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The Absolute Configuration of 1,2-Cyclononadiene and *cis*-3-Acetoxycyclononene

Sir:

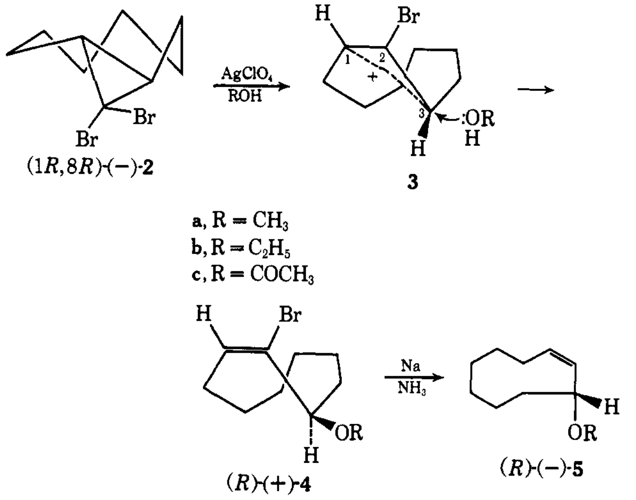
We recently reported the hydroxymercuration[1] and alkoxymercuration[1,2] of optically active 1,2-cyclononadiene[3] to afford optically active products *via* a mercurinium ion[4] intermediate. We now wish to report the absolute configuration of 1,2-cyclononadiene and the products of its oxymercuration. We also wish to present evidence for the intermediacy of a chiral carbonium ion in a cyclopropyl–allyl rearrangement.

The key intermediates in our assignment of the stereochemistry of these compounds are the (+) and (−) enantiomers of 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (**1** and **2**). The (−) enantiomer of *trans*-cyclooctene was treated with $CHBr_3$ and $KOC(CH_3)_3$ in pentane at 0° affording optically pure **1**, $[\alpha]^{25}\mathrm{D}$ +44.2° (*c* 2.49, CH_2Cl_2), mp 51.5–53°.[3] An X-ray study[5] on the tetragonal crystals of **1** showed this compound to exist in a distorted crown conformation. This structure determination established the absolute configuration of (+)-**1**, (1*S*,8*S*) and corroborated the assignment[6] of the absolute configuration of (−)-*trans*-cyclooctene as *R*.

The silver perchlorate induced ring expansion of 9,9-dibromo-*cis*-bicyclo[6.1.0]nonane in methanol affording *trans*-2-bromo-3-methoxycyclononene has recently been reported.[7] The stereospecificity observed in this series of reactions led these authors to suggest that a free allylic cation was *not* involved in the solvolytic process. Orbital symmetry considerations[8] predict that the silver ion promoted ring expansion of the *trans*-dibromocarbene adduct **2** would proceed by a concerted disrotatory process affording the *cis,trans*-allyl cation **3**. Attack by solvent at C_1 would afford *trans*-2-bromo-3-alkoxycyclononene while attack at C_3 would result in the cis isomer **4** (Scheme I).

Treatment of **2**, $[\alpha]^{25}\mathrm{D}$ −43.7°, with an excess of silver perchlorate in anhydrous methanol at 25° for 10 min resulted in quantitative conversion to *cis*-2-bromo-3-methoxycyclononene (**4a**), $[\alpha]^{25}\mathrm{D}$ +42.6°. Reduction of **4a** with sodium in liquid ammonia (1 hr) afforded **5a** (55%) that had $[\alpha]^{25}\mathrm{D}$ −13.1°. The methoxy ether **5a** was identical, except for its optical activity, with an authentic sample prepared by methoxymercuration–demercuration of 1,2-cyclononadiene.[1] The cyclopropyl–allyl transformation with **2** in anhydrous ethanol required 4 hr affording **4b**, $[\alpha]^{25}\mathrm{D}$ +36.0° (92%). Similarily, treatment of **4b** with sodium in liquid ammonia afforded the pure cis isomer **5b**[2] that had $[\alpha]^{25}\mathrm{D}$ −20.2°. Acetolysis of **2** with excess silver perchlorate in glacial acetic acid for 30 min afforded **4c** (80% conversion) that had $[\alpha]^{25}\mathrm{D}$ +8.1°. Reduction of **4c** with lithium aluminum hydride gave *cis*-2-bromo-3-hydroxycyclononene, $[\alpha]^{25}\mathrm{D}$ +9.3°. Esterification of this alcohol with optically pure *O*-methylmandelyl chloride and nmr analysis using the method of Raban and Mislow[9] showed this compound to be of low optical purity (*ca.* 5%).

Scheme I



(1*R*,8*R*)-(−)-**2**

3

a, R = CH_3
b, R = C_2H_5
c, R = $COCH_3$

(*R*)-(+)-**4**

(*R*)-(−)-**5**

The above results preclude the possibility of a long-lived achiral carbonium ion. The rate of racemization of **4a**–**4c** under the reaction conditions is too slow to account for the observed loss of optical activity and a concerted solvolysis of **2** may also be excluded.[10] We may, therefore, conclude that an optically active product arises by preferential attack by solvent on the chiral carbonium ion **3** from the least hindered side. Examination of molecular models clearly indicates that the developing carbonium ion **3** is more accessible to attack from the "outside" of the ring since the opposite approach is effectively shielded by the methylene chain. Since **2** has C_{2v} symmetry, (*R*)-(+)-**4** would be formed regardless of which of the two asymmetric centers in **2** (C-1 or C-8) becomes the asymmetric carbon atom in **4**.

The optical stability of **3** derives from steric inhibition to free rotation of the methylene chain that comprises the ring. Racemization of **3** requires overcoming the steric inhibition to rotation of the planar allyl moiety through the ring. Since the strained *trans,trans*-allyl cation derived from 9,9-dibromo-*cis*-bicyclo[6.1.0]nonane[7] maintained its stereochemical integrity, in all probability the allyl moiety in **3** does not undergo cis,-

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(1) R. D. Bach, *Tetrahedron Lett.*, 5841 (1968).

(2) R. D. Bach, *J. Amer. Chem. Soc.*, **91**, 1771 (1969).

(3) A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *ibid.*, **92**, 1243 (1970); W. R. Moore and R. D. Bach, *ibid.*, in press.

(4) G. A. Olah and P. R. Clifford, *ibid.*, **93**, 1261, 2320 (1971); R. D. Bach and H. F. Henneike, *ibid.*, **92**, 5589 (1970).

(5) We are indebted to Drs. S. H. Simonsen and B. J. Bowen for the X-ray analysis; B. J. Bowen, Ph.D. Thesis, University of Texas, Austin, Tex., 1969.

(6) A. C. Cope and A. S. Mehta, *J. Amer. Chem. Soc.*, **86**, 5626 (1964); P. C. Manor, D. P. Shoemaker, and A. S. Parkes, *ibid.*, **92**, 5260 (1970).

(7) C. B. Reese and A. Shaw, *ibid.*, **92**, 2566 (1970); C. B. Reese and A. Shaw, *Chem. Commun.*, 1365, 1367 (1970).

(8) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); C. H. De Puy, *Accounts Chem. Res.*, **1**, 33 (1968).

(9) M. Raban and K. Mislow, *Top. Stereochem.*, **2**, 199 (1967).

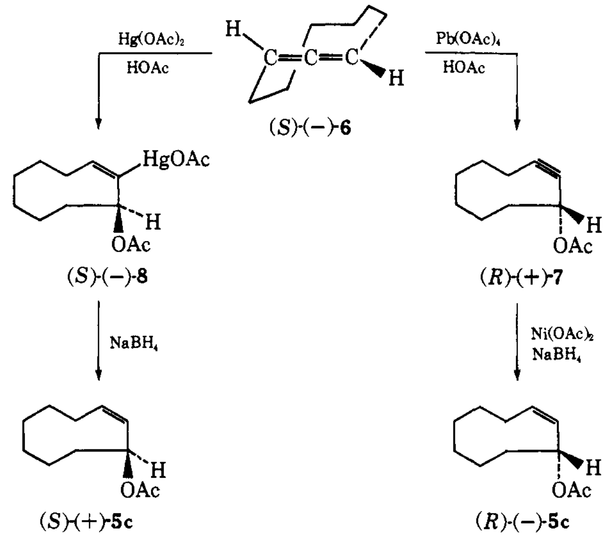
(10) The optical purity of **5a** and **5b** cannot be greater than 86 and 48% since these compounds prepared by oxymercuration of **6** (48% optically pure) had $[\alpha]^{25}\mathrm{D}$ +7.3° and $[\alpha]^{25}\mathrm{D}$ +15.3°,[1] respectively. This is based upon a maximum rotation of 175° for 1,2-cyclononadiene.[11] Doubling the reaction time for the solvolysis of **2** gave rotations of $[\alpha]^{25}\mathrm{D}$ +41.3, +30.4, and +7.6°, for **4a**, **4b**, and **4c**, respectively.

(11) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969).

trans isomerism. The exclusive formation of the cis isomer probably reflects product development control.

The absolute configuration of 1,2-cyclononadiene was established by relating the stereochemistry of the products of lead tetraacetate oxidation and oxymercuration of (−)-**6** to the *cis*-3-alkoxycyclononenes derived from **2**. Treatment of **6**, $[\alpha]^{25}\mathrm{D}$ −14.6°, with lead tetraacetate in acetic acid afforded as the major product (+)-3-acetoxycyclononyne (**7**), $[\alpha]^{25}\mathrm{D}$ +7.6° Stereospecific hydrogenation of **7** ($[\alpha]^{25}\mathrm{D}$ +16.3°) gave (−)-*cis*-3-acetoxycyclononene (**5c**), $[\alpha]^{25}\mathrm{D}$ −9.3° (Scheme II). Acetoxymercuration of (−)-**6**, $[\alpha]^{25}\mathrm{D}$ −14.6°, in glacial acetic acid, afforded (−)-**8** (isolated as the mercuri chloride, $[\alpha]^{25}\mathrm{D}$ −0.8°) which upon demercuration with sodium borohydride gave the *opposite* enantiomer of **5c**, (+)-*cis*-3-acetoxycyclononene, $[\alpha]^{25}\mathrm{D}$ +1.1°.[12] The conversion[1] of (+)-*cis*-3-hydroxycyclononene (**9**) to (+)-**5a** establishes the absolute configuration of (+)-**9** as *S*.[1] Similarly, treatment of (+)-**9** with acetyl chloride gave (+)-**5c** which must also have the *S* configuration. This series of reactions establishes that acetoxy-, alkoxy-, and hydroxymercuration of (−)-**6** all occur principally by an anti addition[13a] with the topology of the reaction such that electrophilic attack by $^{+}$HgX occurs only from the "outside" of the ring.[1,2] However, the reaction of (−)-**6** with lead tetraacetate proceeds by a syn addition to the carbon–carbon double bond.[13b] This is compelling evidence that (−)-1,2-cyclononadiene must have the *S* configuration[13c] in order for the latter reaction to afford (−)-**5c** with the *R* configuration.

Scheme II



The absolute configuration of the oxymercurial **8** was also related to the dibromocyclopropane **2** by electrophilic cleavage of the carbon–mercury bond with bromine. Thus, treatment of (−)-2-acetoxymercurial **8** and the corresponding (−)-2-methoxymercurial with bromine in carbon tetrachloride afforded (−)-**4c** and (−)-**4a**, respectively, which have the *S* configuration.[14]

On the basis of the above data, we may unequivocally conclude that (−)-1,2-cyclononadiene has the *S* configuration and that the (−)-*cis*-3-alkoxycyclononenes above have the *R* configuration. It is significant to note that the absolute configuration assigned to (−)-**6** is the *opposite* to that predicted by Lowe's rule[15] which is based upon the helical model of optical activity originally proposed by Brewster.[16] It is also worthy of note that the chiral cyclopropylidene derived from (−)-**2** by the action of methyllithium[3] affords (−)-**6** by a mode of ring opening that is controlled by relief of torsional strain rather than by steric effects.[17]

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[12] Both **7** and **5c** gave satisfactory elemental analyses and the proposed structures are consistent with their ir, nmr, and mass spectral data.

[13] (a) However, nitratomercuration of (−)-**6** under syn oxymercuration conditions with mercuric nitrate in methylene chloride occurs *via* a syn addition to the carbon–carbon double bond (unpublished results with R. F. Richter). (b) We have established that the lead tetraacetate oxidation of the acyclic allene, (+)-2,3-pentadiene, also occurs *via* a syn addition, affording (+)-4-acetoxy-2-pentyne (unpublished results with R. N. Brummel). (c) Since submission of this communication, (+)-1,2-cyclononadiene has been assigned the *R* configuration on the basis of a rigorous ORD–CD correlation. Our own results corroborate this assignment. We are indebted to Professor Moore for informing us of his results prior to publication: W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **93**, 4932 (1971).

[14] Our results unequivocally establish that bromination of (*S*)-(−)-**6** in methanol proceeds by a trans addition affording (*S*)-(+)-**4a**: L. R. Byrd and M. C. Caserio, *J. Amer. Chem. Soc.*, **93**, 5758 (1971).

[15] G. Lowe, *Chem. Commun.*, 411 (1965).

[16] However, Brewster's more general helical model correctly predicts the sign of the rotation of (+)-**6**, if the estimated contributions to the rotatory power include the methylene chain.:[13c] J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

[17] Consideration of a sterically controlled process leads to the wrong assignment of the absolute configuration of (−)-**6**: G. Krow, *Top. Stereochem.*, **3**, 31 (1970).

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*Book Reviews**

Core Experiments in General Chemistry. By R. S. Drago and T. L. Brown (University of Illinois). Allyn and Bacon, Inc., Boston, Mass. 1970. xii + 196 pp. Limp binding. Price not stated.

This laboratory manual is an abbreviated version of "Experiments in General Chemistry," 3rd edition, and is intended for a course in which laboratory time is limited. Unusual features are the preparation of geometrically isomeric coordination compounds and preparation of organic polymers (cuprammonium rayon; phenol-formaldehyde resin).

Cours de Chimie. Tome 2. By M. Garric (Lycée Michel Montaigne). Dunod, Paris. 1971. xxxii + 464 pp. 84F.

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