Chiral Laser Photochemistry: Photoresolution accompanying Photoisomerization of (±)-1-Acetyl(benzoyl)aminobicyclo[3.2.0]hepta-3,6-dien-2-one to Optically Active 7-Isomers. A Photochemical Procedure for Chirality Enhancement of (−)-(1*S*,5*S*)-7-Acetylaminobicyclo[3.2.0]hepta-3,6-dien-2-one

Marino Cavazza, Gioia Morganti, and Maurizio Zandomeneghi
Istituto di Chimica Generale and Istituto di Chimica Fisica, Università di Pisa, via Risorgimento 35, 56100 Pisa, Italy

Photoisomerization of (±)-1-acetylaminobicyclo[3.2.0]hepta-3,6-dien-2-one (±)-(2b) with u.v. left circularly polarized light up to 36% conversion led to (−)-(1*S*,5*R*)-(2b) [optical purity, o.p. 0.83%; $\Delta\varepsilon_{max.}$ (347) −4.2 $dm^3\ mol^{-1}\ cm^{-1}$] and (−)-(1*S*,5*S*)-7-acetylaminobicyclo[3.2.0]hepta-3,6-dien-2-one (−)-(3b) [o.p. 1.5%; $\Delta\varepsilon_{max.}$ (345) −3.3]. The optical purities obtained allowed us to measure circular dichroism for $\lambda > 260$ nm. An analogous procedure when applied to the benzoylamino-derivatives gave $\Delta\varepsilon_{max.}$ (348) −5.0 and $\Delta\varepsilon_{max.}$ (346) −4.9 for the 1- and 7-derivatives, respectively. Further chirality enhancement to o.p. 2.9% permitted a complete (>200 nm) c.d. spectrum to be obtained for (−)-(3b).

Chiroptical studies of chiral molecules are limited by the accessibility of labile or difficult to resolve molecules and of molecules which are both tedious and time consuming to obtain in an optically active form.

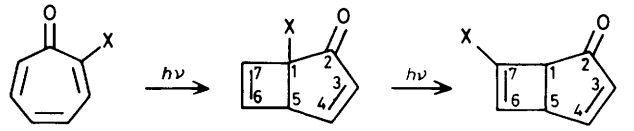
To overcome such difficulties we have recently reported an application [1] of the partial photoresolution of racemates with circularly polarized light (c.p.l.).[2] The method consists in the partial phototransformation of a racemate with c.p.l. and in the measurement of both the differential c.p.l. absorption by the resulting optically active compounds and the extent of the reaction.[1] It is then possible to obtain $\Delta\varepsilon$ for the pure enantiomers from these data. This is a good procedure if there are no sensitization effects and if the excited species do not racemize before collapsing into products.

This method has been applied to the photoresolution of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (2a), which can be obtained by photoisomerization of 2-methoxytropone, leading to optically active, labile 7-methoxybicyclo[3.2.0]-hepta-3,6-dien-2-one (3a), as shown in Scheme 1. We were able to obtain c.d. in the $n \longrightarrow \pi^*$ band, *i.e.* the irradiation band, and the absolute configuration for both (2a) [1a] and (3a) [1b] and to establish that the photoisomerization of (2a) into (3a) is stereospecific and is attained by net inversion of configuration at the bridgeheads [1b] (Scheme 2).

On the other hand, it was impossible to measure the c.d. in the $\pi \longrightarrow \pi^*$ spectral region because of the small ratio $\delta A/A$ [3a] in this region, δA being the differential circular absorbance of the enantiomerically enriched samples. In other words, on account of the sensitivity of the commercial spectropolarimeter used, the optical purities (o.p.) of (2a) and (3a) were insufficient to obtain the c.d. spectrum of $\pi \longrightarrow \pi^*$ bands; greater o.p. for both (2a) and (3a) would be required.

In principle, (2a) of substantially greater o.p. could be produced by c.p.l. irradiaton of (±)-(2a) with a sufficiently high degree of conversion [2] into (3a). Photoconversion of the isolated optically active (2a) would, subsequently, produce optically active (3a) with the same o.p. of (2a) because of the stereospecificity of the phototransformation.[1b]

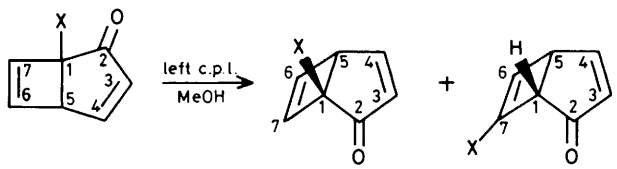
Unfortunately, (3a) could hardly be separated in an unaltered form from the mixture of optically active (2a) and (3a) because of its considerable sensitivity to acid-catalysed hydrolysis,[1b] so we decided to investigate other related systems, *e.g.* (2b and c). These compounds give the same kind of clean photoisomerization as (2a) at a relatively high degree of



(1) (2) (3)

a; X = OMe a; X = OMe a; X = OMe
b; X = NHCOMe b; X = NHCOMe b; X = NHCOMe
c; X = NHCOPh c; X = NHCOPh c; X = NHCOPh

Scheme 1. Examples of photocyclization of 2-X-tropones and photoisomerization of the photoproducts



(±)-(2b) (−)(1*S*, 5*R*)-(2b) (−)(1*S*,5*S*)-(3b)
(±)-(2c) (−)(1*S*, 5*R*)-(2c) (−)(1*S*,5*S*)-(3c)

Scheme 2. Irradiation of (±)-(2b) or (±)-(2c) with c.p.l. and t.l.c. separation of optically active products (3) from residual optically active starting compounds (2) (the absolute configurations and the sign of optical rotation, which is given at 436 nm, refer to the enantiomers present in excess)

conversion (*ca.* 40%). They and their photoproducts (3b and c) respectively, can be separated in an unaltered form by t.l.c. from the reaction mixture and further purified by crystallization. Probably, (2b and c) should have high dissymmetry factors, $g = \Delta\varepsilon/\varepsilon$, of the same order as (2a) (*ca.* 3.5%, at 350—363 nm, the emission lines of the laser).

Under these conditions, it should be possible to reach a sufficient enantiomeric excess for both starting and final compounds so as to obtain complete c.d. spectra.

As described later, only partial information on the $\pi \longrightarrow \pi^*$ c.d. bands has been obtained with *ca.* 40% conversion. A two-step photochemical procedure for chirality enhancement, based on the stereospecificity of the (2) ⟶ (3) transforma-

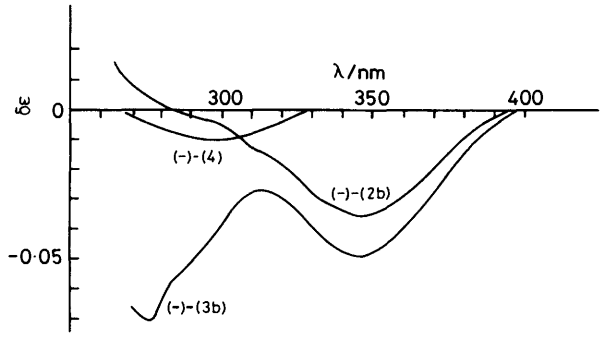


Figure 1. Measured dichroic spectra for (−)-(2b), o.p. 0.83% in MeOH, $\Delta\varepsilon_{max.}$(347) −4.2; (−)-(3b), o.p. 1.5% in MeOH, $\Delta\varepsilon_{max.}$(345) −3.3; (−)-(4), o.p. 0.83% in EtOH, $\Delta\varepsilon_{max.}$(295) −1.2

tion, was then devised. By means of this procedure the goal of a complete (200—400 nm) c.d. spectrum was achieved for photoproduct (3b).

Results and Discussion

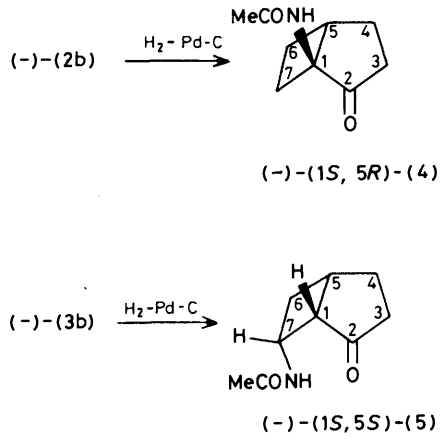
(A) *Photoresolution and Photoisomerization of the Racemate.*—Cyclization to (2), followed by photoisomerization of (2) into (3) (Scheme 1), has already been shown [4] to occur on irradiation of a solution of (1) in ethanol or cyclohexane with a high-pressure mercury lamp.

We have repeated the photosynthesis of (2b and c) by irradiating (1b and c), respectively, with the u.v. linearly polarized light (l.p.l.) of an argon-ion laser source. Then irradiation of a methanolic solution of (2b) with u.v. left c.p.l. up to 36% disappearance of (2b) led to an optically active mixture composed of 64% (2b) and 36% (3b). This mixture could be separated by t.l.c. into the chemically pure components which both exhibited negative optical rotation (Scheme 2). As expected, with this relatively high conversion the o.p. (0.83%) obtained for (2b) enabled us to measure the $n \longrightarrow \pi^*$ band and also the portion of the $\pi \longrightarrow \pi^*$ band † lying in the 260—300 nm range, as shown in Figure 1. In the same Figure the c.d. of the photoproduct (3b), now measured directly [1b] on the isolated compound, is also reported. Here the measured portion of the $\pi \longrightarrow \pi^*$ band has the same sign as the $n \longrightarrow \pi^*$ one, in contrast to the (2b) case.

Analogous irradiation of a methanolic solution of (2c) led to results similar to the (2b) ⟶ (3b) case for the $n \longrightarrow \pi^*$ bands. Owing to the strong absorption associated with the phenyl group for $\lambda < 300$ nm, we were able to obtain only the dichroism of the $n \longrightarrow \pi^*$ transition for both (2c) and (3c).

Optical purities and the c.d. for the pure enantiomers, at the irradiation wavelength, were then obtained by solving a system of two equations ‡ where we inserted both the measured molar circular dichroism (δε) for species (2), and the degree of conversion (x) of (2) into (3). We thus obtained $\Delta\varepsilon_{max.}$ (347) −4.2 dm³ mol⁻¹ cm⁻¹ for (−)-(2b) and $\Delta\varepsilon_{max.}$ (348) −5.0 for (−)-(2c). Then, by assuming that, by analogy with the (2a) ⟶ (3a) case, the (2) ⟶ (3) photoisomerizations are stereospecific, which is reasonable, it was easy to obtain the optical purities for (3b and c) and therefore their c.d. spectra. In fact, if the photoisomerization (2) ⟶ (3) is the only reaction involved, the relationship $c_{(2)}$·o.p.$_{(2)} = c_{(3)}$·o.p.$_{(3)}$ holds. Here $c_{(2)}$ and $c_{(3)}$ represent the concentrations of species (2) and (3) at the end of the irradiation.

At this point it was possible to obtain $\Delta\varepsilon_{max.}$ (345) −3.3 for (−)-(3b) and $\Delta\varepsilon_{max.}$ (346) −4.9 dm³ mol⁻¹ cm⁻¹ for (−) -(3c).



Scheme 3. Hydrogenation of (−)-(2b) and (−)-(3b)

(B) *Absolute Configurations for Both Photoresolved and Photoisomerized Products and Steric Course of the Photoisomerization.*—Both (2b) and (3b) exhibit negative $n \longrightarrow \pi^*$ c.d. bands as for (2a) and (3a) under identical (left) helicity of the irradiating light. However, since the octant rule [5] cannot be applied with confidence to α,β-unsaturated enones, both (−)-(2b) and (−)-(3b) have been hydrogenated to give the corresponding saturated ketones (4) and (5), respectively § (Scheme 3). Both (4) and (5) display negative $n \longrightarrow \pi^*$ c.d. bands and, by application of the octant rule, the (1*S*,5*R*) and (1*S*,5*S*) absolute configurations, respectively, can be assigned. Consequently, we can assign the absolute configuration (1*S*,5*R*) and (1*S*,5*S*) to (−)-(2b) and (−)-(3b), respectively (Scheme 2).

It can be thus concluded that there is inversion of configuration at the bridgeheads on going from (2b) to (3b) as in the case (2a) ⟶ (3a).[1b] Concerning the (2) ⟶ (3) isomerization, these results are clearly compatible with either the ketene [7a] or the concerted mechanism.[7b]

As regards the benzoylamino derivatives (2c) and (3c), the hydrogenation of (3c) proved to be troublesome so that no firm stereochemical conclusions could be drawn for the (2c) ⟶ (3c) photoisomerization.

(C) *Chirality Enhancement Procedure for the Photoproducts.*—As shown above a 36% conversion of (2b) led to o.p. 0.83% and 1.5% for (2b) and (3b) respectively, which allowed the measurement of the $\pi \longrightarrow \pi^*$ c.d. only in the 260—300 nm region. For a significant extension of the measureable c.d. spectrum an o.p. of *ca.* 3% for both (2b) and (3b) was deemed necessary. Then, assuming ideal behaviour of the photoprocess, compound (2b) would require some 80% photocon-

† For brevity, we designate as $\pi \longrightarrow \pi^*$ all absorptions in the 200—300 nm range.

‡ o.p. $= |\delta\varepsilon/\Delta\varepsilon|$ $\quad |\Delta\varepsilon| = \left|\dfrac{\varepsilon \ln[(1 + \text{o.p.})/(1 - \text{o.p.})]}{\ln(1 - x) + 0.5 \ln[(1 + \text{o.p.})(1 - \text{o.p.})]}\right|$

The above system was derived from the kinetic equations describing the c.p.l. induced photolysis of an initially racemic mixture. ε, δε, and Δε are given at the laser wavelength.

§ Structure (5) is probably the *endo*-7-acetylamino epimer. In fact, catalytic hydrogenation of (3b) is expected to add hydrogen to the convex *exo*-face of the olefin.[6] In any case, the problem of the stereochemistry at C(7) is not relevant to our conclusions, about the absolute stereochemistry of the ring fusion. In fact, the *endo* and *exo* substituents lie in the same octant.

$$(\pm)\text{-(2b)} \xrightarrow[55\%]{\text{right c.p.l.}} (+)\text{-(1}R,5S\text{)-(2b)}\ (\text{o.p. } 1{\cdot}3\%) + (+)\text{-(1}R,5R\text{)-(3b)}\ (\text{o.p. } 1{\cdot}1\%)$$

$$(+)\text{-(1}R,5S\text{)-(2b)}\ (\text{o.p. } 1{\cdot}3\%) \xrightarrow[16\%]{\text{left c.p.l.}} (+)\text{-(1}R,5S\text{)-(2b)}\ (\text{o.p. } 0{\cdot}7\%) + (+)\text{-(1}S,5S\text{)-(3b)}\ (\text{o.p. } 2{\cdot}9\%)$$

Scheme 4.

version.[2] Because of the competitive absorption of light by (3b) formed, the irradiation time needed grows in proportion to $|\ln(1-x)|$, x being the degree of photoconversion of (2b), so that parasitical photoreactions, otherwise negligible due to their low quantum yield, become more and more important as $x \longrightarrow 1$. A text experiment showed that conversion up to *ca.* 75% required more than three times the energy needed for the 36% conversion and, above all, that the separation of (2b) from optically active by-products was difficult.

As far as photoproduct (3b) is concerned, it must be observed that its enantiomeric excess decreases as the phototransformation of (2b) proceeds to completion, starting from the maximum value $g_{(2b)}/2$ (*i.e.* 1.8%).[3b] So we devised a two-step photochemical procedure leading to o.p. *ca.* 3% for photoproduct (3b), and avoiding the above purification problems.

In the first step, (2b) is partially resolved with, for example, *right* c.p.l. up to the maximum extent possible, taking into due account the fact that a sufficient quantity of chemically pure (2b) has to be separated from the reaction mixture. In the second step this non-racemic (+)-(1*R*,5*S*) enriched (2b), purified from photoproducts, is irradiated with *left* c.p.l., that is with the polarity which causes preferential absorption of the light by the (+)-(2b) enantiomer present in excess. Because of the stereospecificity of the reaction this enantiomer will be transformed into the (−)-(1*S*,5*S*)-(3b) enantiomer. The o.p. of the resulting (−)-(1*S*,5*S*)-enriched (3b) will, obviously, be enhanced with respect to (3b) obtained from simple left c.p.l. irradiation of (±)-(2b). With a low degree of conversion the o.p. of the resulting (−)-(3b) approaches the value of $\text{o.p.}_{(2b)} + g_{(2b)}/2$ as shown in the Experimental section.

In other words, the chiral photodiscrimination effected by c.p.l. and the subsequent stereospecific reaction result in a transfer to (3b) of the o.p. acquired by (2b) in the first step, enhanced by half the precursor dissymmetry factor.

Accordingly (Scheme 4), (+)-(2b) (o.p. 1.3%) was obtained by converting 55% of racemate (2b) with right c.p.l. and by t.l.c. separation from (+)-(3b) (o.p. 1.1%) and from by-products. Subsequent irradiation of (+)-(2b) with left c.p.l. up to 16% conversion gave a mixture of (2b) and (3b) practically inactive from a polarimetric point of view. After t.l.c. separation, the o.p. of (−)-(3b) was *ca.* 2.9%, to be compared with 1.3% + 1.8% = 3.1% expected from the above equation.

In Figure 2 the c.d. spectrum of (−)-(3b) enantiomer, now measurable up to 210 nm, is reported. The exciton-like shape of this spectrum in the high frequency spectral region (210—250 nm) is to be noted because it shows the presence of, at least, one transition in addition to the classical $\pi \longrightarrow \pi^*$ one. A consequence of the exciton-like shape of the c.d. absorption in the 210—260 nm region is that the measured optical rotation at 436 nm, is, almost entirely, due to c.d. absorption for $\lambda > 260$ nm as is easily calculable by Kronig–Kramers transformation;[1b,8] in fact one obtains $[\varphi]_{436}$ −40° while the experimental value is −38°.

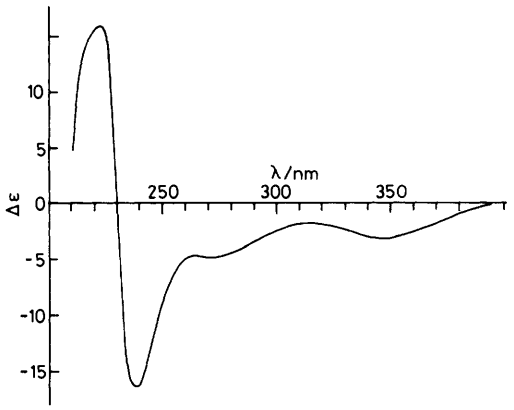


Figure 2. C.d. spectrum of (−)-(3b) obtained from the sample with o.p. 2.9%

Experimental

Kinetic Treatment in the Second Step of the Chirality Enhancement Procedure.—If c_{+2} is the concentration of the prevailing (+)-(1*R*,5*S*)-(2b) enantiomer which preferentially absorbs left c.p.l. with molar extinction coefficient ε_{+2} at the laser wavelength, we have relations (1) and (2). If the isomerization is stereospecific and (+)-(2b) $\longrightarrow$ (−)-(3b) $-dc_{+2}/dt = dc_{-3}/dt$ and $-dc_{-2}/dt = dc_{+3}/dt$. The o.p. of (3b) produced at any instant will be given by equations (3) which are deduced from relations (1) and (2).

$$\varepsilon_{+2} - \varepsilon_{-2} = \Delta\varepsilon_2\ (>0);\ \varepsilon_{+2} + \varepsilon_{-2} = 2\varepsilon_2$$
$$c_{+2} = c_2(1 + |\text{o.p.}_2|)/2;\ c_{-2} = c_2(1 - |\text{o.p.}_2|)/2 \quad (1)$$

$$\frac{dc_{+2}}{dt} \propto c_{+2}\varepsilon_{+2}/(c_{-2}\varepsilon_{-2} + c_{+2}\varepsilon_{+2} + \cdots)$$
$$\frac{dc_{-2}}{dt} \propto c_{-2}\varepsilon_{-2}/(c_{-2}\varepsilon_{-2} + c_{+2}\varepsilon_{+2} + \cdots) \quad (2)$$

$$\text{o.p.}_3 = \left(\frac{dc_{-3}}{dt} - \frac{dc_{+3}}{dt}\right)\Big/\left(\frac{dc_{-3}}{dt} + \frac{dc_{+3}}{dt}\right) = \left(\frac{dc_{+2}}{dt} - \frac{dc_{-2}}{dt}\right)\Big/\left(\frac{dc_{+2}}{dt} + \frac{dc_{-2}}{dt}\right) = \frac{\Delta\varepsilon_2 + 2\text{o.p.}_2\cdot\varepsilon_2}{2\varepsilon_2 + \text{o.p.}_2\cdot\Delta\varepsilon_2} = \frac{g_2 + 2\text{o.p.}_2}{2 + \text{o.p.}_2 g_2} \quad (3)$$

At the very beginning of the (2) $\longrightarrow$ (3) conversion the value for (3) will also be the o.p. of (3) produced and this value can safely be approximated by $\text{o.p.}_3 = g_2/2 + \text{o.p.}_2$.

Instrumentation and Photochemical Methodology.—C.d. spectra were taken with a JASCO J 500C spectropolarimeter while polarimetric measurements were carried out on a Perkin-Elmer 141 polarimeter, using a cell of 10 cm optical path length. U.v. and i.r. spectra were taken with Pye Unicam SP8 150 and Perkin-Elmer 337 spectrometers, respectively. ^{1}H N.m.r. spectra were taken with a Varian 360 spectrometer at 60 MHz in $CDCl_3$ and chemical shifts are given in δ with respect to internal $(CH_3)_4Si$. L.p.l. was from a Spectraphysics 171—19 argon-ion laser, using both the 350 and the 363 nm emissions, jointly, as before.[1b] C.p.l. was obtained, as before, by polarizing the above emissions through a silica Fresnel rhomb. Both l.p.l. and c.p.l. irradiations were carried out under total light absorption conditions, using the previously described reactor, with efficient stirring.[1b] The irradiations, as well as u.v. and c.d. spectra were carried out in Erba RS methanol or ethanol as solvents. Merck Kieselgel 60 PF_{254} was used to prepare 2 mm thick silica gel plates for preparative t.l.c.

1-*Acetylamino*[3.2.0]*hepta*-3,6-*dien*-2-*one* (±)-(2b).—A solution of 2-acetylaminotropone (1b) (0.250 g, 1.53 mmol) in methanol (360 ml) was irradiated with l.p.l. (0.8 W) up to 50% disappearance of the troponoid. The mixture was evaporated at reduced pressure and the residue was taken up in chloroform and then subjected to t.l.c. [eluant Et_2O–MeOH (95 : 5)]. Chloroform extraction of the bands at R_F 0.65 and 0.25 led to, respectively, unchanged (1b) (0.120 g), and (±)-(2b) (0.040 g, 32%), pale yellow crystals, m.p. 158 °C (lit.,[4] 158 °C) (Found: C, 66.2; H, 5.5; N, 8.45. Calc. for $C_9H_9NO_2$: C, 66.2; H, 5.6; N, 8.6%); $\lambda_{max.}$ (MeOH) 345 nm (ε 117); δ_H ($CDCl_3$) 7.62 (1 H, dd, $J_{3,4}$ 6.1, $J_{4,5}$ 2.7 Hz, 4-H), 6.9br (1 H, NH), 6.78 (1 H, dd, $J_{6,7}$ 2.6, $J_{5,6}$ 0.9 Hz, 6-H), 6.20 (1 H, d, $J_{6,7}$ 2.6 Hz, 7-H), 6.12 (1 H, d, $J_{3,4}$ 6.1 Hz, 3-H), 3.92 (1 H, dd, $J_{4,5}$ 2.7, $J_{5,6}$ 0.9 Hz, 5-H), and 2.00 (3 H, s, CH_3). On irradiation at δ 3.9, both δ 7.62 and 6.78 became doublets with, respectively, $J_{3,4}$ 6.1 and $J_{6,7}$ 2.6 Hz.

1-*Benzoylaminobicyclo*[3.2.0]*hepta*-3,6-*dien*-2-*one* (±)-(2c).—A solution of 2-benzoylaminotropone (1c) (0.553 g, 2.46 mmol) in methanol (100 ml) was irradiated as in the above case. Evaporation of the mixture and t.l.c. as above [Et_2O–n-pentane (90 : 10)] led to (±)-(2c), R_F 0.21 (0.060 g, 22%), pale yellow crystals, m.p. 173 °C (lit.,[4] 170 °C) (Found: C, 75.0; H, 4.9; N, 6.3. Calc. for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.9; N, 6.2%), besides unchanged (1b) (0.20 g), R_F 0.55, and much tar; $\lambda_{max.}$ (MeOH) 342 nm (ε 156); δ_H ($CDCl_3$) 7.85br (1 H, NH), 7.55 (1 H, dd, $J_{3,4}$ 6.0, $J_{4,5}$ 2.6 Hz, 4-H), 7.5—7.1 (5 H, m, Ph), 6.68 (1 H, dd, $J_{6,7}$ 2.5, $J_{5,6}$ 1.0 Hz, 6-H), 6.15 (1 H, d, $J_{6,7}$ 2.5 Hz, 7-H), 6.08 (1 H, d, $J_{3,4}$ 6.0 Hz, 3-H), and 3.92 (1 H, dd, $J_{4,5}$ 2.6, $J_{5,6}$ 1.0 Hz, 5-H). On irradiation at δ 7.5, both δ 6.08 and 3.92 doublets became singlets.

C.p.l. Irradiation of (±)-(2b).—A 1.08×10^{-2}M solution of (±)-(2b) in methanol (20 ml) was irradiated with left c.p.l. (*ca.* 0.3 W) during 7 min up to α_{436} −0.033° (polarimetry), corresponding to 36% change of (2b) into (3b) (n.m.r. analysis). The irradiated mixture was then evaporated at reduced pressure and the residue was taken with chloroform and then subjected to t.l.c. as above [Et_2O–MeOH (95 : 5)]. No tar was detected. The R_F 0.25 band was extracted with chloroform to give (−)-(1*S*,5*R*)-1-acetylaminobicyclo[3.2.0]hepta-3,6-dien-2-one (−)-(2b) (0.0064 g, 15.2%), m.p. 158 °C, α_{436} 0.013° (0.0064 g per 5 ml MeOH), corresponding to an optical purity of 0.83%. The R_F 0.56 band, on chloroform extraction gave (−)-(1*S*,5*S*)-7-acetylaminobicyclo[3.2.0]hepta-3,6-dien-2-one (−)-(3b), pale-yellow crystals (0.0053 g, 15%), m.p. 179 °C (Found: C, 66.3; H, 5.5; N, 8.5. Calc. for $C_9H_9NO_2$: C, 66.2; H, 5.6; N, 8.6%), α_{436} −0.025° (0.0053 g per 5 ml MeOH), corresponding to an optical purity of 1.5%; $\lambda_{max.}$ (MeOH) 345 nm (ε 94); δ_H ($CDCl_3$) 8.1br (1 H, NH), 7.68 (1 H, dd, $J_{3,4}$ 6.0, $J_{4,5}$ 2.5 Hz, 4-H), 5.95 (1 H, dd, $J_{3,4}$ 6.0, $J_{1,3}$ 0.9 Hz, 3-H), 5.90 (1 H, d, $J_{5,6}$ 0.9 Hz, 6-H), 3.78 (1 H, m, $J_{4,5}$ 2.5, $J_{1,5}$ 2.9, $J_{5,6}$ 0.9 Hz, 5-H), 3.45 (1 H, dd, $J_{1,5}$ 2.9, $J_{1,5}$ 2.9, $J_{1,3}$ 0.9 Hz, 1-H), and 2.00 (3 H, s, CH_3).

C.p.l. Irradiation of (±)-(2c).—A 1.40×10^{-2}M solution of (±)-(2c) in methanol (20 ml) was irradiated with left c.p.l. (*ca.* 0.3 W) during 8 min up to α_{436} −0.041° and 40% conversion of (2c) into (3c) (n.m.r. analysis). The mixture was evaporated and the residue was subjected to t.l.c. No tar was detected. The R_F 0.27 band, on chloroform extraction, gave (−)-(2c) (0.0126 g, 20%), m.p. 173 °C, α_{436} −0.020° (0.0126 g per 5 ml MeOH), corresponding to an o.p. of 0.85%. The R_F 0.42 band gave (−)-(3c) (0.012 g, 19%) as crystals, m.p. 169 °C (Found: C, 74.8; H, 4.9; N, 6.35. Calc. for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.9; N, 6.2%), α_{436} −0.035° (0.012 g per 5 ml MeOH), corresponding to an o.p. of 1.3%, $\lambda_{max.}$ (MeOH) 274 and 230 nm (ε 4 900 and 10 000) whilst no absorption band maximum was detectable in the 300—350 nm region; δ_H ($CDCl_3$) 8.7br (1 H, NH), 7.72 (1 H, dd, $J_{3,4}$ 5.6, $J_{4,5}$ 2.8 Hz, 4-H), 7.6—7.3 (5 H, m, Ph), 6.1 (1 H, d, $J_{5,6}$ 1.0 Hz, 6-H), 6.0 (1 H, dd, $J_{3,4}$ 5.6, $J_{1,3}$ 0.9 Hz, 3-H), 3.90 (1 H, m, $J_{4,5}$ 2.8, $J_{1,5}$ 2.8, $J_{5,6}$ 1.0 Hz, 5-H), 3.63 (1 H, dd, $J_{1,5}$ 2.8, $J_{1,3}$ 0.9 Hz, 1-H).

(−)-(1S,5R)-1-*Acetylaminobicyclo*[3.2.0]*heptane* (−)-(4).—To a solution of (−)-(2b) (α_{436} 0.013°, o.p. 0.83%; 0.0064 g, 0.039 mmol), in EtOH (5 ml) was added 5% Pd–C (0.005 g). It was hydrogenated at 1 atm. overnight at room temperature. When (2b) was no longer detected by t.l.c. the mixture was filtered and then subjected to polarimetric, u.v., and c.d. analyses; α_{436} −0.016°, $\lambda_{max.}$ (EtOH) 295 nm (ε 44), $\delta\varepsilon_{max.}$ (295) −0.0098. The solvent was then evaporated to leave an oil (Found: C, 65.1; H, 7.65; N, 8.25. $C_9H_{13}NO_2$ requires C, 64.65; H, 7.8, N, 8.4%); $\nu_{max.}$ (neat) 3 260 (NH), 2 920, and 1 740 cm^{-1} (CO); δ_H ($CDCl_3$) 2.0 (3 H, s, CH_3) and 2.3—1.5 (9 H, m,ring protons).

(−)-(1S,5S)-endo-7-*Acetylaminobicyclo*[3.2.0]*heptane* (−)-(5).—A solution of (−)-(3b) (α_{436} −0.025°, o.p. 1.5%; 0.0053 g, 0.032 mmol), was hydrogenated as above to give, after work-up, crystals, m.p. 124—126 °C (Found: C, 64.3; H, 7.9; N, 8.2. $C_9H_{13}NO_2$ requires C, 64.65; H, 7.85; N, 8.4%); $\nu_{max.}$ (Nujol) 3 330 (NH), 1 740 [C(1)O], and 1 665 cm^{-1} (amide CO); δ_H ($CDCl_3$) 6.1br (1 H, s, NH), 4.5 (1 H, m, 7-H), 3.0—1.2 (9 H, m, ring protons), and 2.0 (3 H, s, CH_3).

Chirality Enhancement of (3b).—A 1.1×10^{-2}M solution of (±)-(2b) in methanol (160 ml) was irradiated with right c.p.l. (0.3 W) during 175 min up to 55% conversion of (2b) into (3b) (n.m.r. analysis). Evaporation of the mixture and t.l.c. led to (+)-(1*R*,5*R*)-(3b), $\delta\varepsilon_{max.}$ (345) 0.037, in CH_3OH, corresponding to an o.p. 1.1% and to (+)-(1*R*,5*S*)-(2b) (0.071 g, 54%), $\delta\varepsilon_{max.}$ (347) 0.055, o.p. 1.3%. (+)-(1*R*,5*S*)-(2b) was then dissolved in methanol (40 ml) and irradiated with left c.p.l. during 7 min (0.3 W), up to 16% conversion. Work-up of the mixture as above led to (+)-(1*R*,5*S*)-(2b), $\delta\varepsilon_{max.}$ (347) 0.029, o.p. 0.7%, and to (−)-(1*S*,5*S*)-(3b) (0.0072 g, 63%) $\delta\varepsilon_{max.}$ (345) −0.095 corresponding to an o.p. of 2.9%.

Acknowledgements

We thank the M.P.I., Roma, for a grant within the Progetti di Interesse Nazionale, the C.N.R., Roma, for financial support, the Istituto di Chimica Quantistica ed Energetica Molecolare, the Istituto di Biofisica, and the Centro per le Macromolecole Stereoordinate of the C.N.R., Pisa, for laboratory facilities.

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Received 10*th May* 1983; *Paper* 3/741