trans Doubly-bridged Ethylene. Preparation of (±)-*trans*-Bicyclo-[10.8.0]eicos-1(12)-ene

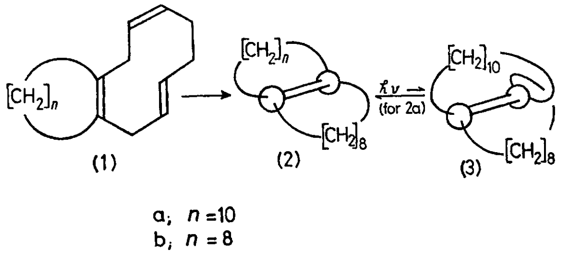
By Masao Nakazaki,* Koji Yamamoto, and Junichiro Yanagi
(*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan*)

Summary (±)-*trans*-Bicyclo[10.8.0]eicos-1(12)-ene (**3**) was prepared by photochemical isomerization of the *cis*-precursor (**2a**), and is the first example of a *trans* doubly bridged ethylene.

We have been interested in the preparation and chiroptical properties of high symmetry chiral molecules[1] having a twisted and strained π-electron system, and have reported the syntheses of (−)-(*RRRR*)-[6]chochine[2] and (+)-(*S*)-[8][8]paracyclophane.[3]

Although the chemistry of *trans*-cycloalkenes has been extensively studied by Cope,[4] the preparation of a *trans* doubly bridged ethylene has not been reported. We report here the synthesis of (±)-*trans*-bicyclo[10.8.0]-eicos-1(12)-ene (**3**) which can be regarded as an ethylene analogue of [*m*][*n*]paracyclophanes.

Co-oligomerization[5] of cyclodecyne[6] with 2 mol of butadiene afforded the bicyclic triene (**1a**) which was partially hydrogenated with Raney nickel to give *cis*-bicyclo[10.8.0]eicos-1(12)-ene (**2a**),[5] m.p. 63—64 °C. A cyclohexane solution of (**2a**) containing xylene as photosensitizer[7] was irradiated with a Toshiba SHL-100 u.v. medium-pressure mercury lamp under N_2. Monitoring the reaction by g.l.c. indicated that irradiation for 12 h yielded a 2.4:1 mixture of the *cis*- and *trans*-isomers and this ratio remained unchanged after further irradiation. After several unsuccessful attempts to separate these isomers by various chromatographic methods, eventually the *trans*-isomer was obtained by treating the isomers with dichlorocarbene; (**2a**) was found to be more reactive towards dichlorocarbene than (**3**). The isomeric mixture when stirred with 50% aqueous NaOH, $CHCl_3$, and cetyltrimethylammonium chloride (phase transfer catalyst)[8] yielded (preparative t.l.c.) the unchanged *trans* isomer (**3**) (26%) and the dichlorocarbene adduct of the *cis* isomer (m.p. 120—121 °C, from hexane) (46%). A 1:1 mixture of the *cis–trans* isomers was obtained after irradiating the pure *trans* isomer (**3**) (m.p. 37—38 °C, from acetone) for 48 h. The inertness of (**3**) towards dichlorocarbene may be attributed to the steric shielding of the unsaturated centre from both sides by the [8] and [10]bridges, and this effect was further demonstrated by catalytic hydrogenation (PtO_2, AcOH–EtOAc; 60—65 °C; 32 h); (**2a**) was converted into a mixture of dihydro-derivatives[5] whereas (**3**) was recovered unchanged.†



The n.m.r. spectra of the two isomers reflect their symmetries; the *cis* isomer (**2a**) with C_{2v} symmetry exhibits peaks at δ 1·00—1·82 (28H, CH_2) and 1·87—2·50 (8H,

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† Satisfactory elemental analyses and mass spectral data have been obtained for all new compounds.

CH_2:CH.CH_2-), while the *trans*-isomer (**3**) with C_2 symmetry shows a rather complex pattern consisting of peaks at δ 0·92—1·58 (28H, CH_2) and three separate groups of peaks corresponding to allylic protons at δ 1·58—1·82 (2H), 1·85—2·10 (2H), and 2·22—2·76 (4H).

The photochemical *cis–trans* isomerization of *cis*-bicyclo-[8.8.0]octadec-1(10)-ene (**2b**) (m.p. 105—106 °C) has proved to be unsuccessful so far.

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[1] M. Nakazaki, 'Syntheses and Stereochemistry of Twisted Organic Compounds,' Invited Lecture at 30th National Meeting of the Chemical Society of Japan, Osaka, April, 1974, Abstract V, p. 1.

[2] M. Nakazaki, K. Yamamoto, and S. Tanaka, *J.C.S. Chem. Comm.*, 1972, 433; M. Nakazaki, K. Yamamoto, S. Tanaka, and H. Kametani, *J. Org. Chem.*, 1977, **42**, 287.

[3] K. Yamamoto and M. Nakazaki, *Chem. Letters*, 1974, 1051.

[4] A. C. Cope, C. R. Ganellin, and H. W. Johnson, Jr., *J. Amer. Chem. Soc.*, 1962, **84**, 3191; A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, 1963, **85**, 3276; A. C. Cope and B. A. Pawson, *ibid.*, 1965, **87**, 3644, 3649.

[5] W. Brenner and P. Heimbach, *Angew. Chem. Internat. Edn.*, 1966, **5**, 961; *Annalen*, 1975, 660.

[6] I. Lalezari and A. Shafiee, *J. Heterocyclic Chem.*, 1972, **9**, 1411.

[7] J. S. Swenton, *J. Org. Chem.*, 1969, **34**, 3217.

[8] J. Dockx, *Synthesis*, 1973, 441.