Asymmetric Synthesis of an Optically Active *trans* Doubly Bridged Ethylene, (−)-(*R*)-D_2-Bicyclo[8.8.0]octadec-1(10)-ene

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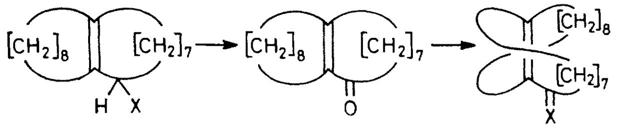
Summary U.v. irradiation of the *cis* bicyclic αβ-unsaturated ketone (**5**) in diethyl L_g-(+)-tartrate afforded a 1 : 7 mixture of the *cis* (**5**) and the *trans* ketone (**6**) enriched in the (−)-enantiomer; Wolff–Kishner reduction of (**6**) yielded (−)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**7**) (optical purity 0·5—1·0%) with the (*R*)- configuration.

IN previous papers,[1] we reported a successful photochemical isomerization of the *cis*-[8][8]doubly bridged ethylene (**1**) into the *trans* isomer (**7**) with D_2 symmetry. To prepare (**7**) in an optically active modification seemed desirable to demonstrate its gyrochiral nature, as well as to provide a counterpart to Cope's classical resolution of *trans*-cyclo-octene.[2]

We now report the chiral solvent-induced asymmetric *cis–trans* photoisomerization of the *cis* bicyclic $\alpha\beta$-unsaturated ketone (**5**) into the (—)-*trans* ketone (**6**) which was eventually transformed into the (—)-*trans*-[8][8] doubly bridged ethylene (**7**)



(1) X=H
(2) X=Br
(3) X=OAc
(4) X=OH

(5)

(–)–(6) X=O
(–)–(*R*)–(7) X=H_2

The conventional sequence of transformations[3] involving bromination with *N*-bromosuccinimide of (**1**)[1] to give the bromide (**2**), conversion of (**2**) into the acetate (**3**) using silver acetate, followed by alkaline hydrolysis gave the unsaturated alcohol (**4**), m p 94—95 °C Jones' oxidation of (**4**) afforded the *cis* $\alpha\beta$-unsaturated ketone (**5**), m p 125—126 °C, i r ν 1674 cm^{-1} (C=O), u v (hexane) λ_{max} 240 nm (ϵ 9570)

A solution of (**5**) (20 mg) in diethyl L_g-(+)-tartrate[4] (10 g) was irradiated with a medium-pressure mercury lamp (Toshiba SHL-100UV) at room temperature, and g l c analysis of the product indicated that irradiation for 3 h had yielded a 1 : 7 equilibrium mixture of the *cis*-(**5**) and the *trans*-(**6**)

Preparative g l c of the combined aliquots, freed of the diethyl tartrate by washing with water, followed by column chromatography (SiO_2) gave a 40% yield of (**6**),[5] an oil, *m/e* 262 (M^+), i r ν 1725 cm^{-1} (C=O), u v (hexane) λ_{max} 307 nm (ϵ 60), $[\alpha]_D^{24}$ $-13°$ (*c* 0 46, hexane), $[\theta]_{307\ nm}$ $-2\ 2 \times 10^3$ (hexane) The negative specific rotation indicates that (**6**) is not racemic but is enriched in the (—)-enantiomer

We had found[1] that dichlorocarbene reacted preferentially with the *cis* isomer (**1**) and this proved convenient for isolating the *trans* isomer (**7**), the combined aliquots freed from the chiral solvent after irradiation were directly treated with hydrazine hydrate and KOH in diethylene glycol to give a mixture of the *cis*-(**1**) and *trans*-(**7**) When stirred with 50% aqueous NaOH, $CHCl_3$, and cetyltrimethylammonium chloride this mixture provided a 64% yield [from (**5**)] (preparative t l c) of D_2-bicyclo[8 8 0]-octadec-1(10)-ene (**7**) enriched in the (—)-enantiomer,† $[\alpha]_D^{24}$ $-2\ 3°$ (*c* 0 60, iso-octane), $[\theta]_{222\ 5\ nm}$ $-1\ 8 \times 10^3$ (iso-octane) whose identity was established by comparison with an authentic sample[1] (g l c and i r , u v , and mass spectra)

C d spectral comparison with (—)-(*R*)-*trans*-cyclo-octene[6] and (—)-(*S*)-bicyclo[3 3 1]-1(2)-nonene[7] together with Scott's octant projection rule[8] indicated an (*R*)-configuration for (**7**)

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† Comparison with the reported $[\alpha]_D$ — 458° (neat) (ref 2) and $[\theta]_{196\ nm}$ — 1 41 × 10^5 (hexane) (ref 8) of (—)-*trans*-cyclo-octene seems to suggest *ca* 0 5—1 0% optical purity for this specimen

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[2] A C Cope, C R Ganellin, and H W Johnson, Jr , *J Am Chem Soc* , 1962, **84**, 3191, A C Cope, C R Ganellin, H W Johnson, Jr , and T V van Auken, *ibid* , 1963, **85** 3276

[3] A C Cope and L L Esters, *J Am Chem Soc* , 1950, **72**, 1129, A C Cope, M R Kinter, and R T Keller, *ibid* , 1954, **76**, 2757

[4] An asymmetric synthesis of optically enriched hexahelicene (optical yield 1 1%) has been reported, W H Laarhoven and Th J H Cuppen, *J Chem Soc , Chem Commun* , 1977, 47

[5] An 80% photochemical conversion of *cis*-2-cyclo-octenone into the *trans* isomer has been reported (P E Eaton and K Lin, *J Am Chem Soc* , 1964, **86**, 2087), and the spectral data of (**5**) and (**6**) were found to be parallel to those of these *cis* and *trans* isomers

[6] A C Cope and A S Metha, *J Am Chem Soc* , 1964, **86**, 1268

[7] M Nakazaki, K Naemura, and S Nakahara, *J Org Chem* , 1979, **44**, 2438

[8] A I Scott and A D Wrixon, *Tetrahedron*, 1970, **26**, 3695