Optical Rotatory Dispersion and Circular Dichroism of Some Optically Active Iodides

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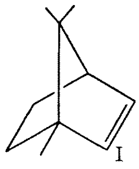
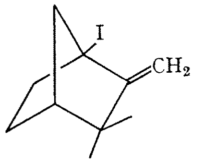
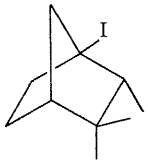
DURING a general study of hydrazone oxidations, we have prepared some bicyclic optically active iodo-compounds and present here their rotatory properties, including the first recorded Cotton effect associated with an iodo-chromophore.†

The oxidation of (+)-camphor hydrazone[1] with iodine in the presence of triethylamine (a procedure discovered by Barton[2] in the steroid series) gave two products separable by liquid chromatography on silica gel. The first product was 2-iodo-1,7,7-trimethylbicyclo[2,2,1]hept-2-ene (2-iodoborn-2-ene) (1); λ (film), μ) 6·39 (C=C); λ (EtOH) 248 nm. (ϵ 104); δ ($CDCl_3$) 0·85 (6H, s, Me), 0·97 (3H, s, Me), 6·39 (1H, d; vinyl H); $[\phi]_{240}$ -6600 (*c*, 0·023, MeOH). This product is expected from Barton's work as well as from other work done in these laboratories. The second product was the result of Wagner–Meerwein rearrangement of a cationic intermediate that has been suggested to occur during oxidations of the present type.[2] The rearrangement product has been assigned the structure 1-iodo-3,3-dimethyl-2-methylenebicyclo[2,2,1]heptane (1-iodocamphene) (2); λ (film, μ) 6·05 (=CH_2), 11·25 (=CH_2); λ (EtOH) 253 nm. (ϵ 590); δ ($CDCl_3$) 1·08 (3H, s, Me), 1·12 (3H, s, Me), 4·80 (1H, s, vinyl H), 5·13 (1H, s, vinyl H); $[\phi]_{228}$ $-18{,}750$ (*c*, 0·015, MeOH); $[\theta]_{214}$ $-29{,}230$ (*c*, 0·3, MeOH).


(1)



(2)



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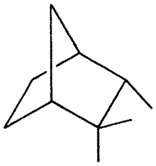
(4)

Although the u.v. spectra of the above unsaturated iodo-compounds showed the expected absorption mazima at 248 and 253 nm., respectively, as well as strong end-absorption, the o.r.d. and c.d. spectra‡ showed no Cotton effects at the iodo-chromophore and only the beginnings of Cotton effects for the π–π* transition of the appropriate double bonds.[3] The influence of the bridgehead iodo-group on the energy of the exocyclic double bond transition in 1-iodocamphene is interesting and indicates a possible interaction between the two groups.

When 1-iodocamphene (2) was reduced with di-imide (hydrazine–oxygen[4]), a saturated iodo-compound was

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† Not, however, the first observed (C. Djerassi and P. Laur, personal communication).

‡ The o.r.d. and c.d. measurements were made with a Cary 60 spectropolarimeter and a Japan Spectroscopic Co. automatic recording spectropolarimeter with c.d. attachment. The measurements were made on methanolic solutions in 1 cm. cells.

obtained; δ ($CDCl_3$) 0·89 and 1·00 (9H, two s, Me); λ (EtOH), 253 nm. (ϵ 690); $[\phi]_{260}$ -419, $[\phi]_{250}$ -1251, $[\phi]_{240}$ -998 (*c*, 0·04, MeOH); $[\phi]_{250}$ -830 (*c*, 0·26, MeOH). The compound was assigned the structure 1-iodo-2-*endo*-3,3-trimethylbicyclo[2,2,1]heptane (3), with assumption of steric control of the di-imide reduction.[4] Hydrogenolysis of the saturated iodo-compound (sodium–alcohol) afforded a known hydrocarbon, isocamphane (4), the methyl resonances of which were identical with those of the major isomer derived from the catalytic reduction of camphene that had previously been assigned the *endo*-configuration.[4] The methyl resonances of the lesser (*exo*)-isomer are easily distinguishable in a mixture of the two isomers; thus the saturated iodo-compound (3) is probably configurationally pure *endo*.

The o.r.d. and c.d. spectra of 1-iodo-2-*endo*-3,3-trimethylbicyclo[2,2,1]heptane (3) are recorded in the Figure. At the position of the weak iodo-absorption, an anomaly is observed. This observation is particularly important as it holds the potential for direct determination of absolute configuration of optically active centres convertible stereospecifically into the iodo-chromophore.

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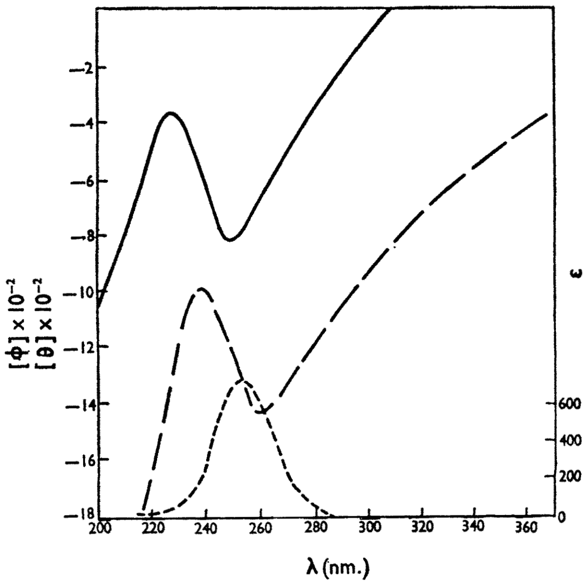

FIGURE. *O.r.d.* (— —), *c.d.* (——), *and u.v.* (- - - - -) *absorption of* 1-*iodo*-2-endo-3,3-*trimethylbicyclo*[2,2,1]*heptane.*

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[2] D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 1962, 470.

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[4] E. E. van Tamelen and R. J. Timmons, *J. Amer. Chem. Soc.*, 1962, **84**, 1067.