Epoxidation. II. Stereoselective Epoxidation of Methylenecyclohexanes *via* Bromohydrins[1]

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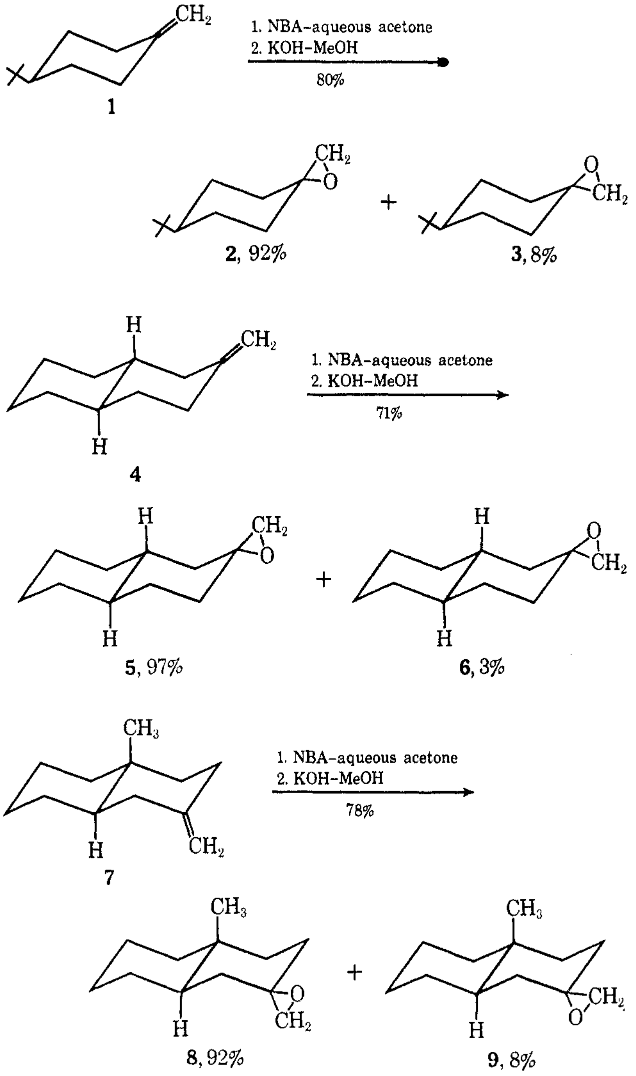
Our interest in the use of isomeric methylenecyclohexane oxides (*e.g.*, **2** and **3**) as intermediates for the synthesis of amino alcohols required for ring expansion reactions[3] prompted an earlier study[1] of methods for the stereoselective preparation of compounds of this type. This study revealed that epoxides with an equatorial methylene group (*e.g.*, **3**) could be prepared in good yield and with high stereoselectivity by treatment of the corresponding cyclohexanone with dimethyloxosulfonium methylide.[4] The isomeric epoxides with an axial methylene group (*e.g.*, **2**) were best prepared by epoxidation of the corresponding olefin with the alkaline hydrogen peroxide–benzonitrile system. This method gave at best a mixture of epoxides containing only about 70% of the epoxide with an axial methylene group and further purification, although possible, was quite tedious. We now wish to report that epoxides with an axial methylene group can be readily prepared from unhindered methylenecyclohexanes *via* bromohydrins.

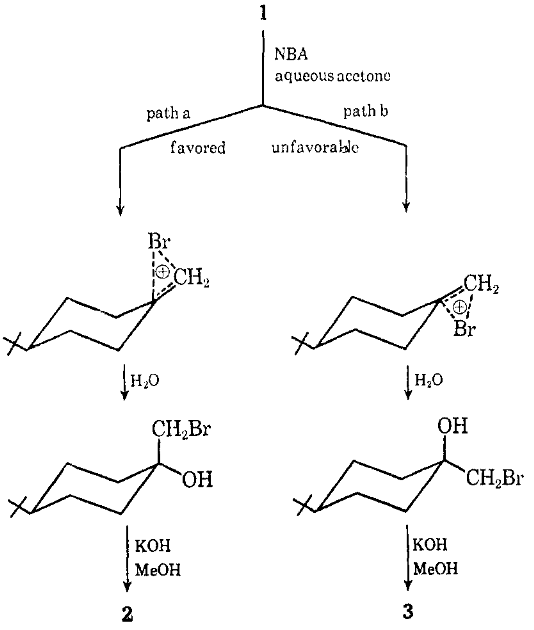
Treatment of the three representative olefins **1**, **4**, and **7** with *N*-bromoacetamide (NBA) in aqueous acetone produced the corresponding bromohydrins[5] which, without further purification, were converted to the epoxides by treatment with potassium hydroxide in methanol. This two-step procedure gave the corresponding epoxides **2**, **5**, and **8** in good yield and with a high degree of stereoselectivity (see Scheme I). Although a brief examination of the use of other solvent systems for the formation of the bromohydrins was made, aqueous acetone proved to be the most satisfactory.

These stereochemical results indicate that bromonium ion formation by electrophilic attack of NBA on the olefin occurs preferentially from the axial direction (path a, Scheme II) and in this respect is similar to other addition reactions to methylenecyclohexanes and cyclohexanones.[6]

Scheme I



Scheme II



Experimental Section

The preparation of the olefins and characterization of the epoxides has been previously reported.[1] The following general procedure was used for the preparation of the epoxides.

General Procedure.—To a solution of 4.14 g (30 mmol) of *N*-bromoacetamide and 3.75 g of sodium acetate in 120 ml of water was added a solution of the olefin (6.0 mmol) in 300 ml of acetone. The resulting mixture was stirred overnight at room temperature and extracted thoroughly with ether. The combined ether extracts were dried ($MgSO_4$) and evaporated to give the crude bromohydrin (91–96%). The crude bromohydrin was dissolved in 10 ml of methanol, 10 ml of a 5% solution of potassium hydroxide in methanol was added, and the resulting mixture stirred for 90 min. The reaction mixture was diluted with water and ex-

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[1] For part I, see R. G. Carlson and N. S. Behn, *J. Org. Chem.*, **32**, 1363 (1967).

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[3] R. G. Carlson and N. S. Behn, *J. Org. Chem.*, **33**, 2069 (1968).

[4] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

[5] For comments on the structure of the bromohydrin derived from methylenecyclohexane, see A. J. Sisti, *J. Org. Chem.*, **33**, 3953 (1968).

[6] For a recent discussion, see M. Cherest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968).

tracted with ether. The combined ether extracts were washed with brine, dried ($MgSO_4$), and evaporated with ether to give the epoxide mixture which was analyzed by vpc.[1] The results are summarized in Scheme I.

Registry No.—1, 13294-73-0; **2,** 7787-79-3; **4,** 7787-72-6; **5,** 7787-77-1; **7,** 7787-73-7; **8,** 7787-80-6.

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Nuclear Magnetic Resonance Analysis of 5,12*H*-Dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene

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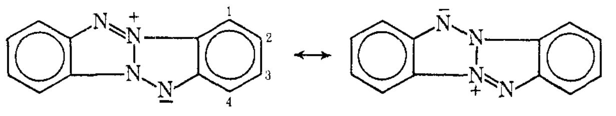
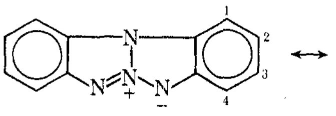
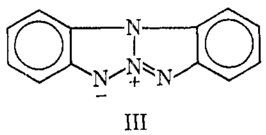
In an earlier paper,[1] the nmr spectrum of 5,6*H*-dibenzo[*b*,*f*]-1,3a,4,6a-tetraazapentalene (I) and two of its methyl derivatives was reported. In this paper, the analysis of the nmr of the isomeric 5,12*H*-dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene (II) is described.



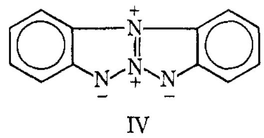
I



II



III



IV

Compound II was prepared by essentially the same procedure as has been reported by Carboni, *et al.*,[2] from 1-(2-azidophenyl)benzotriazole. The nmr spectrum of II was obtained in deuteriochloroform. The spectrum is shown in Figure 1. The experimental spectrum was matched with the calculated spectrum shown in Figure 1 using the LAOCN-3 program.[3] The calculated coupling constants and chemical shifts for II are tabulated in Table I. The data reported previously[1] for I are also tabulated in Table I for comparison purposes.

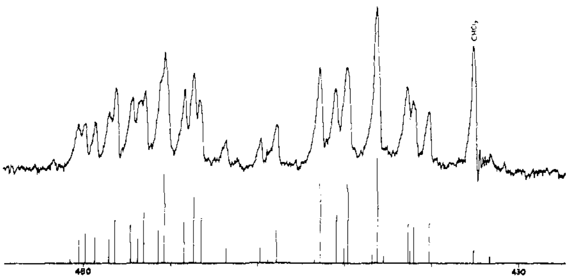


Figure 1.—Experimental and calculated spectra of 5,12*H*-dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene (II) in deuteriochloroform.

TABLE I

COUPLING CONSTANTS AND 60-MHz CHEMICAL SHIFTS

Chemical shifts[a]	Compd I[b]	Compd II
H_1	486.7	474.8
H_2	440.0	443.6
H_3	453.1	450.7
H_4	471.5	471.0
Coupling constants		
$J_{1,2}$	8.47	8.38
$J_{1,3}$	1.05	0.98
$J_{1,4}$	0.79	0.69
$J_{2,3}$	7.00	7.32
$J_{2,4}$	0.93	0.85
$J_{3,4}$	8.73	8.68

[a] Chemical shifts are in hertz downfield relative to internal tetramethylsilane. The values in this table were obtained by an iterative fitting using the LAOCN-3 program.[3] [b] Reference 1.

The coupling constants for both I and II are similar and of the order of magnitude expected for a normal benzenoid ring. The chemical shift of H_2 in each compound is furtherest upfield, a reflection of its location para to N-5, which carries a partial negative charge as seen in structures II–IV. H_4, which is ortho to N-5, is at nearly the same position in both I and II and in both cases is over 27 Hz downfield from H_2, a reflection of its closer proximity to the electronegative nitrogen. Apparently the inductive effect of the nitrogen in the ortho position decreases the effect of the partial negative charge on N-5 and results in the downfield shift. In both I and II, H_3 is located further downfield than H_2; however, in the II the difference between H_2 and H_3 is 7 cycles compared to 13 cycles in compound I. This result suggests that, whereas in compound I H_3 is located para to a nitrogen carrying a partial positive charge, in II the positive charge is much reduced; *i.e.*, structure IV contributes very little to the resonance hybrid. H_1 in compound II is 12 cps upfield compared to H_1 in compound I. This again suggests little contribution of structure IV to the resonance hybrid.

It is interesting to compare the observed chemical shifts of the protons in I and II with the molecular orbital calculations of Chia and Simmons.[4] In Figure 2 is shown a plot of the calculated electron densities *vs.* the observed chemical shifts. The chemical shifts of protons H_2 and H_3 in both I and II seem to correlate very well with the calculated electron densities. H_4 in both compounds falls nearly at the same point. This is not unexpected, since examination of structures I and II shows that in both H_4 has a similar electronic relationship to the nitrogens of the heterocyclic system. On the other hand H_1 in the compounds is in quite

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[1] J. H. Hall, J. G. Stephanie, and D. K. Nordstrom, *J. Org. Chem.*, **33**, 2951 (1968).

[2] R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2618 (1967).

[3] A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964).

[4] Y. T. Chia and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2638 (1967).