



Effects of heteroatoms in heterocyclic molecules
by Kao-rong Sun

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemistry
Montana State University
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Abstract:

By utilizing data obtained from chemical and spectroscopic studies, the ground state conformation of an oxygen-containing heterocyclic compound, cis-8-oxabicyclo [4.3. 0]non-3-ene, has been established. A long-range electronic participation from the π -system of the double bond to the nonbonded electrons of the oxygen was proposed from the spectroscopic study.

Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0]non-3-ene was prepared, and the conformation of this molecule was proposed by utilizing chemical and spectroscopic data. Furthermore, the spectroscopic study indicated the blockage of the electronic participation between the π -system of the alkene and the nonbonded electrons of the oxygen atom due to the steric factor of the four methyl groups.

A similar spectroscopic study was extended to the nitrogen analogs, the cis-N-substituted-8-azabicyclo [4. 3. 0]non-3-ene systems. The primary data led to the proposal of the nitrogen inversion and the similar electronic participation was obtained.

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Date June 16, 1972

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by

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A thesis submitted to the Graduate Faculty in partial
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in

Chemistry

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iii

To
My Parents, Wife, and Daughter

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TABLE OF CONTENTS

| | <u>Page</u> |
|---|-------------|
| VITA | ii |
| ACKNOWLEDGEMENT | iv |
| LIST OF TABLES | vii |
| LIST OF FIGURES | ix |
| ABSTRACT | xii |
| PART I. The Conformation of Cis-8-oxabicyclo [4.3.0] non-3-ene | |
| I. 1 Introduction | 1 |
| I. 2 Synthesis | 6 |
| I. 3 nmr Spectroscopic Data | 9 |
| I. 4 Hydroboration | 16 |
| I. 5 Cis-8-oxabicyclo [4.3.0] nonan-3-one | 19 |
| PART II. Synthesis and Reactivity of Cis-7,7,9,9-tetra- methyl-8-oxabicyclo [4.3.0]non-3-ene | |
| II. 1 Introduction | 23 |
| II. 2 Molecular Model | 23 |
| II. 3 Synthesis | 24 |
| II. 4 nmr Spectroscopic Data | 26 |
| II. 5 Oxymercuration | 27 |
| II. 6 nmr Study for the Electronic Participation | 30 |
| PART III. Cis-N-substituted-8-azabicyclo [4.3.0] non-3-ene Systems | |
| III. 1 Introduction | 36 |
| III. 2 Synthesis | 37 |
| III. 3 nmr study for the Electronic Participation | 38 |

TABLE OF CONTENTS (CONTINUED)

| | | |
|---------------------|---|----|
| III. 4 | Relation to the Corresponding Oxygen Systems | 50 |
| EXPERIMENTAL | | |
| | General Information | 51 |
| | Part I | 51 |
| | Part II | 59 |
| | Part III | 64 |
| APPENDIX | | |
| I. | The Analysis of Gas Liquid Chromatography | 67 |
| II. | The Commonly Used Gas Liquid Chromatography Columns | 68 |
| III. | The Commonly Used Names of Some of the Heterocyclic Compounds | 69 |
| IV. | The nmr Spectra of Some of the Heterocyclic Compounds | 70 |
| | REFERENCES | 89 |

LIST OF TABLES

| <u>Table</u> | | <u>Page</u> |
|--------------|--|-------------|
| 1. | Competition Results of Oxymercuration Reaction | 2 |
| 2. | Tentative Coupling Constants From Conformations of Cis-8-oxabicyclo [4.3.0]non-3-ene | 15 |
| 3. | Results From Reduction of Cis-8-oxabicyclo [4.3.0]nonan-3-one | 19 |
| 4. | Report of Elemental Analysis of 3,5-dinitrobenzoate Derivative of Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0]nonan-3-ol | 30 |
| 5. | The Observed Chemical Shifts of Protons in Cis-8-oxabicyclo [4.3.0]non-3-ene From nmr Studies | 32 |
| 6. | The Observed Chemical Shifts of Hydrogens in Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0]non-3-ene From nmr Studies | 32 |
| 7. | The Observed Chemical Shifts of Hydrogens in Cis-8-oxabicyclo [4.3.0]nonane From nmr Studies | 34 |
| 8. | The Observed Chemical Shifts of Hydrogens in Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0]non-3-ene at Different Concentrations in Acidic Solvent | 35 |
| 9. | The Observed Chemical Shifts of Hydrogens in Cis-8-phenyl-8-azabicyclo [4.3.0]non-3-ene From nmr Studies | 39 |
| 10. | The Observed Chemical Shifts of Hydrogens in Cis-8-phenyl-8-azabicyclo [4.3.0]nonane From nmr Studies | 40 |
| 11. | The Comparison of Observed Chemical Shifts of Hydrogens in Cis-8-phenyl-8-azabicyclo [4.3.0]non-3-ene and its Quaternary Methiodide Salt | 41 |
| 12. | The Comparison of Observed Chemical Shifts of Hydrogens in Cis-8-phenyl-8-azabicyclo [4.3.0]nonane and its Quaternary Methiodide Salt | 41 |

LIST OF TABLES (CONTINUED)

| | | |
|-----|---|----|
| 13. | The Observed Chemical Shifts of Hydrogen in Cis-8-propyl-8-azabicyclo [4.3.0]non-3-ene From nmr Studies | 42 |
| 14. | The Comparison of Observed Chemical Shifts of Hydrogens in Cis-8-propyl-8-azabicyclo [4.3.0] non-3-ene and its Quaternary Methiodide Salt | 43 |
| 15. | The Observed Chemical Shifts of Hydrogens in Cis-7,7,9,9-tetradeutero-8-propyl-8-azabicyclo [4.3.0] non-3-ene From nmr Studies | 47 |
| 16. | The Comparison of Observed Chemical Shifts of Hydrogens in Cis-7,7,9,9-tetradeutero-8-propyl-8-azabicyclo [4.3.0]non-3-ene and its Quaternary Methiodide Salt | 48 |
| 17. | The Observed Chemical Shifts of Hydrogens in Cis-8-phenyl-8-azabicyclo [4.3.0] non-3-ene in Solvents of Different Acidities | 49 |
| 18. | The Relative Retention Time of Compounds From Cis-8-oxabicyclo [4.3.0]non-3-ene System From Analytical Gas Chromatography | 56 |
| 19. | The Observed Yield of Reactions From Cis-8-oxabicyclo [4.3.0]non-3-ene System When Analyzed by Gas Chromatography | 56 |
| 20. | The Relative Retention Time of Compounds From Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0] non-3-ene System From Analytical Gas Chromatography | 63 |

LIST OF FIGURES

| <u>Figure</u> | | <u>Page</u> |
|---------------|---|-------------|
| 1. | The Cis-8-hetero-bicyclo [4.3.0] non-3-ene Systems | 1 |
| 2. | The Long-range Oxygen Participation | 3 |
| 3. | The Products From Oxymercuration-demercuration Reaction of Cis-8-oxabicyclo [4.3.0] non-3-ene | 3 |
| 4. | Suggested Possible Conformations of Cis-8-oxabicyclo [4.3.0] non-3-ene | 4 |
| 5. | Suggested Possible Conformations of Cis-bicyclo [4.3.0] non-3-ene and Cis-bicyclo [4.2.0] oct-3-ene | 4 |
| 6. | Preparation of Cis-8-oxabicyclo [4.3.0] non-3-ene | 6 |
| 7. | The Main- and By-product of Lithium Aluminum Hydride Reduction of Cis-1,2,3,6-tetrahydrophthalic Anhydride | 6 |
| 8. | Mechanism of Cyclization to the Bicyclic System | 7 |
| 9. | Preparation of Cis-7,7-dideutero-8-oxabicyclo [4.3.0] non-3-ene | 7 |
| 10. | The Protons Adjacent to the Ether Oxygen in Cis-8-oxabicyclo [4.3.0] non-3-ene and Cis-7,7-dideutero-8-oxabicyclo [4.3.0] non-3-ene | 9 |
| 11. | Possible Conformations of Cis-8-oxabicyclo [4.3.0] non-3-ene | 10 |
| 12. | The Observed Dihedral Angles in Models of Conformation <u>2-I</u> | 11 |
| 13. | Partial nmr Spectrum of Hydrogens Adjacent to the Ether Oxygen of Cis-8-oxabicyclo [4.3.0] non-3-ene | 12 |
| 14. | The Angular Dependence of the Geminal and Vicinal Proton-proton Coupling Constants | 13 |
| 15. | The Observed Dihedral Angles in Conformation <u>2-II</u> and <u>2-III</u> , From Space-filling Molecular Models | 14 |
| 16. | Possible Conformations of Thujopsene | 16 |

LIST OF FIGURES (CONTINUED)

| | | |
|-----|---|----|
| 17. | The Transition States of Hydroboration of Cis-8-oxabicyclo [4.3.0] non-3-ene | 17 |
| 18. | The Products From Hydroboration of Cis-8-oxabicyclo [4.3.0] non-3-ene | 18 |
| 19. | Steric Approach Control <u>vs.</u> Product Development Control | 20 |
| 20. | Torsional Strain <u>vs.</u> Steric Strain | 21 |
| 21. | Possible Conformations of <u>23</u> , and the Possible Approach of the Metal Hydrides to the Carbonyl Function | 22 |
| 22. | Possible Conformations of Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0] non-3-ene | 23 |
| 23. | Preparation of Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0] non-3-ene | 24 |
| 24. | The Grignard Reaction of Dimethyl-cis-4-cyclohexene-1,2-dicarboxylate | 25 |
| 25. | Cis- and Trans-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0] non-3-ene | 26 |
| 26. | Possible Product or Product Mixture From Hydration of Conformation <u>3-II</u> and <u>3-III</u> | 28 |
| 27. | The Observation of the Product Mixture From the Oxymercuration of Cis-7,7,9,9-tetramethyl-8-oxabicyclo [4.3.0] non-3-ene by an Analytical Gas Chromatography | 29 |
| 28. | The Long-range Electronic Participation Between the π -system of the Double Bond and the Nonbonded Electrons of the Oxygen Atom in Cis-8-oxabicyclo [4.3.0] non-3-ene | 31 |
| 29. | Cis-8-oxabicyclo [4.3.0] nonane | 33 |
| 30. | The Cis-N-substituted-8-azabicyclo [4.3.0] non-3-ene Systems | 36 |
| 31. | Preparation of Cis-N-substituted-8-azabicyclo [4.3.0] non-3-ene Systems | 37 |

LIST OF FIGURES (CONTINUED)

| | | |
|-----|---|----|
| 32. | Preparation of the Quaternary Methiodide Salt of the Cis-N-substituted-8-azabicyclo [4.3.0] non-3-ene Systems | 37 |
| 33. | Cis-8-phenyl-8-azabicyclo [4.3.0] nonane and its Quaternary Methiodide Salt | 38 |
| 34. | Possible Conformations of Nitrogen Inversion of Cis-8-propyl-8-azabicyclo [4.3.0] non-3-ene | 44 |
| 35. | The Quinolizidine Ring System | 44 |
| 36. | The Aziridine System | 45 |
| 37. | The N-substituted-2,2-dimethyl Aziridine Systems | 45 |
| 38. | The Cis-7-chloro-7-azabicyclo [4.3.0] heptane System | 46 |
| 39. | Stereospecific Synthesis of Cis-8-oxabicyclo [4.3.0] nonan-3-ol-endo | 54 |
| 40. | The Observation of Compounds in Table 18 From an Analytical Gas Chromatography | 56 |
| 41. | The Observation of the Product Mixture From Dehydration of Cis- $\alpha, \alpha', \alpha', \alpha'$ -tetramethyl-4-cyclohexene-1,2-dimethanol From an Analytical Gas Chromatography | 60 |
| 42. | The Observation of Compounds in Table 20 From an Analytical Gas Chromatography | 63 |

ABSTRACT

By utilizing data obtained from chemical and spectroscopic studies, the ground state conformation of an oxygen-containing heterocyclic compound, *cis*-8-oxabicyclo [4.3.0]non-3-ene, has been established. A long-range electronic participation from the π -system of the double bond to the nonbonded electrons of the oxygen was proposed from the spectroscopic study.

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A similar spectroscopic study was extended to the nitrogen analogs, the *cis*-N-substituted-8-azabicyclo [4.3.0]non-3-ene systems. The primary data led to the proposal of the nitrogen inversion and the similar electronic participation was obtained.

PART I

THE CONFORMATION OF CIS-8-OXABICYCLO[4.3.0]NON-3-ENE

INTRODUCTION

Compounds containing a ring made up of more than one kind of atom are called heterocyclic compounds, and are often found in drugs, natural products, and many biologically important molecules. The role of the heteroatoms in the molecule is important, and is different from that of a carbon atom. Yet, the influence of the heteroatom to the conformation, stereochemistry, and reactivity of the whole molecule is still unknown in many heterocyclic systems.

In this laboratory, some simple heterocyclic systems, as shown in figure 1, have been studied. The main interest of the investigation concerns the influence between the heteroatoms and the alkene bond.

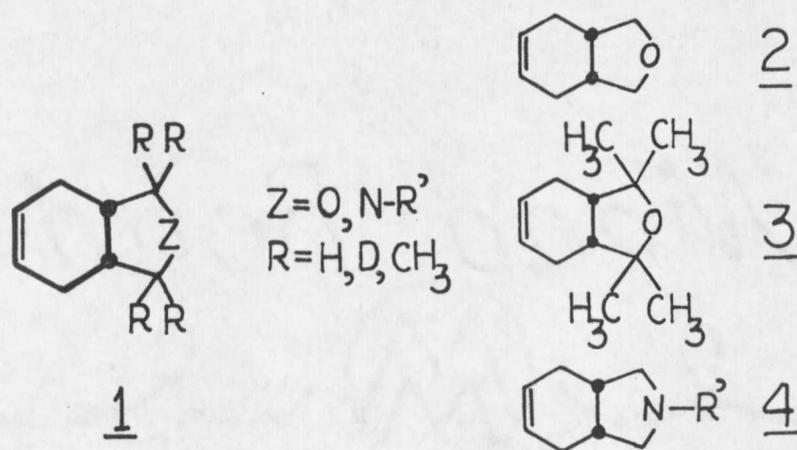


Figure 1: The Structure of Cis-8-hetero-bicyclo[4.3.0]non-3-ene Systems.

Cis-8-oxa-bicyclo[4.3.0]non-3-ene, (2), has been used as a model for the corresponding carbocyclic compound¹. It has been assumed that this oxygen-containing heterocycle will exhibit steric and conformational characteristics similar to the corresponding carbocycle, especially in reactions on the cyclo-

