Tetrahedron Vol. 41, No. 10, pp. 1989 to 1990, 1985
Printed in Great Britain

0040–4020/85 \$3.00 + .00
Pergamon Press Ltd.

CHIROPTICAL STUDIES OF SATURATED KETONES PARTIALLY PHOTORESOLVED BY CHIRAL LASER PHOTOCHEMISTRY

Marino Cavazza, Maurizio Zandomeneghi and Gigliola Ciacchini
Istituti di Chimica Generale e Chimica Fisica, Università di Pisa, 56100 Pisa, Italy

and

Francesco Pietra
Istituto di Chimica, Università di Trento, 38050 Provo-Trento, Italy

(*Received in UK* 27 *January* 1984)

Abstract—Partial photoresolution of tricyclo[5.4.0.0^{1,5}]undecan-5-one ((±)-1) with circularly-polarised 333.6 nm light from an Ar-ion c.w. laser led to $\Delta\varepsilon_{max} = -0.40$ and $\Delta\varepsilon/\varepsilon_{max} = 1.8\%$ at 300 nm in n-hexane and 1*S*, 7*R*, 5*R* configuration for (−)-1.

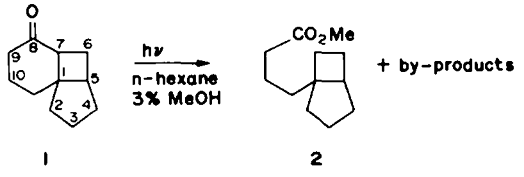
Chiroptical studies have been largely devoted to saturated chiral ketones.[1] In fact, the generally high dissymmetry factors for easily available natural ketones made the study accessible even to low-sensitivity, early CD instrumentation. This contrasts with the situation of non-natural chiral ketones where the problems connected with either the optical resolution of the racemic ketone,[2] or its asymmetric synthesis, have posed serious limitations to chiroptical studies.

We have recently reported successful chiroptical studies of α,β-unsaturated ketones obtained by either partial photoresolution of the racemate or asymmetric photosynthesis with circularly polarised UV laser light (CPL).[3] We were assisted by the fact that the photochemically-active 350 nm enone $n \rightarrow \pi^*$ absorption band only occurs at the emissions of commercially available continuous-wave lasers.[3,4] We have now attacked, along similar lines, the problem of the photoresolution of saturated ketones. The method proved successful, albeit limited by the fact that, with a large proportion of saturated ketones, the $n \rightarrow \pi^*$ absorption occurs at too short a wavelength for commercially available continuous wave lasers.

We have first selected a ketone (1) (i) for which chiroptical data are not available, (ii) which has appreciable tail absorption at the laser emissions and (iii) which, being acid-labile, would be difficult to resolve.[5] Thus, well stirred, *ca.* 0.1 M, solutions of (±)-1 in n-hexane–3% methanol were irradiated with 333.6 nm (0.2–0.4 W)[6] left CPL produced from a continuous wave laser. Under these conditions, 1 gave 2 as the main product, as in the irradiation of 1 with an Hg-lamp,[7] besides unidentified by-products (Scheme 1). Mixtures after irradiation for various time intervals were first GLC analysed for 1 in order to obtain the degree of conversion,[8] and then evaporated *in vacuo* to leave an oily residue which was subjected to preparative TLC (2 mm thick Merck Kieselgel 60 PF$_{254}$; solvent, n-pentane–ethyl ether 80:20). This allowed us to isolate residual 1 (R_F 0.39), 2 (R_F 0.73) and unidentified by-products.[9] Dichroic measurements on recovered 1 in n-hexane gave $\delta\varepsilon_{334}$ (percentage degree of conversion of 1) = −0.00014 mol^{-1} cm^{-1} (18), −0.00020 (26), −0.00039 (38), −0.00055 (54), the full spectrum related to the last case being shown in Fig. 1. The δε values, which are affected by a large (±10%) error due to the small elongation (*ca* 10 mm) at 334 nm, allowed us to calculate the molar dichroism for pure (−)-1 from eqn (1),[10] where *x* stands for 1 − % degree of conversion/100.

$$|\Delta\varepsilon_{334}| = \sqrt{2\varepsilon_{334}|\delta\varepsilon_{334}/\ln x|}. \qquad (1)$$

We thus obtained the mean value $\Delta\varepsilon_{334} = -0.055$, with a deviation (±0.002) smaller than the error on δε. This gives the maximum dichroism $\Delta\varepsilon_{300} = -0.40$ and a 1.8% dissymmetry factor at 300 nm, for (−)-1 in n-hexane (ε = 22 at the absorption maximum, 290 nm; $\varepsilon_{334} = 2.1$). According to the octant rule[1] the configuration is (−)-(1*S*, 7*R*, 5*R*) (Fig. 2). Confidence in this dichroism value, which has the expected order of magnitude, is given by its notable independence of the degree of conversion of 1.[11]



Scheme 1.

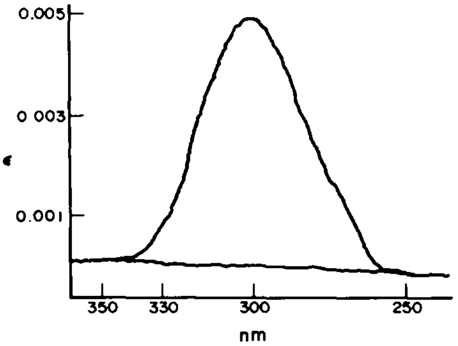


Fig. 1. Measured dichroism (δε) at 54% conversion of starting (±)-1.

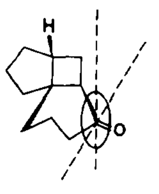


Fig. 2. (−) (1*S*, 7*R*, 5*R*)-tricyclo[5.4.0^{1,5}]undecan-5-one.

We then turned to (±)-camphor in order to deal with a saturated ketone, of known chiroptical data, having such a slight absorption ($\varepsilon = 0.2$ at 334 nm in n-hexane and nil at the other laser emissions)[6] to be at the limits of the practical possibility of carrying out a photochemical transformation. Operating as with **1** above, with 10–20% conversion of the starting racemate, the dichroism at the irradiation wavelength was too small to be measured, so that eqn (1) could not be used. However, from the measured maximum dichroism $\delta\varepsilon_{303} \simeq 0.003$, the optical purity could be calculated in accordance with the literature values.[12]

CONCLUSIONS

We have shown here that, provided the ketone has appreciable absorption at the source emissions, CPL irradiations with a UV continuous-wave laser[4] offer a rapid method, which only needs little starting racemate, for chiroptical studies of saturated ketones.[13] This is especially attractive for difficult-to-resolve and/or labile ketones.

EXPERIMENTAL

Circularly polarised light (CPL) was produced from a Spectra-Physics mod. 171-19 Ar-ion continuous-wave laser through a silica Fresnel rhomb. The photochemical reactor has been previously described.[3] NMR spectra were taken with a Varian CFT 20 spectrometer modified for proton. UV spectra were recorded with a Pye-Unicam SP8 150 spectrophotometer. Polarimetric measurements and CD spectra were made with, respectively, a Perkin–Elmer 141 polarimeter and a Jasco J 500C spectropolarimeter. IR spectra were taken with a Perkin–Elmer 983 spectrometer.

Acknowledgements—We thank MPI and CNR, Roma, for financial support, the Istituto di Chimica Quantistica, CNR, Pisa, for laser facilities and the Centro di Chimica delle Macromolecole Stereoordinate, CNR, Pisa, for CD facilities.

REFERENCES AND NOTES

[1] S. F. Mason, *Molecular Optical Activity and the Chiral Discriminations*. Cambridge University Press, Cambridge (1982).

[2a] F. Toda, K. Tanaka, T. Omata, K. Nakamura and T. Oshima, *J. Am. Chem. Soc.* **105**, 5151 (1983); J. Jaques, A. Collet and S. H. Wilen, *Enantiomers, Racemates and Resolutions*. Wiley, New York (1981); [b] W. R. Adams, O. L. Chapman, J. B. Siega and W. J. Welstead, Jr., *J. Am. Chem. Soc.* **88**, 162 (1966).

[3] M. Zandomeneghi, M. Cavazza, C. Festa and F. Pietra, *J. Am. Chem. Soc.* **105**, 1839 (1983).

[4] The shortest-wavelength emissions of commercially available continuous-wave lasers are 333.6 nm (Ar-ion laser) and 337.4 nm (Kr-ion laser). Emissions at shorter wavelength can be obtained with commercially-available excimer- and frequency-multiplier-lasers. However, with such pulsed emissions non-linear phenomena might well come into play. This is in fact the case of the phototransformation of carvone into carvonecamphor where biphotonic photochemistry plays an important role when high-power, pulsed lasers are used (V. Malatesta, C. Willis and P. A. Hackett, *J. Org. Chem.* **47**, 3117 (1982); U. Brackmann and F. P. Schäfer, *Chem. Phys. Letters* **87**, 579 (1982)). In contrast, when continuous-wave UV lasers are used, only single photon photochemistry is involved (M. Zandomeneghi, M. Cavazza, L. Moi and F. Pietra, *Tetrahedron Letters* 213 (1980). This urges studies as to the scope of chiral photochemistry with the use of pulsed lasers.

[5] In fact, in our hands, attempted resolution of (±)-**1**,[7] according to a widely used method for acid-labile ketones[2b] failed to give detectable optical activity.

[6] Actually, the 333.6, 351.1, 351.4 and 363.8 nm laser emissions were used jointly. However, both **1** and its photoproducts absorb only the 333.6 nm emission.

[7] R. L. Cargill, J. R. Dalton, S. O'Connor and D. G. Michels, *Tetrahedron Letters* 4465 (1978).

[8] SE-52 C. Erba 25 m, 0.2 mm capillary column, 160°, N_2, 2 ml min^{-1}, retention time for **1** 16.7 min (with carvone as internal reference standard).

[9] Recovered **1** proved chemically pure (free, in particular, from isomers) according to both spectra and capillary column GLC.[8] Particularly significant was a clean ^{13}C-NMR (20 MHz) spectrum: δ_{TMS} (C_6D_6) 212.2, *s* (C=O), 50.3, *s* (C-1), 47.2, *d* (C-7), 40.6, *t* (C-9), 39.8, *d* (C-5), 21.5, *t* (C-6), besides triplets at 39.5, 33.3, 33.0, 26.9 and 25.2 ppm for the remaining methylenes (where multiplicities are from off-resonance decoupling). While it is obvious that the two smaller rings of **1** must be *cis*-fused, *cis*-fusion between the six- and the four-membered ring is indicated by the following facts. Thus, the carbonyl stretching frequency of **1** (liquid film) occurs at 1697 cm^{-1} as expected for similar, *cis*-fused systems.[14,15] Moreover, **1** did not undergo any change on 2 hr refluxing in methanol–K_2CO_3 whereas, under such conditions, similar, *trans*-fused systems undergo isomerisation to the *cis*-analogues.[14]

[10] Equation (1) has been derived from the kinetic equations governing the disappearance of the enantiomers during the irradiation of a racemic mixture with CPL (M. Cavazza, M. Zandomeneghi, C. Festa, E. Lupi, M. Sammuri and F. Pietra, *Tetrahedron Letters* **23**, 1387 (1982). Though approximate, eqn (1), for low optical purities, applies up to higher conversions than was the case with the corresponding eqn (2) in ref. 3.

[11] The fact that $\Delta\varepsilon$ is independent of the degree of conversion of the starting racemate fits the requirements of the kinetic equations governing CPL photoresolutions.[1,3,10]

[12] G. Balavoine, A. Moradpour and H. B. Kagan, *J. Am. Chem. Soc.* **96**, 5152 (1974).

[13] Other causes for failure of the CPL method, not considered above, can be envisaged in, for example, excitation transfers among molecules. This would lead to $\delta\varepsilon$ values governed by both the concentration of the reagent and the nature of the solvent, rather than by the chiral photodiscrimination alone.

[14] M. C. Pirrung, *J. Am. Chem. Soc.* **103**, 82 (1981).

[15] W. Oppolzer, *Acc. Chem. Res.* **15**, 135 (1982).