45 at the maximum of the CD band, 365 nm. This means that (−)-**1** was formed during the above chiral irradiation of (±)-**1** with 0.28% optical purity. It must be noticed that the $\Delta\epsilon^1$ value obtained here is in excellent agreement with the value (−2.1 at 355 nm) we have previously obtained indirectly through the hydrogenated derivative (−)-**3**.

We have seen that, in the case of **1**, the knowledge of $\delta\epsilon^1$ leads directly to $\Delta\epsilon^1$, at least as far as the $n \rightarrow \pi^*$ band is concerned. In the case of **2**, in order to arrive at $\Delta\epsilon^2$ from a knowledge of $\delta\epsilon^2$ (curve $\delta\epsilon(t{=}0) - \delta\epsilon(t{=}\infty)$ in Figure 1), we must also know the degree of stereoselectivity for the $\mathbf{1} \rightarrow \mathbf{2}$ photoisomerization. Assuming that, as will be proved later, the isomerization is stereospecific, the optical purity (OP) for enantiomeric **1** and **2** is given by respectively eq 3 and 4. Here c_l and c_r represent respectively the concentrations of the enantiomers preferentially absorbing left and right CPL, δc_l or δc_r represents the variation of the concentration of a particular enantiomer, and δc is the sum of the change of the concentrations of both enantiomers. At zero irradiation time the relationships $c_l = c_r = c_0/2$ holds. Thus

$$\mathrm{OP}(1) = \frac{|c_l^1 - c_r^1|}{c_l^1 + c_r^1} = \frac{|(c_0^1/2 + \delta c_l^1) - (c_0^1/2 + \delta c_r^1)|}{c_0^1/2 + \delta c_l^1 + c_0^1/2 + \delta c_r^1} = \frac{|\delta c_l^1 - \delta c_r^1|}{c_0^1 + \delta c^1} \qquad (3)$$

and, since

$$|\delta c_l^2 - \delta c_r^2| = |\delta c_l^1 - \delta c_r^1|$$

and

$$\delta c_l^2 + \delta c_r^2 = |\delta c^1|$$

we have

$$\mathrm{OP}(2) = \frac{|\delta c_l^2 - \delta c_r^2|}{\delta c_l^2 + \delta c_r^2} = \mathrm{OP}(1)\frac{c_0^1 + \delta c^1}{|\delta c^1|} \qquad (4)$$

Equation 4 immediately gives 0.28(0.85/0.15) = 1.6% for the optical purity of (−)-**2** formed during the above chiral irradiation of (±)-**1**. From the value of $\delta\epsilon^2$ at 350 nm we now obtain $\Delta\epsilon^2 = -2.0$ at the center of the dichroic band.

We have seen above that the dichroic spectrum of (−)-**1**, as reported in Figure 1, $\delta\epsilon(t{=}\infty)$, is deformed, albeit slightly, by the contribution of (−)-**7** in the high-frequency zone. On the other hand, we are now in a position to obtain the CD spectrum of chemically pure **1**. To this end, we irradiated (±)-**1** with left CPL as above, but for a longer time. Acidic workup of the irradiated mixture, followed by TLC separation (Scheme II), afforded chemically pure (−)-**1** having 1.2% optical purity. The actual dichroic spectrum obtained from this sample is shown in Figure 2a.

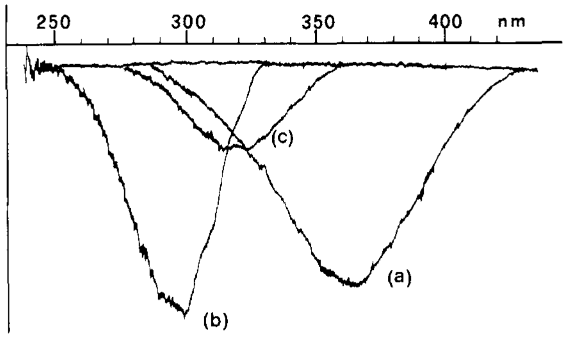

Figure 2. Actual dichroic spectra in arbitrary ordinate units: (a) (−)-**1**, OP ≃ 1.2%, 0.089 M in MeOH, 0.2-cm-cell optical path length, $\Delta\epsilon_{\max}(365) = -2.45$; (b) (−)-**8**, OP ≃ 1.6%, 0.0195 M in EtOH, 1-cm-cell optical path length, $\Delta\epsilon_{\max}(297) = -1.82$; (c) (+)-**7**, OP ≃ 1.6%, 0.060 M in MeOH, 0.5-cm-cell optical path length, $\Delta\epsilon_{\max}(320) = -0.39$.

C. Absolute Configuration for the Product of Phototransformation of the Racemate. As already discussed in section II.B, the absolute configuration of **2** is directly correlated to that of either **7** or **8** (Scheme II). Since the absolute configuration for **8** is independently known,[11a] from chiroptical data for **2**, **7**, and **8**, we can arrive at the absolute configuration for **2**. To this end, we repeated the photoresolution of (±)-**1**, at the same laser frequencies and power as in the experiments in section II.B, but with light of opposite chirality. So, a solution of (±)-**1**, 0.385 g in 50 mL of methanol, was irradiated with right CPL until a ca. 40% conversion of **1** into **2**, giving α_{436} 0.145° and α_{589} 0.037°. Acidic workup and repeated TLC purifications led to chemically pure (+)-**7**, 0.038 g, which was dissolved in 10 mL of methanol to give α 0.010, 0.006, 0.006, and 0.006° at respectively 436, 546, 578, and 589 nm. Catalytic hydrogenation of (+)-**7**, 0.038 g in 5 mL of ethanol, which went to completion, as shown by GLC, gave (−)-**8** with α −0.065, −0.031, −0.016, −0.015, and −0.015° at respectively 365, 436, 546, 578 and 589 nm. This enabled us to assign the absolute configurations (−)(1*S*)-**8**, (+)(1*S*)-**7**, and (+)(1*R*,5*R*)-**2** from the known (1*R*) absolute configuration for (+)-**8**.[11a] We can conclude that the (−)-**1** → (+)-**2** photoisomerization involves inversion of configuration at the brigdeheads[12] (Scheme II).

It is now interesting to evaluate the optical purities of (+)-**2**, (+)-**7**, and (−)-**8** obtained in the above irradiation. From the value reported above, we obtain the specific rotation $[\alpha]_D{}^{20} = -2.0$ deg·cm^3 dm^{-1}·g^{-1} (*c* 0.76, EtOH) for (−)-**8**. This can be compared with the value $[\alpha]^{18}{}_D = -115.4$ (*c* 1.13, MeOH) for, reportedly,[11b] enantiomerically pure (−)-**8**, to deduce an optical purity of 1.7% for our sample of (−)-**8**.

The optical purity of (−)-**8** can also be obtained from CD data. Thus, from the CD spectrum in Figure 2b we calculate $\delta\epsilon_{\max} = -0.029$. Comparison with the value $\Delta\epsilon_{\max}(291) = -1.82$ (CH_3OH) for, reportedly,[11b] enantiomerically pure (−)-**8** gives 1.59% optical purity. This can be taken as a more reliable estimate of the optical purity of (−)-**8** than the value obtained above from polarimetric measurements. The latter, in fact, being concerned with very small angles of rotation, are affected by relatively large errors.

The value we have obtained for the optical purity of (−)-**8**, 1.59%, can be compared with the value calculated from eq 4 and

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(11) (a) Hill, R. K.; Edwards, A. C. *Tetrahedron* **1965**, *21*, 1501–1507. (b) Kuritani, H.; Takaoka, Y.; Shingu, K. *J. Org. Chem.* **1979**, *44*, 452–454.

(12) This is true within the limits of validity of the absolute configuration assignment to **1** from the octant rule.[1] Should (+)-**1** have the opposite configuration to that assigned, the (+)-**1** → (−)-**2** photoisomerization would involve complete retention of configuration at the bridgeheads. However, the assignment of configuration to **1** by the octant rule can be taken with great confidence in the case of a rigid, saturated ketone like **3**, which is configurationally related to **1**.

5. Equation 4 assumes total stereospecificity for the **1** → **2**

$$c_r^{\mathbf{1}} = (c_l^{\mathbf{1}})^{(\epsilon_r^{\mathbf{1}}/\epsilon_l^{\mathbf{1}})}(c_0^{\mathbf{1}}/2)^{1-\epsilon_r^{\mathbf{1}}/\epsilon_l^{\mathbf{1}}} \qquad (5)$$

photoisomerization, which will be proved later to be the case. Equation 5, which is derived by integration of previously given equations,[1] is valid also in the case where **2** absorbs CPL. The ϵ_r and ϵ_l values can be obtained from both the $\Delta\epsilon^{\mathbf{1}}$ values reported in section II.B and the molar extinction coefficients $\epsilon_l^{\mathbf{1}} = \epsilon^{\mathbf{1}} - |\Delta\epsilon^{\mathbf{1}}/2|$ and $\epsilon_r^{\mathbf{1}} = \epsilon^{\mathbf{1}} + |\Delta\epsilon^{\mathbf{1}}/2|$. We thus get 1.22% for the optical purity of (+)-**2**, (+)-**7**, and (−)-**8**.

The discrepancy observed here as to the values for the optical purity of (+)-**2**, (+)-**7**, and (−)-**8** (1.59 vs. 1.22%), according to the evaluation method used, needs some comment. The higher value, 1.59%, might be an artifact arising from an actually lower optical purity then the 100% assigned to (−)-**8**.[11b] If, however, (−)-**8** was really obtained, as stated,[11b] in optically pure form, the above discrepancy should merely reflect a normal accumulation of errors in the measurements. In any case, however, the values obtained here for the optical purity of **2** point to a completely stereospecific photoisomerization of **1** into **2**.

Let us now examine the case of **7**. From the optical purity given above for (+)-**7**, and from the dichroism of the isolated species, we obtain the dichroism of the n → π* band. As anticipated in section II.B, the dichroic band is centered at 320 nm and has the low value $\Delta\epsilon_{\max}(320) = -0.39$ (Figure 2c) if the OP is 1.59%.

As said in section II.B, with both **1** and **2** the optical rotation at 436 nm is determined in part, ca. 50%, by the n → π* CD band, and α_{436} and $\Delta\epsilon_{n\to\pi^*}$ have the same sign. The same sign of $\Delta\epsilon$ and α_{436} also occurs with **8** where the optical activity at 436 nm is totally determined by the n → π* dichroic band. Indeed, the value of $[\Phi]_{436}$, as can be calculated by the Kronig–Kramers transform of measured $\delta\epsilon$ for (−)-**8**, is −6.8. This has to be compared with the experimental value −6.4. In sharp contrast, with **7** the sign of α_{436} is opposite to that of the n → π* CD band. Application of the Kronig–Kramers transforms (eq 1) to the data for (−)-**7** gives $[\Phi]^{20}_{436} = -1.7$. This value has to be compared with the experimental value of +4.2 which can be computed from the α_{436} value in section II.C. Such contrasting values for the molar rotation of **7** are most reasonably interpreted in terms of an overriding contribution of the π → π* band to the optical rotation at 436 nm.

The difference in optical properties for the molecules considered above probably arises from a combination of factors. In fact, with **1** and **2** there are two chiral centers and there may be overlapping olefin and enone chromophores, while with **7** there is only one chiral center and only the enone chromophore. Also, **1** and **2**, on one side, and **7**, on the other side, may differ as regards to the contribution of the allylic bond polarization to the optical activity.[13] However, the observed behavior may be related to the conformation of the enone chromophore which, according to molecular models, is constrained into a plane with both **1** and **2**, but can be partially relaxed from planarity in the case of **7** by skewing of the enone chromophore.

D. Steric Course of the Phototransformation of the Racemate. We have shown in previous sections that when (±)-**1** is irradiated with left CPL, light of that chirality is preferentially absorbed by (1*R*,5*S*)-**1**. This leads to formal C(1)–C(2) and C(5)–C(4) bond breaking and C(7)–C(2) and C(6)–C(4) bond re-formation from the fragments with inversion of configuration at both the C(4) and C(7) center whereby (1*S*,5*S*)-enantiomerically enriched **2** is formed (Scheme II). Thus, residual **1** is (1*S*,5*R*)-enantiomerically enriched (Scheme II).

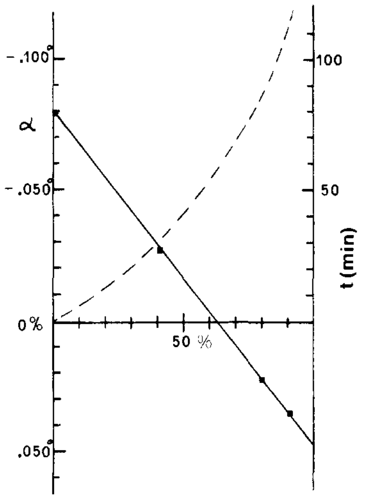
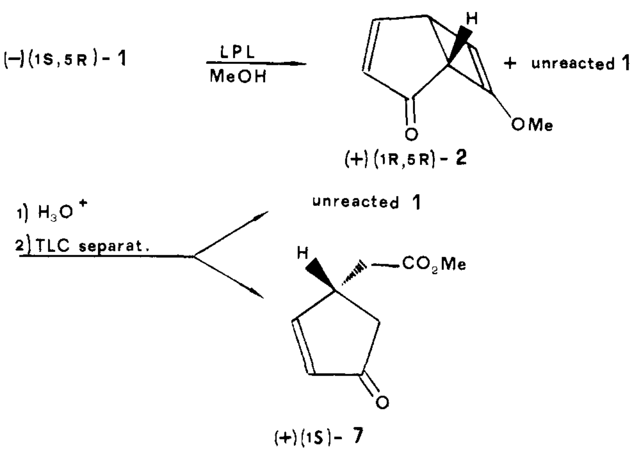


Figure 3. Irradiation of (−)-**1** of optical purity ca. 1% with LPL. Plot of the percentage of **2** in the resulting mixture of **1** and **2** against (left ordinate; heavy line) the optical rotation or (right ordinate; broken line) the irradiation time.

Scheme III. Irradiation of Enantiomerically Enriched **1** with Linearly Polarized Light (LPL)[a]



[a] Structural formulas or configuration notations represent the absolute configuration for the enantiomer in excess; the sign of optical rotation is given at 436 nm.

We have also offered some evidence that the **1** → **2** photoisomerization is stereospecific. We now consider further both this and the preceding problems. In fact, we prepared, by chiral photoresolution of (±)-**1**, a solution of (1*S*,5*R*)-enantiomerically enriched **1**, 0.091 g in 15 mL of methanol, α_{436} −0.079°, corresponding to an optical purity of ca. 1.0%. This solution was irradiated with LPL (laser source, 350 and 363 nm, jointly, 0.4 W) monitoring, at time intervals, the chemical composition by ^{1}H NMR spectroscopy and the optical activity polarimetrically. The optical rotation data, when plotted vs. the percentage of **2** in the mixture of **1** and **2** (Figure 3, heavy line), show that α_{436} is a linear function of the percentage conversion of **1** into **2**. Figure 3 also shows that, on increasing the percentage of **2** in the mixture of **1** and **2**, the irradiation time needed to convert **1** into **2** increases more than linearly. Actually, the irradiation time increases with the logarithm of $c^1/(c^1 + c^2)$. This trend is easily rationalized on admitting that **2** competes with **1** for light absorption, the more effectively as the concentration of **2** increases. This is a light-wasting process because **2** is photostable.

That **2** is photostable under the conditions of the **1** → **2** photoisomerization is apparent from the linear trend of α_{436} vs. percentage of **2** in Figure 3. In fact, any appreciable photodegradation of **2**, leading to disappearance of optical activity, would

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(13) Anderson, N. H.; Costin, C. R.; Syrdal, D. D.; Svedberg, D. P. *J. Am. Chem. Soc.* **1973**, *95*, 2049–2051.

(14) The mechanism for the **1** → **2** photoisomerization has received attention by various authors[4] (see also Miyashi, T.; Nitta, M.; Mukai, T. *J. Am. Chem. Soc.* **1971**, *93*, 3441–3447. Kende, A. S.; Goldschmidt, Z.; Izzo, P. T. *Ibid.* **1969**, *91*, 6858–6868) without, however, any specific mention to the stereochemical problems involved. The latest view, from experiments of irradiations of either **1** or **2** in glass matrices at −195 °C with a Hg lamp,[4b] is that the photoisomerization occurs through the ketene intermediate. Our results, as to the configuration inversion at the bridgeheads on going from **1** to **2** are clearly compatible with either the ketene mechanism[4b] or the concerted one.[4a]

have produced a nonlinear trend of α vs. percentage of **2**.

Acidic workup of the mixture of LPL irradiation, followed by TLC separation, afforded (+)(1*S*)-**7** (Scheme III). According to previous discussions, this leads to the (1*R*,5*R*) configuration for (+)-**2** (Scheme III).

Therefore, the whole body of the above results shows that, for our irradiation times, **1** → **2** is the only process which occurs. This involves chirality transfer from **1** to **2**, resulting in optical rotations and dichroism values of opposite signs for **1** and **2**.[14] As we have measured $\alpha_{\text{total}} = 0$ for $c^1/c^2 \simeq 40/60$ (Figure 3), the ratio of specific rotations between enantiomerically enriched **1** and **2**, which has received chirality from **1**, must be ca. 60/40.

III. Conclusions

The successful application of the partial resolution of racemates with CPL presented here owes much to recent innovations in instruments. In fact, the high sensitivity of modern dichrographs, together with the special features of the linearly polarized UV laser light, which is ideally suited to circular polarization, have been indispensable tools. They made possible, in fact, the production of optical activity at a sufficiently high, and strictly controlled level, and to detect it with great accuracy. This was needed in order to carry out our treatment leading to chiroptical data which enabled us to solve stereochemical problems for both molecules (even labile ones) and reactions.

Various alternative modern techniques are available to produce optical activity much more effectively, and to measure the enantiomeric composition of the optically active mixture. However, our technique surpasses all other ones in one respect. In our technique, in fact, the intrinsic molecular spectroscopic dissymmetry (e.g., $\Delta\epsilon$) and the observed dissymmetry of the products (e.g., $\delta\epsilon$) are, conceptually, most directly connected together.

Our technique and the instruments used here are capable to deal with a large variety of compounds. The extension to chromophores absorbing at wavelengths shorter than 300 nm needs to exploit other suitable laser sources, perhaps an excimer laser or a frequency-multiplied neodymium laser.

As a divertissement regarding the $n \rightarrow \pi^*$ transitions with enones and ketones, the optical rotation is determined by the $n \rightarrow \pi^*$ dichroism totally with compound **8**, only partially with both **1** and **2**, while with **7** there is an overriding contribution by more energetic dichroic bands, probably the $\pi \rightarrow \pi^*$ band. The octant rule[5] can be applied with little confidence to enones.[1] However, in the case of **7**, the use of polarimetric data in combination with the octant rule would lead, in any case, to erroneous results so that either CD or ORD data are required.

IV. Experimental Section

General. UV and IR spectra were taken with respectively Pye-Unicam SP8 150 and Perkin-Elmer 337 spectrometers. ^{1}H NMR spectra were taken with a Varian 360 spectrometer at 60 MHz in $CDCl_3$–$(CH_3)_4Si$ and chemical shifts are given in δ (ppm) with respect to internal $(CH_3)_4Si$. Polarimetric measurements were carried out on a Perkin-Elmer 141 polarimeter, with a cell of 10 cm optical-path length. CD spectra are from a Jasco J 500C spectropolarimeter. LPL was obtained from a Spectraphysics 171-19 Ar ion, continuous wave laser, using both the 350- and the 363-nm emission, jointly (0.4–1.5 W). CPL was obtained by polarizing, through a fused silica Fresnel rhomb, the above emissions. The photochemical reactor was made of an Erlenmeyer flask provided with a strain-free optical window. Efficient stirring was ensured by a magnetic bar. LPL and CPL irradiations, as well as CD spectra and polarimetric measurements, were carried out using spectroscopic grade Erba RS methanol as a solvent. Both LPL and CPL irradiations were always carried out under conditions of total absorption.

1-Methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (1). A well-stirred, ca. 2×10^{-2} M solution of 2-methoxytropone[6] in methanol (280 mL) was irradiated with LPL (333, 350, and 363 nm, jointly, 1.5 W) with up to 50–60% conversion of 2-methoxytropone. Under these conditions **1** is the main product, with traces of **2**. The solvent was evaporated at reduced pressure and the oily residue was distilled, using a short, efficient column, at 0.02 torr, bath temperature 60 °C. The central fractions were constituted of pure **1**. **1** was further purified by preparative TLC (Merk Kieselgel 60 PF_{254}, 2 mm thick) eluent ethyl ether–*n*-pentane 60:40. **1** was collected from the R_F 0.41 band by extraction with chloroform (0.3 g, yield 39%). Analytical and spectral data agreed with those of the literature.[4a]

Irradiation of (±)-1 with CPL and Isolation of both Methyl 4-Oxo-2-cyclopentene-1-acetate (7) and Methyl 3-Oxocyclopentane-1-acetate (8). A well-stirred solution of (±)-**1** (0.385 g, 2.83 mmol) in 50 mL of methanol was irradiated with right CPL until 40% conversion of **1** into **2** (as shown by ^{1}H NMR analysis of a portion of the mixture, which was evaporated at reduced pressure and the residue was taken with $CDCl_3$), corresponding to α_{436} 0.145°. The solvent was evaporated at reduced pressure, and the residue was added to 3 mL of water acidified with a few drops of 0.75 M sulfuric acid. The aqueous mixture was added to sodium sulfate and then repeatedly extracted with chloroform. The organic layer was evaporated and the residue was subjected to preparative TLC, as above, to give (+)-**1**, 0.143 g (1.05 mmol) from the $R_f = 0.41$ band. The $R_f = 0.27$ band gave (+)-**7** which was further purified by TLC to give a pure sample of 0.045 g (0.29 mmol): IR[4a] $\nu_{\max}^{\text{neat}}$ 1740, 1710, 1580 cm^{-1}; UV $\lambda_{\max}^{\text{MeOH}}$ 217 (10 500), 313 (ϵ 33); ^{1}H NMR ($CDCl_3$) δ 7.40 (1 H, dd, $J_{2,3} = 5.4$, $J_{1,2} = 2.4$ Hz, H(2)), 5.96 (1 H, dd, $J_{2,3} = 5.4$, $J_{1,3} = 1.8$ Hz, H(3)), 3.60 (3 H, s, OCH_3), 3.22 (1 H, m, H(1)), 2.8–1.8 (4 H, m, methylene protons). On irradiation at δ 3.22, both the δ 7.40 and 5.96 dd became doublets with $J_{2,3} = 5.4$ Hz. The above sample of (+)-**7**, 0.038 g (0.25 mmol), in 5 mL of 95% ethanol and 10 mg of 5% Pd–C was hydrogenated at atmospheric pressure for 6 h. Conversion to (–)-**8** was quantitative, as shown by GLC (2 mm × 3 mm column, 15% silicone on Chromosorb W (80 – 100 mesh, N_2 20 mL min^{-1}, 165 °C, retention time 7.5 min): IR $\nu^{\text{neat}}{}_{\max}$ 1740 cm^{-1}; UV $\lambda^{\text{EtOH}}{}_{\max}$ 285 nm (ϵ 25); the ^{1}H NMR spectrum is in accordance with the literature.[11b]

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Infrared Photochemistry of Bicyclopropyl

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Abstract: The decomposition of bicyclopropyl (C_6H_{10}) induced by multiphoton absorption from an infrared laser has been investigated. The reaction produces a complex product mixture consisting mainly of C_6H_{10} isomers. A mechanism is proposed that can rationalize all of the existing infrared photochemical and thermal data on the basis of a single primary step, C–C bond cleavage to a 1,3-biradical. The product mixture results from competitive decay channels of the biradical and successive reactions of the "hot" products. This system provides a striking example of the influence of "hot molecule effects" on the product distributions in infrared multiphoton dissociation.

Polyatomic molecules decompose under the influence of high-power infrared laser radiation. The phenomenon is well characterized[1-3] and theoretical models capable of rationalizing most of the existing data, at least qualitatively, have been developed.[4-6]

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