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REACTION OF N-BENZENESULFONYL-9-AZABICYCLO[3.3.1]NONA-2,6-DIENE WITH DIBORANE: FAILURE OF CYCLIC HYDROBORATION IN THE INTRAMOLECULARLY FACED DIENE SYSTEM

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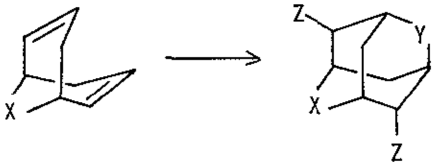
Hydroboration of N-benzenesulfonyl-9-azabicyclo[3.3.1]-nona-2,6-diene gave 2,6-diols and exo,exo-2,7-diol in the ratio of ca. 2.3 : 1, but neither exo,exo-3,7-diol nor the products derived from a boraadamantane were formed. A marked site-selectivity in the hydroxylation was discussed in terms of inductive or spatial effects of the N-substituent.

Cis,cis-cycloocta-1,5-diene usually undergoes a transannular ring closure on electrophilic addition reactions.[1] The reactions of bicyclo[3.3.1]nona-2,6-diene systems have also been reported[2] to afford heteroadamantane derivatives via the first exo-attack of electrophiles and subsequent endo-addition of nucleophiles. The hydroboration of bicyclo[3.3.1]nona-2,6-diene has been reported[3] to afford a boraadamantane via a bisborane adduct, the result implying, however, that the first endo-attack of the boron atom is involved in the transannular addition.

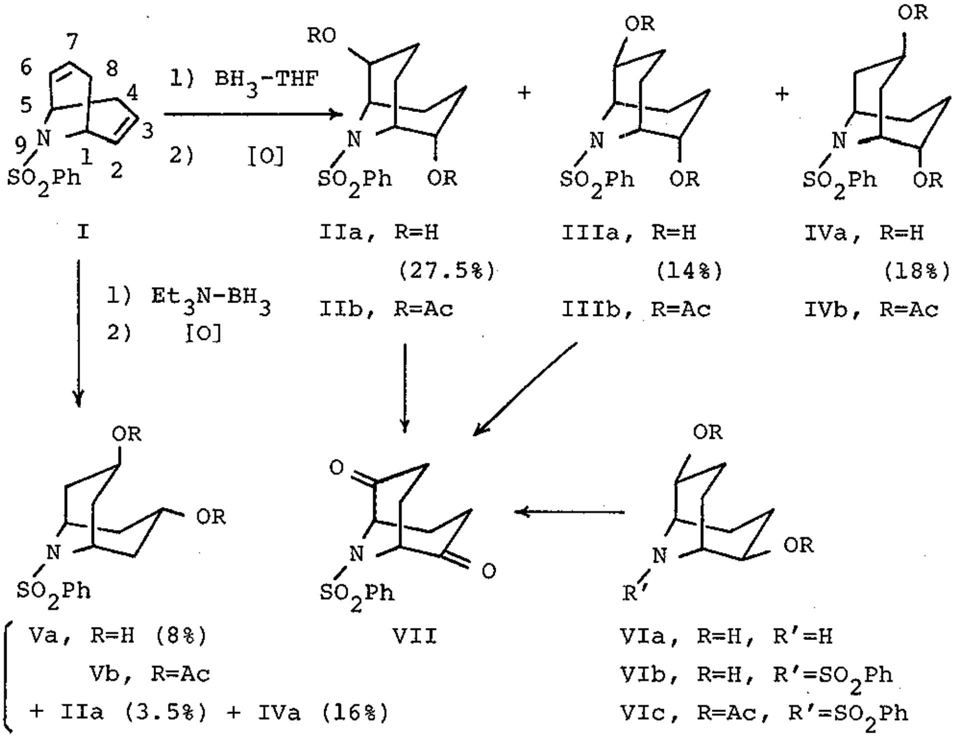
X= N-, S, O, B-
Y= Br, Cl, OH, H



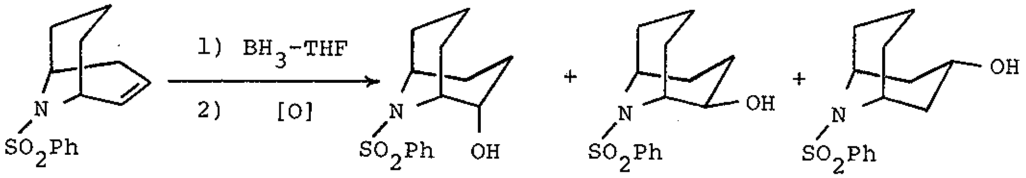
X= CH_2, N-, S, O
Y= N-, S, O, B-
Z= Br, Cl, I, OH, Hg-, H

In the studies associated with a 3,7-bisfunctionalization[4] of 9-azabicyclo[3.3.1]nonane systems via hydroboration, we have found a predominant exo-attack of the boron without any bridge formation between two olefin bonds and a marked regioselectivity in the hydroxylation of this bicyclic system.

Hydroboration-oxidation of N-benzenesulfonyl-9-azabicyclo-[3.3.1]nona-2,6-diene (I)[5] gave three products, exo,exo-2,6-diol (IIa), exo,endo-2,6-diol (IIIa), and exo,exo-2,7-diol (IVa), but neither exo,exo-3,7-diol (Va) nor the alcohol derived from 3,7-endo-addition of the boron was obtained. Their structures were assigned on the basis of ^{1}H-nmr spectra[6] of the corresponding diacetates. The 2,6-diacetate (IIb) showed nmr signals of C_2-H and C_6-H as a multiplet ($W_{\frac{1}{2}}$=8Hz) at δ 4.73ppm, and those of two acetyl methyls as a singlet at δ 1.81ppm. The diacetate (VIc) of endo,endo-2,6-diol (VIb), prepared by N-benzenesulfonylation of a known amino alcohol (VIa)[5] followed by O-acetylation, showed nmr signals of C_2-H and C_6-H as a multiplet ($W_{\frac{1}{2}}$=16Hz) at δ 4.91ppm, and those of two acetyl methyls as a singlet at δ 2.04ppm, the feature of which suggests that two acetoxy groups in IIb were in axial position. The 2,6-diacetate (IIIb) showed nmr signals of C_2-H and C_6-H as a multiplet at δ 4.62-4.94ppm, and those of two acetyl methyls as two singlets at δ 1.99ppm and δ 2.02ppm. In addition, oxidation of IIa or IIIa with CrO_3-pyridine gave a 2,6-dione (VII) identical with the authentic specimen prepared by oxidation of VIb. In the nmr spectrum of 2,7-diacetate (IVb), two acetyl methyls at C_2 and C_7 position appeared as two singlets at δ 1.89ppm and δ 1.97ppm, respectively. The C_2-H signal appeared as a multiplet ($W_{\frac{1}{2}}$=8Hz) at δ 4.79ppm, and C_7-H signal as a multiplet ($W_{\frac{1}{2}}$=21Hz) at δ 5.40 ppm, the feature of which suggests an axial orientation for the C_2-acetoxy group and an equatorial one for the C_7-acetoxy group.

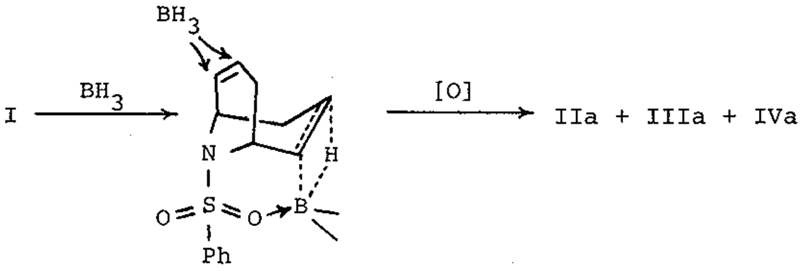


In the hydroboration-oxidation[7] of I using triethylamine borane[8], alcohols IIa, IVa and Va were obtained. In the diacetate (Vb), the ^{1}H-nmr spectrum displayed a singlet at δ 1.98ppm due to two acetyl methyls and a multiplet ($W_{\frac{1}{2}}$=22Hz) at δ 5.20ppm due to C_3-H and C_7-H.



VIII (39%) (~20%) (27%)

From the result in the mono-olefinic system (VIII)[9] shown in the scheme, the preferential attack of the boron at C_6 position rather than at C_7 position in I can be explained in terms of an inductive effect[10] derived from the electron-withdrawing N-sulfonyl group. However, the selective attack of the boron at the C_2 position may be favored through a six-membered transition state (IX)[11] derived from a participation of the boron and N-sulfonyl group. Support for this possible participation might be found in the result of the hydroboration of I using amine borane of reduced ability in coordination.



IX

This is a rare example[12] of a failure of transannular bridge formations in the electrophilic addition reactions to this diene system, and is the first example of a possible role of N-sulfonyl group in the hydroboration of azabicyclic olefins.

NOTES AND REFERENCES

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4. Construction of the 3,7-bisfunctionalized system from previously oxy-functionalized moieties has been described: see H. Stetter and R. Mehren, *Liebigs Ann. Chem.*, 1967, **709**, 170.
5. Prepared according to the method similar to the Stetter's one;

ref. 2d. An alternative synthesis has been reported: see ref. 2j.

6. ^{1}H-nmr spectra were measured for the $CDCl_3$ solution with TMS as an internal standard on a Hitachi R-22 spectrometer operating at 90MHz.

7. Carried out according to the procedure of Štern et al.; P. Štern, P. Trška, and M. Ferles, Coll. Czech. Chem. Comm., 1974, **39**, 2267.

8. U. S. Borax & Chemical Corporation: Brit. Pat. 952,811 (1964) [C. A., 1964, **61**, 2970g].

9. The olefin (VIII) was prepared from 3-granatanone by successive benzenesulfonylation, reduction, mesylation, and elimination reaction.

10. The hydroboration of carbocyclic bicyclo[3.3.1]nonene systems has been reported to give a mixture of the 2- and 3-ol with predominance of the latter: see J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, J. Org. Chem., 1967, **32**, 1372; M. R. Vegar and R. J. Wells, Tetrahedron Letters, 1969, 2565. For discussions of the effects of nearby functional groups on the orientation in hydroboration of cyclic olefins, see H. O. House, Modern Synthetic Reactions, 2nd Ed., Benjamin, Menlo Park, 1972, pp.115-123; J. Klein, E. Dunkelblum, and D. Avrahami, J. Org. Chem., 1967, **32**, 935; L. A. Paquette, A. A. Youssef, and M. L. Wise, J. Am. Chem. Soc., 1967, **89**, 5246; J. M. Davies and S. H. Graham, J. Chem. Soc. (C), 1968, 2040.

11. The orientation control via participation of a carbonyl oxygen has been postulated: see H. C. Brown and K. A. Keblys, J. Am. Chem. Soc., 1964, **86**, 1795; D. N. Butler and A. H. Soloway, ibid., 1966, **88**, 484.

12. The only example of a non-bridged product was reported for aminomercuration of 9-oxabicyclo[3.3.1]nona-2,6-diene using a less reactive nucleophile: see V. G. Aranda, J. B. Mur, and G. A. Aguilar, Rev. Acad. Cienc. Exactas, Fis.-Quim. Natur. Zaragoza, 1973, **28**, 215 [C. A., 1974, **80**, 83174k].

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