The first step is considered to involve the catalytic deoxygenation of the nitro compound to a nitrene (II), discrete or complexed, whose subsequent addition to the carbonyl compound, present in solution, would furnish the oxazirane IIIa, and correspondingly the isomeric nitrone IIIb.

The intermediacy of nitrene and nitrenoid intermediates has been invoked by previous investigators[4,7,8] in an attempt to rationalize the formation of an array of products from catalytic coversions of nitro compounds with carbon monoxide. Even in formation of isocyanates,[5] nitrene intervention is made very probable by the analogous reaction of azides.[9] One might thus expect *in situ* trapping of the reactive intermediate by aldehyde (*vide supra*) to prevail over transformation to isocyanate and subsequent reaction (eq 3). As additional persuasive evidence for the first two steps may be cited the formation of Schiff bases by thermolysis of phenyl azide in aldehydes or ketone, reported by Neiman, *et al.*[10,11] The expected nitrone or oxazirane, however, remained elusive in these latter reactions. This fact is ascribed by the authors to probable oxidation of excess carbonyl compound by the oxygenated intermediates, which in the process become reduced to Schiff base.

Once formed, III can be reduced by carbon monoxide in the presence of rhodium carbonyl to the Schiff base I, as could also be verified experimentally.[12]

Experimental Section

Materials.—Commercial carbon monoxide was used without further purification. Benzaldehyde and various nitro compounds were freshly distilled prior to reaction. Hexarhodium hexadecacarbonyl was prepared by the reductive carbonylation of rhodium chloride in the presence of iron pentacarbonyl.[14] Pyridine and *N*-methylpyrrolidine were additionally dried and distilled over potassium hydroxide. Authentic samples of Schiff bases for comparison of physical constants were synthesized by usual condensation[2] of benzaldehyde with corresponding amines.

General Procedure for Schiff Bases.—All reactions were carried out in a stainless steel autoclave of 500-ml capacity, heated by an external rocking electric oven. Only one experiment, with benzaldehdye and *p*-nitrobiphenyl, will be described here to exemplify the general procedure adopted; the effect of varying conditions can be seen from the data presented in Table I. A solution of benzaldehyde (0.1 mol), *p*-nitrobiphenyl (0.11 mol), and hexarhodium hexadecacarbonyl (10^{-5} mol) in 50 ml of anhydrous pyridine was allowed to react with carbon monoxide (150 atm). The content of the autoclave was heated during 40 min to 165–170° and held at this temperature for 3 hr. After cooling, the autoclave was discharged and pyridine was evaporated from the mixture under vacuum. The residue was swirled with *ca.* 40–50 ml of methanol and filtered to give in 84% yield substantially pure crystals of *N*-benzylidene-*p*-phenylaniline (Ig), mp 147°. Identity of the compound was confirmed by mixture melting point, ir, and nmr spectroscopic comparison with an authentic sample. Yields and physical properties of further azomethine derivatives are compiled in Table I.

Registry No.—Ia, 538-51-2; Ib, 783-08-4; Ic, 889-38-3; Id, 5877-55-4; Ie, 5877-58-7; If, 2272-45-9; Ig, 13924-28-2; carbon monoxide, 630-08-0.

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(7) J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).

(8) T. Kajimoto and J. Tsuji, *Bull. Chem. Soc. Jap.*, **42**, 827 (1969).

(9) R. P. Bennett and W. B. Hardy, *J. Amer. Chem. Soc.*, **90**, 3295 (1968).

(10) L. A. Neiman, V. I. Maimind, and M. M. Shemyakin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1498 (1962).[11]

(11) Compare also *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1831 (1964).

(12) For example, α-phenyl-*N*-phenylnitrone[13] was smoothly deoxygenated by hexarhodium hexadecacarbonyl at 150° and 130 atm carbon monoxide pressure to *N*-benzylideneaniline.

(13) O. H. Wheeler and P. H. Gore, *J. Amer. Chem. Soc.*, **78**, 3363 (1956).

(14) B. L. Booth, M. J. Else, R. Fields, H. Goldwhite, and R. N. Haszeldine, *J. Organometal. Chem.*, **14**, 417 (1968).

Conformational Preference of *cis*-8-Oxabicyclo[4.3.0]non-3-ene

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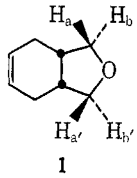
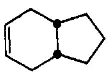
cis-8-Oxabicyclo[4.3.0]non-3-ene (**1**) has found occasional use as a model of *cis*-bicyclo[4.3.0]non-3-ene (**2**), primarily due to the ease of preparing **1**.[2] As part of our effort to test the validity of using an oxygen-containing molecule as a model for its carbocyclic analog,[3] we examined the ground-state conformation of **1**.



1



2

Using results based on the steric course of epoxidation, previous investigations have suggested that **5** is the preferred ground-state conformer of **2**[4] (Scheme I[5]). We have examined the products from epoxidation of **1** and find a fortuitously similar product ratio (Scheme I). These data would appear to support, based on steric data alone, conformer **8** as the ground-state conformer. Furthermore, this would be consistent with the steric course of oxymercuration and the oxygen participation noted for this reaction.[6] However, the nmr spectrum of **1** is better accommodated by conformer **9**.

The spectrum of **1** exhibited a multiplet for the pro-

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(1) NDEA Predoctoral Fellow, 1968–1971. Abstracted, in part, from the Ph.D. Thesis of Rodney D. Otzenberger, Montana State University, 1971.

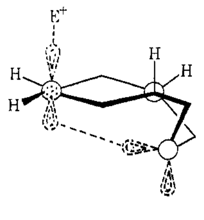
(2) (a) E. L. Eliel and C. Pillar, *J. Amer. Chem. Soc.*, **77**, 3600 (1955); (b) B. Rickborn and S. Y. Lwo, *J. Org. Chem.*, **30**, 2212 (1965).

(3) (a) B. P. Mundy, A. R. DeBernardis, and R. D. Otzenberger, *ibid.*, **36**, 3830 (1971); (b) B. P. Mundy and R. D. Otzenberger, *ibid.*, **37**, 677 (1972).

(4) J. C. Jallageas and E. Casadevall, *C. R. Acad. Sci., Ser. C*, **268**, 449 (1969).

(5) We did not analyze the epoxides, but rather compared the alcohols resulting from lithium aluminum hydride reduction of the epoxide mixture. The stereochemistry of the alcohols had been previously assigned,[3b] and the known stereospecificity of reductive opening of the epoxide moiety assured us that we were analyzing an alcohol mixture representative of the epoxide mixture.

(6) See ref 3b. The stereospecificity and oxygen participation is best explained by invoking an intermediate for reactions proceeding *via* carbonium ion intermediates.



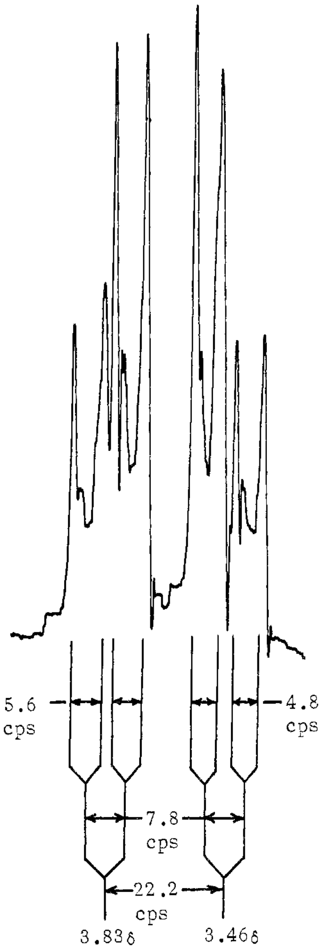
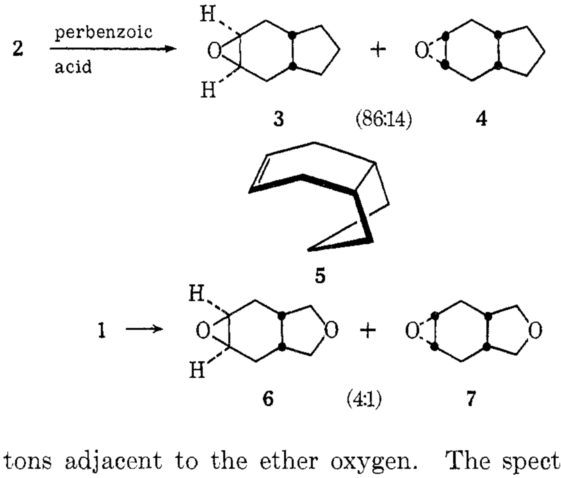
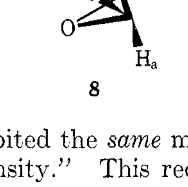


Figure 1.—Partial nmr spectrum of *cis*-8-oxabicyclo[4.3.0]-non-3-ene.

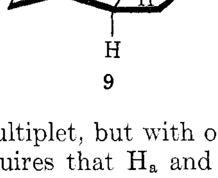
SCHEME I
STERIC COURSE OF EPOXIDATION[5]



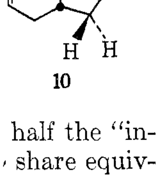
tons adjacent to the ether oxygen. The spectrum of *cis*-8-oxabicyclo[4.3.0]7,7-dideuterionon-3-ene (**10**) exhibited the *same* multiplet, but with only half the "intensity." This requires that H_a and $H_{a'}$ share equivalent magnetic environments, as must H_b and $H_{b'}$. An analysis of the coupling of these protons with each other and with the protons at the ring juncture (Figure 1) suggests that **9** will be the stable conformer.



8



9



10

A very simple ABX pattern for the spectrum of **1** can be analyzed. Protons H_a ($H_{a'}$) and H_b ($H_{b'}$) exist in different magnetic environments, leading to different chemical shifts of δ 3.46 and 3.83, respectively. H_a couples with H_b to give a coupling constant of $J = 7.8$ cps. The only other coupling available now can be between the proton at the ring juncture. At this point we face interpretative problems because coupling constant–dihedral angle relationships have not been well studied for heterocyclic systems. However, we will assign the larger coupling constant to the trans coupling of H_b with the ring juncture proton. Additional chemical evidence supports the necessary conformation, **9**, resulting from this assignment. If **8** were the ground-state conformer, proton H_b would be expected to be upfield from H_a because it would be influenced by the shielding cone of the alkene system. Another argument for **9** being the ground-state conformer might be suggested from the simple suggestion that in **8** there would be extensive repulsion of the π electrons with the nonbonding electrons of oxygen. The effects of interacting dipoles of oxygen heteroatoms has been well documented in the field of carbohydrate chemistry.[7]

Although the use of molecular models does not always solve conformational problems, their use can be instructive in the sense that certain conformations are readily noted to be improbable. Space-filling models are particularly useful in this study and it can be readily suggested that only two conformations, **8** and **9**, are reasonable, both maintaining a boat conformation of the cyclohexene moiety. As we have already noted, nmr evidence is consistent with, but does not prove, the assumption that **9** is the ground-state conformer. We next sought chemical evidence to substantiate our assignment.

Buttressing our argument for **9** being the ground-state conformer are the results from our studies related to the steric course of hydroboration. Because the transition state for hydroboration has a structure similar to that of the reactants, it has been suggested that the stereochemistry of the reaction products can be correlated with the ground state of the reactants.[8] Brown[8c] has convincingly argued that the observed high reactivity for diborane addition is most consistent with a low activation energy, and with thujopsene has suggested that the energy of interconversion of conformations would be greater than the energy of activation for diborane addition. Although we do not have the necessary thermodynamic data, we suggest that, in our fused ring system, conformational interconversions might be also expected to be higher than the activation energy for diborane addition. With this reasonable assumption we can consider transition states **11** and **12**, resembling **9** and **8**, respectively. The ex-

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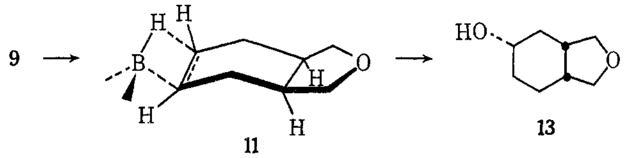
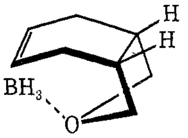
[7] See, for example, R. V. Lemieux in "Molecular Rearrangements," Vol. 2, P. de Mayo, Ed., Interscience, New York, N. Y., 1964, Chapter 12.

[8] (a) F. Frinquelli and A. Taticchi, *J. Chem. Soc. C*, 2011 (1971); (b) J. Klein and D. Lichtenbert, *J. Org. Chem.*, **35**, 2654 (1970); (c) S. P. Acharya and H. C. Brown, *ibid.*, **35**, 3874 (1970).

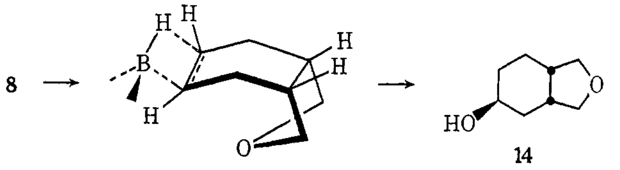
pected major product resulting from **11** would be **13**[9] and from **12** would be **14**.[10] We find **13** to make up 72% of the reaction product after addition of diborane. The apparent insensitivity of **1** to steric demands of the reactants is most consistent with **9** being the ground-state conformer.[11]



11 **13**



15



12 **14**

Diborane is known to complex with tetrahydrofuran.[12] That our results from diborane addition are not merely a reflection of simple coordination with the ether oxygen of **1**, followed by a rapid transfer to the π system, can best be seen by examining space-filling models. Steric crowding around the π system of **8** is so great that it precludes the possibility of addition, as might be suggested by **15**. If complexing were to occur, it would most certainly have to take place on the other face of the tetrahydrofuran moiety. This brings us to another argument against an intermediate such as **15**. Since the reaction is carried out in an ether, a consideration of the high reactivity of diborane with alkene bonds coupled with the necessary and unfavorable competition of solvent and the oxygen of **1** would suggest that preferential complexing, as in **15**, is not reasonable.

The results of this work, coupled with our previous investigations relating to the directive[3a] and electronic effects of the oxygen heteroatom,[3b] clearly demonstrate that there can be serious consequences resulting from the use of heterocyclic molecules as models for the carbocyclic analogs.

Experimental Section

The nmr spectra were recorded on a Varian A-60 instrument, using deuteriochloroform as solvent and tetramethylsilane as standard.

Epoxidation of *cis*-8-Oxabicyclo[4.3.0]non-3-ene (1).—To 5 ml of chloroform containing 5 mmol of perbenzoic acid[13] was added 0.5 g of **1**. The reaction mixture was maintained at 0° for 3 days, after which it was washed with a solution of 10% bicarbonate. The chloroform solution was dried and reduced in volume to yield 0.56 g of crude product. Distillation yielded 240 mg of a water-clear liquid, bp 94–98° (9 mm). The epoxide mixture was immediately reduced with 20 mg of lithium aluminum hydride in 10 ml of dry tetrahydrofuran. The known alcohols[3b] resulting from this procedure were analyzed by analytical glc.

Synthesis of *cis*-8-Oxabicyclo[4.3.0]7,7-dideuterionon-3-ene (10).—Following the method of Bailey,[14] 7.7 g of *cis*-1,2,3,6-tetrahydrophthalic anhydride in 40 ml of anhydrous tetrahydrofuran were slowly added to a cooled solution prepared from 2.0 g of sodium borohydride in 10 ml of tetrahydrofuran. After 1 hr, 20 ml of 6 *M* hydrochloric acid was cautiously added to the reaction mixture. After the addition had been completed, the reaction mixture was extracted with dichloromethane. The combined extracts were dried, filtered, and distilled, yielding 1.7 g of product, bp 129–132° (10 mm). This lactone was taken directly onto the next step, where 0.5 g of lithium aluminum deuteride and 30 ml of anhydrous tetrahydrofuran reduced it to the 1,4-diol (0.75 g). Cyclization by the method of Eliel[2a] was affected with 1 g of *p*-toluenesulfonyl chloride in 10 ml of pyridine. The product, identical by glc with **1**, exhibited an nmr spectrum identical with that of **1**, except that the portions of the spectrum assigned to the protons at C-7 and C-9 exhibited only half the intensity.

Hydroboration of *cis*-8-Oxabicyclo[4.3.0]non-3-ene (1).—To a reaction mixture prepared from 1.5 g of sodium borohydride and 3.6 g of **1** in 17 ml of anhydrous diglyme was slowly added 3 ml of a freshly distilled sample of boron trifluoride etherate. The reaction mixture was maintained at 20° and under a nitrogen atmosphere during the addition. After stirring for 30 min, 3.5 ml of 2 *N* sodium hydroxide was slowly added. This was followed by the slow addition of 3.5 ml of 30% hydrogen peroxide. After stirring for an additional 1 hr the reaction mixture was extracted with ether, and the resulting crude alcohol mixture was compared with the known products[3b] by analytical glc.

Registry No.—**1,** 3471-41-8; **10,** 34959-69-8.

Acknowledgments.—We acknowledge the support of the Endowment and Research Foundation of Montana State University and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Helpful discussions with Dr. Arnold Craig have also been appreciated.

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[9] Attack of the other side of the π system would be less favorable due to interference of the protons at the ring juncture. Being in a boat, this interaction would be of critical importance, similar to that found in the lack of endo addition to nonbornene.

[10] Space-filling models clearly indicate that in conformation **12** there is no possibility of attack from the other side of the π system.

[11] We find an almost identical product ratio after the addition of disiamylborane.

[12] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 42.

[13] G. Braun, "Organic Syntheses," Collect. Vol. I., Wiley, New York, N. Y., 1941, p 431.

[14] D. M. Bailey and R. E. Johnson, *J. Org. Chem.*, **35**, 3574 (1970).