



Ethereal oxygen effects on structure and reactivity  
by David Kent Johnson

A thesis submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy in Chemistry  
Montana State University  
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Abstract:

The role the oxygen atom plays in influencing the stereochemistry of electrophilic additions to cis-8-oxabicyclo[4.3.0]non-3-ene, [1] and 8-oxatricyclo[4.3.3.0]undec-3-ene, [7], was examined. A complete absence of stereoselectivity was observed in [7]. This was consistent with calculations completed on the olefin that suggest: (1) there are two boat conformers existing for the alkene in approximate equilibrium abundances, (2) the conformers have HOMOs of equal energy and as a result should have equal reactivity, and (3) there is no contribution by the oxygen atom in the HOMOs of either conformer which could possibly have directed the addition. The modest stereoselectivity observed in [1] was attributed to simple steric effects.

The role of the oxygen atom in imparting reactivity during solvolysis on the syn- and anti-tosylates derived from [1] and [7] was examined. Identical reactivities and products were observed in the solvolysis of the syn and anti-tosylates of [1]. This was interpreted to mean oxygen does not influence reactivity in these compounds. A slight rate enhancement (1.53) was observed for the anti tosylate of [7] relative to the syn-isomer. A stabilized hydrogen bonded intimate ion pair (IIP) was used to rationalize this increased reactivity.

The role of the oxygen atom to influence the stereochemistry of catalytic hydrogenation in 3-methyl-8-oxabicyclo[4.3.3.0]undec-3-ene, [35], was studied and modest stereoselectivity was observed (3:1). This is suggestive of an oxygen/catalysts interaction (haptophilicity).

The olefins resulting from the palladium induced bond isomerization of [1] were characterized and examined by the MM2 and MNDO methods. These olefins were found to exhibit increasing thermodynamic stability as measured by heats of formation and hyperstability. This stability was used to rationalize the bond isomerization on the basis of the Polanyi mechanism. A correlation between hyperstability and HOMO n bond order was observed in this system.

The major ions in the EI mass spectrum of [1] were determined from an examination of the mass spectra of a series of deuterium labelled analogues of [1] which were prepared. Fragmentation mechanisms were proposed for the formation of these ions.

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A thesis submitted in partial fulfillment  
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of

Doctor of Philosophy

in

Chemistry

MONTANA STATE UNIVERSITY  
Bozeman, Montana

May 1988

D378  
J6307

APPROVAL

of a thesis submitted by

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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To my mom and dad for their constant love and support.

"The real cycle you're working on  
is a cycle called 'yourself'."

"The study of the art of motorcycle maintenance [or chemistry] is really a miniature study of the art of rationality itself. Working on a motorcycle [or in chemistry], working well, caring, is to become part of a process, to achieve an inner peace of mind. The motorcycle [The chemistry] is primarily a mental phenomenon."

- Robert M. Pirsig

Zen and the Art of Motorcycle Maintenance

### ACKNOWLEDGEMENTS

This endeavor could not have been completed without the help of a number of people. Special thanks are extended to Joe Sears, Dave Theiste, and Tim Schram for their unselfish assistance, respectively, on the mass spectrometer, the computer, and the NMR; to Ray Larson and Dr. Fitzgerald for their assistance with x-ray crystallography; and to Montana Interface and especially Dr. Howald for their assistance with our kinetic experiments. Special thanks is also extended to Dr. Craig for his helpful discussions on physical-organic chemistry and for the interest and enthusiasm he has shown in my career; and to Dr. Mundy for his integrity, his support of students, and for his deep devotion and love of chemistry that he has openly exhibited during my graduate years. Lastly my deepest appreciation is extended to my dear wife, Andrea, for her assistance with word processing and her everpresent love and companionship.

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## ABSTRACT

The role the oxygen atom plays in influencing the stereochemistry of electrophilic additions to cis-8-oxabicyclo[4.3.0]non-3-ene, [1] and 8-oxatricyclo[4.3.3.0]undec-3-ene, [7], was examined. A complete absence of stereoselectivity was observed in [7]. This was consistent with calculations completed on the olefin that suggest: (1) there are two boat conformers existing for the alkene in approximate equilibrium abundances, (2) the conformers have HOMOs of equal energy and as a result should have equal reactivity, and (3) there is no contribution by the oxygen atom in the HOMOs of either conformer which could possibly have directed the addition. The modest stereoselectivity observed in [1] was attributed to simple steric effects.

The role of the oxygen atom in imparting reactivity during solvolysis on the syn- and anti-tosylates derived from [1] and [7] was examined. Identical reactivities and products were observed in the solvolysis of the syn and anti-tosylates of [1]. This was interpreted to mean oxygen does not influence reactivity in these compounds. A slight rate enhancement (1.53) was observed for the anti tosylate of [7] relative to the syn-isomer. A stabilized hydrogen bonded intimate ion pair (IIP) was used to rationalize this increased reactivity.

The role of the oxygen atom to influence the stereochemistry of catalytic hydrogenation in 3-methyl-8-oxabicyclo[4.3.3.0]undec-3-ene, [35], was studied and modest stereoselectivity was observed (3 : 1). This is suggestive of an oxygen/catalysts interaction (haptophilicity).

The olefins resulting from the palladium induced bond isomerization of [1] were characterized and examined by the MM2 and MNDO methods. These olefins were found to exhibit increasing thermodynamic stability as measured by heats of formation and hyperstability. This stability was used to rationalize the bond isomerization on the basis of the Polanyi mechanism. A correlation between hyperstability and HOMO  $\pi$  bond order was observed in this system.

The major ions in the EI mass spectrum of [1] were determined from an examination of the mass spectra of a series of deuterium labelled analogues of [1] which were prepared. Fragmentation mechanisms were proposed for the formation of these ions.

## CHAPTER 1

## INTRODUCTION

Neighboring Group Participation by Oxygen


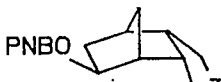
Oxygen containing heterocycles are ubiquitous to organic chemistry and, therefore, the effects that an oxygen atom imparts on reactivity and structure of the molecule are of great importance to the organic chemist. Classically, this reactivity has been widely studied through the use of absolute and relative kinetics, providing insights into reaction mechanisms and elucidating oxygen's role in the chemical transformation.<sup>1,2,3,4,5</sup> Surprisingly, these studies have often shown conflicting influences imparted by oxygen! In some cases the oxygen atom has been shown to enhance reaction rates; while in other compounds, oxygen has been shown to retard reaction rates. Interpreting oxygen's effect in imparting reactivity on the molecule has also been difficult because oxygen does not easily share its lone pair electrons in the stabilization of positive charges, a consequence of its high electronegativity. As a result, the various effects oxygen imparts on structure and reactivity are not completely understood.

In solvolytic reactions oxygen has been shown to stabilize positive charges with its lone pair electrons through neighboring group participation<sup>5</sup> (NGP). This stabilization typically results in an enhanced rate (anchimeric assistance). Oxygen's influence, however, has been shown to be more subtle than that of nitrogen or sulfur, due to their lower



electronegativities and more diffuse lone pair orbital. This makes nitrogen and sulfur better able to stabilize positive charges.<sup>6,7,8</sup> Gratz and Wilder<sup>9</sup> have compared such heteroatom influences for oxygen and sulfur (Table 1). Note the large 752 rate enhancement of the exo-tricyclic sulfide relative to the carbon analog compared to the subtle 2.53 rate enhancement of the exo-tricyclic ether relative to the carbon analog. The authors have attributed the large rate enhancements to lone pair NGP by the heteroatom, and a stabilized intermediate with delocalized positive charge is proposed (Figure 1). Albeit subtle, oxygen's effect can be considered significant as Schleyer<sup>10</sup> suggests, "the detection of any rate enhancement due to anchimeric assistance, no matter how small, is indicative of strong (not weak!) participation by the neighboring group".

Table 1. Solvolytic rate influences by oxygen and sulfur.

	<u>Z</u>	<u>Relative Rate</u>
	S	0.80
	CH <sub>2</sub>	0.70
	S	752
	O	2.53
	CH <sub>2</sub>	1.00

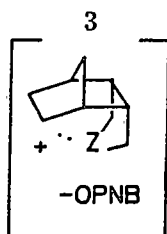


Figure 1. Heteroatom stabilization in a norbornyl system.

Closson et al.<sup>11</sup> also has found anchimeric assistance by the tetrahydrofuranlyl group. This rate enhancement was shown to be greater than that for the methoxyl group, which in turn was far greater than the corresponding straight chain alkane (Table 2). Unlike the conformationally rigid norbornyl systems of Wilder, in these systems great conformational flexibility exists. As a result, oxygen is better able to stabilize positive charge through NGP (Figure 2).

Table 2. Relative rates of solvolysis of p-bromobenzenesulfonates in acetic acid at 50 C.

<u>Compound</u>	<u>Relative Rate</u>
Me-(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> -OBs	1.00
MeO-(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> -OBs	657
n = 1	13.1
n = 2	26.3
n = 3	1510
n = 4	12400
n = 5	1380

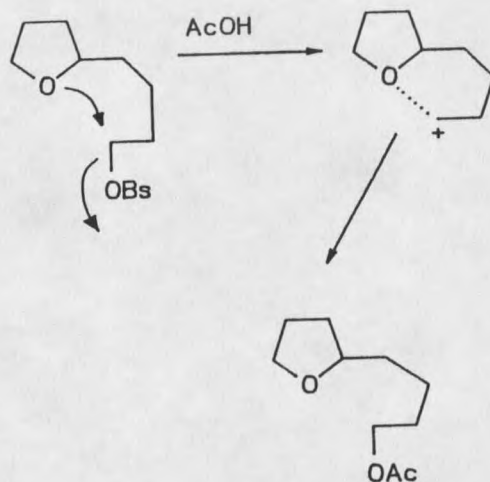


Figure 2. Oxygen intermediate stabilization.

Paquette et al<sup>12</sup> observed a 24 fold rate enhancement in the rate of solvolysis of endo-9-oxabicyclo[4.2.1]-2-yl-p-bromobenzenesulfonates compared to its exo-isomer. The endo-isomer was found to produce the oxonium ion upon acetolysis, while the exo-isomer reacted by the carbocation intermediate which rearranges to the oxonium ion (Figure 3).

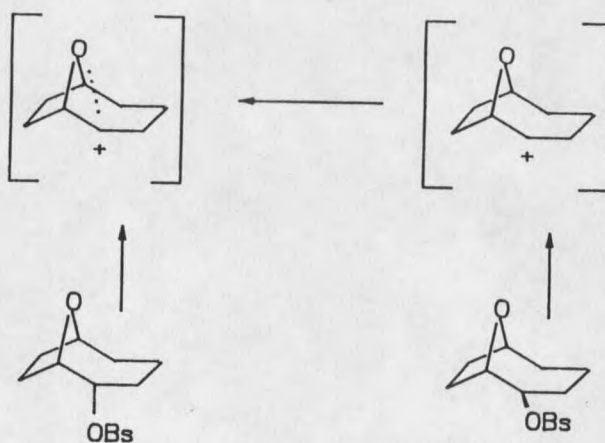


Figure 3. Oxygen participation in endo-9-oxabicyclo[4.2.1]-2-yl-p-bromobenzenesulfonate.

Sunko<sup>13</sup> recently has illustrated oxygen participation in 2-(ethoxybenzyl)-3-methyl-2-cyclohexyl-p-nitrobenzoate. Although he observed a subtle 1.14 rate increase over the corresponding carbon analog, a significantly reduced (1.164) secondary  $\alpha$ -deuterium isotope effect was observed, a strong indication of oxygen participation in the ionization of the ester (Figure 4).

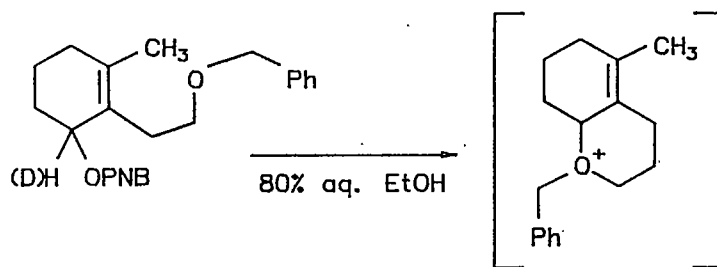

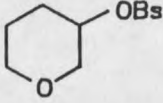
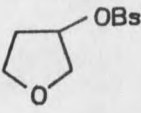
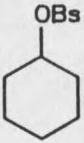
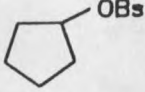


Figure 4. Oxygen participation in 2-ethoxybenzyl-3-cyclohexyl-p-nitrobenzoate.

Conversely, Tarbell and Hazen<sup>14</sup> observed a rate retarding effect by oxygen. They investigated the role oxygen played in the solvolysis of simple oxygen heterocycles (Table 3) and found the rates of solvolysis were an order of magnitude slower than would be expected from an inductive effect by oxygen. This information led them to believe that they were dealing with a transannular dipole effect (Figure 5). The dipole associated with ether oxygen was destabilizing the incipient carbonium ion in the solvolysis, thus retarding the rate.

Table 3. Acetolysis of arenesulfonates.

				
1.4	2.47	0.55	13.6	--
rate x 10 <sup>5</sup> sec. <sup>-1</sup>				

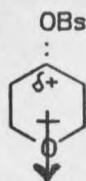
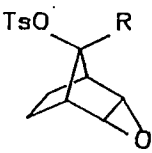
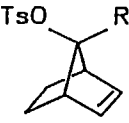
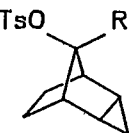
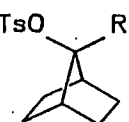


Figure 5. Transannular dipole effect.

Using the method of "increasing electron demand", Gassman<sup>15</sup> examined through bond NGP of the carbon-carbon bond of an epoxide, cyclopropyl group, and a  $\pi$ -system (Table 4). By examining the  $\alpha$ -methyl/hydrogen ratio, the changing electronic effects could be isolated from the changing steric effects of the molecule. This method is based on the assumption that if the electron demand of the incipient carbonium ion in the transition state is satisfied by the electron density donated by a substituent on the carbon atom, then a remote function group will not participate in the reaction. The relative ability of a functional group to be involved in NGP was determined by comparing the rate when the electron demand was satisfied by substituents (tertiary carbocations) to the ratio when electron demand was satisfied by a remote functional group (secondary carbocations).



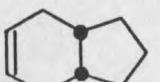
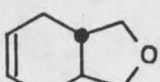

Table 4. Oxygen's inductive effect on carbon-carbon bond participation.

<u>Compound</u>	<u>Relative Ratio (Me/H)</u>
	$10^8$
	$10^{11}$
	$10^{14}$
	1

Great anchimeric assistance was observed for all functional groups. Note, however, the significantly reduced rate enhancement of the epoxide relative to its cyclopropyl group analog. This is attributed to oxygen's inductive effect on carbon-carbon bond participation.

The Mundy group also maintains an aggressive program directed toward the study of the role oxygen plays in imparting structure and reactivity on the molecule. Otzenberger<sup>16</sup> (1971) initiated this investigation by completing a competitive oxymercuration study. A part of this study is represented in Table 5.

Table 5. Oxymercuration competition results.

<u>Compound</u>	<u>Relative Rate <math>\pm</math> 10%</u>
	1.00
 1	0.81
 2	0.11
 3	0.40
 4	0.15

From this study he concluded that any substitution on the ring retards the rate. More interestingly, Otzenberger noted that cis-8-oxabicyclo[4.3.0]non-3-ene, [1], was nearly eight times as reactive as cis-bicyclo[4.3.0]non-3-ene, [2]. A similar, though smaller, rate enhancement was observed for trans-8-oxabicyclo[4.3.0]non-3-ene, [3]. This data seemed to suggest a rate enhancing effect imparted by oxygen.

In considering the preferred conformation of [1], Otzenberger reasoned that the repulsion between the oxygen non-bonding electrons and the  $\pi$ -electrons of the double bond would favor conformation [1A] as shown in Figure 6. He used an  $^1\text{H}$ NMR argument and the work of Cope<sup>17</sup> and Casadevall<sup>18</sup> (who concluded that [2] and cis-bicyclo[4.2.0]oct-3-ene, respectively, exist in pseudo-boat conformations) to support this conclusion.

























































































































































































































































































