Stereoselective 1,4 Bromination of Semibullvalene and Tri-n-butyltin Hydride Reduction of the Dibromide

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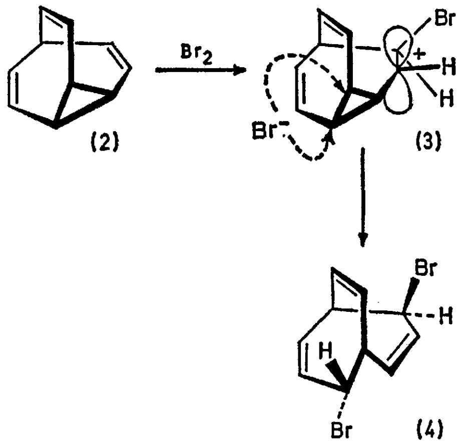
Summary Bromination of semibullvalene proceeds with stereoselective *cis,exo*-1,4-addition in contrast to bullvalene where kinetically controlled *trans*-1,4-addition occurs.

Following the report of a practical synthesis of semibullvalene (**1**),[1] we became interested in its bromination. Unusual results had previously been found in the bromination of bullvalene (**2**), stereoselective formation of the less stable *trans* dibromide (**4**) occurring.[2] This and related observations have been interpreted on the basis of kinetically controlled attack by nucleophile (*e.g.*, bromide ion) on a cyclopropylmethyl cation intermediate such as (**3**).[3] Since the *p* orbital in (**3**) bisects the remaining divinylcyclopropane part of the molecule, the reason(s) for the highly discriminatory capture of this intermediate by one of the illustrated pathways remain unknown.

When semibullvalene (**1**) was treated with bromine in methylene chloride solution at −78°, there was obtained in 67% yield a crystalline dibromide, m.p. 71—71·5°. Since the n.m.r. spectrum provided little definitive stereochemical evidence, a three-dimensional *X*-ray crystal structure analysis was obtained. The molecule belongs to the space group F_{dd2} and sits on a crystallographic two-fold axis; a = 17·979(5), b = 6·216(9) Å. Solution of the structure was by the heavy-atom method, and the ultimate *R*-factor was 0·09. The final *X*-ray model of (**6**) shown in the Figure shows that both bromine atoms are *cis* relative to the bridgehead hydrogens of the two *cis*-fused cyclopentene rings.



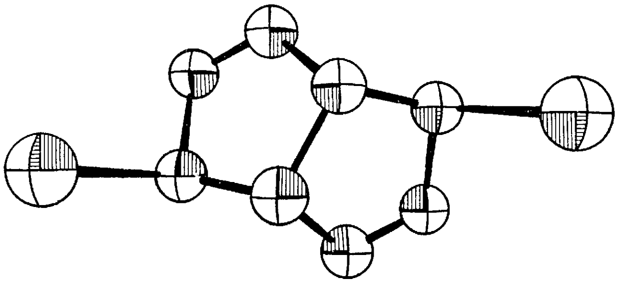
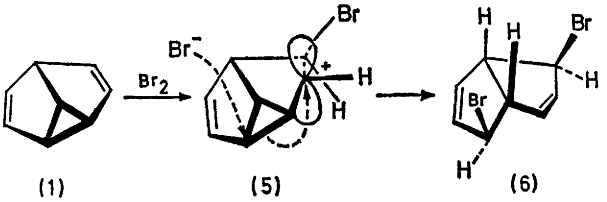
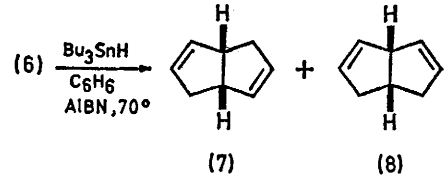


FIGURE. *A structural view of* (**6**) *as determined by* X*-ray analysis.*

When steric factors are considered, initial *exo* attack by bromine on (**1**) is expected to be preferred. Whether the resulting intermediate is (**5**) or its bromonium ion equivalent is not known. However, subsequent attack of bromide ion on the species is seen to occur preferentially from the *cis* direction, *i.e.*, opposite to the situation in (**3**). Kinetically controlled zwitterion annihilation in (**5**) may be sterically controlled and as a result may not be as suitable for multiple-site attack as in (**3**).



When exposed to bases such as potassium t-butoxide, (**6**) was transformed into tarry products. No evidence for the intermediacy of pentalene was found. Treatment of (**6**) with a two-fold excess of tri-n-butyltin hydride in benzene at 70° [4] led to the formation of dienes (**7**) and (**8**) (ratio 3 : 1) in 78% yield. The i.r. spectrum of the product was identical to that reported earlier for a similar mixture.[5,6b] Separation was achieved with a g.l.c. column packed with 10% silver nitrate on 60/80 mesh firebrick at 60°. Hydrocarbon (**7**) which was the less rapidly eluted (t_{ret} 41·2 min) isomer had i.r. and n.m.r. properties in accord with the literature.[6] Diene (**8**) (t_{ret} 16·2 min) also had the expected[6] spectral features. No products of skeletal rearrangement were detected, although some polymer was formed.



(*Received*, 30*th October* 1972; *Com.* 1834.)

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