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SYNTHESIS AND CHIROPTICAL PROPERTIES OF AN OPTICALLY ACTIVE DOUBLY BRIDGED ALLENE. [8][10]SCREW[2]ENE

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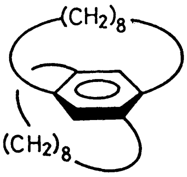
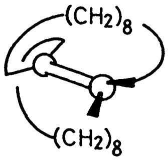
The dichlorocyclopropane derivative **6** prepared from **5** was treated with (-)-sparteine modified butyllithium to afford (+)-(R)-[8][10] doubly bridged allene (**4**) whose absolute configuration was assigned by its CD analysis.

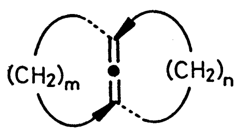
Our continuing interests on twisted π-electron systems have led us to report the first synthesis and absolute configuration determination of (+)-(S)-[8][8]paracyclophane (**1**)[1] and (-)-(R)-[8][8] trans doubly bridged ethylene (**2**),[2] and a natural extension of these studies prompted us to prepare the doubly bridged allene (**3**) whose unique axial chirality as well as its gyrochiral nature has been much discussed.[3] In this communication, we wish to report our successful synthesis of (±)- and (+)-(R)-[8][10] doubly bridged allene ([8][10]screw[2]ene) (**4**)[4] together with latter's chiroptical properties.



(+)-(S)-(1)



(-)-(R)-(2)

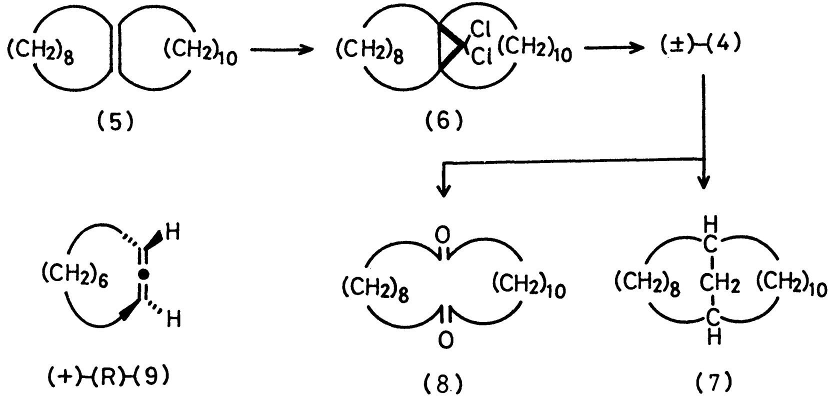


(3) m=n
(+)-(R)-(4) m=8,n=10

Dichlorocarbene insertion reaction of bicyclo[10.8.0]eicos-1(12)-ene (**5**)[6] with chloroform, 50% NaOH, and cetyltrimethylammonium chloride provided an 84% yield of the dichlorocyclopropane derivative **6**, mp 120-121°C which was treated with butyllithium in diethyl ether at -78°C.[7] Purification through vacuum distillation (bp 125-135°C/0.1 mmHg) followed by chromatography over 5% $AgNO_3$ immersed silica gel gave the (±)-[8][10] doubly bridged allene (**4**)[8] which was recrystallized from acetone to afford a 5% yield of needles, mp 72-74°C, MS(m/e) 288(M^+), UV (isooctane) λmax 213.5 nm (ε 9400).

Making a striking contrast to the corresponding [8][10] trans doubly bridged ethylene which was found inert to both catalytic hydrogenation and ozonolysis,[6,9] (±)-**4** could be smoothly hydrogenated with PtO_2 catalyst in ethyl acetate-acetic acid solution to the tetrahydro derivative **7**, mp 41-42°C, MS(m/e) 292(M^+). Isolation of 1,10-cycloeicosanedione (8)[10], mp 51-53°C, from the ozonolysis product of (±)-**4** also confirmed the proposed structure **4**.

In securing **4** in an optically active modification, the dichlorocyclopropane derivative 6 was reacted with a mixture of butyllithium (2 mol equiv) and (-)-sparteine[11] (4 mol equiv) in diethyl ether at -78°C, and the same procedure for the preparation of the racemic modification including AgNO$_3$-silica gel chromatography yielded (+)-4 (9% yield), mp 59-64°C, $[\alpha]_D^{18}$ +4.3°(c 1.6 in hexane); $[\alpha]_{365}^{18}$ +13° (c 1.6 in hexane)[12] whose identification was established by the spectral comparison with the racemic 4. The dextrorotatory 4 exhibits, in common with (+)-(R)-1,2-cyclononadiene (9),[13] a characteristic Cotton curve with respective (-) and (+)-Cotton effect at shorter and longer wavelength region (c 1.48×10^{-3}, isooctane; $[\theta]$ (nm) +1.4×10^2(220), -2.0×10^2(231)), and this, when coupled with the "sector rule",[14] assigns the (R)-configuration to (+)-4.



References and Notes

1) M. Nakazaki and K. Yamamoto, Chem. Lett., 1051 (1974); M. Nakazaki, K. Yamamoto, M. Itho, and S. Tanaka, J. Org. Chem., 42, 3468 (1977).
2) M. Nakazaki, K. Yamamoto, and M. Maeda, J. Chem. Soc., Chem. Commun., 294 (1980); J. Org. Chem., 45, 3229 (1980).
3) R. S. Cahn, C. K. Ingold, and V. Prelog, Angew. Chem. Int. Ed. Engl., 5, 385 (1966).
4) The IUPAC name is bicyclo[10.8.1]heneicos-1(21),12(21)-diene. To circumvent these long and awkard namings and to emphasis their inherent gyrochiral symmetry (C_2 or D_2), we proposed[5] to call a series of these chiral doubly bridged cumulenes by the name of [m][n]screw[p]ene where m and n indicate number of methylene groups constructing the two bridges while p indicates number of cumulative double bonds. As an extension of this nomenclature, the trans doubly bridged ethylene 2 may be called as [8][8]screw[1]ene.
5) In a seminar entitled "Syntheses, Stereochemistry and Microbial Stereo-differentiating Reactions in High-Symmetry Chiral Molecules," held on Sept 30, 1977 at Institut Le Bel, Université Louis Pasteur, Strasbourg.
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8) Satisfactory elemental analyses and mass spectral data have been obtained for all new compounds.
9) V. Ceré, C. Paolucci, S. Pollicino, E. Sandri, and A. Fava, J. Chem Soc., Chem. Commun., 755 (1980); J. A. Marshall and T. H. Black, J. Am. Chem. Soc., 102, 7581 (1980).
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12) A tentative 2.5% optical purity can be assigned to this dextrorotatory specimen 4 based on the alleged absolute rotation[13] reported for the monocyclic allene 9, $[\alpha]_D^{25}$ +170° (CH_2Cl_2).
13) W. R. Moore, R. D. Bach, and T. M. Ozretich, J. Am. Chem. Soc., 91, 5918 (1969).
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