



Heteroatom influences on structure and reactivity  
by John James Theodore

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF  
PHILOSOPHY in Chemistry  
Montana State University  
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**Abstract:**

Influences of heteroatoms on the structure and reactivity of the cis-8-heterobicyclo[4.3.0]non-3-ene series are examined through catalytic hydrogenation, sulfide oxidation reactions, lanthanide induced shift studies, and CNDO/2 calculations. Relative rates of hydrogenation and relative catalyst affinities of a series of bicyclic compounds are presented, accompanied by a discussion of their significance relative to heteroatom and structural effects. An experimental and theoretical analysis is made of the factors influencing the stereochemistry and stability of the sulfoxides formed from the oxidation of cis-8-thiabicyclo[4.3.0]non-3-ene. The utility of lanthanide shift reagents in conformational analysis is examined and a comparison is made between conformations determined by lanthanide induced shift studies and CNDO/2 calculations.

i

to  
my parents

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## ABSTRACT

Influences of heteroatoms on the structure and reactivity of the cis-8-heterobicyclo[4.3.0]non-3-ene series are examined through catalytic hydrogenation, sulfide oxidation reactions, lanthanide induced shift studies, and CNDO/2 calculations. Relative rates of hydrogenation and relative catalyst affinities of a series of bicyclic compounds are presented, accompanied by a discussion of their significance relative to heteroatom and structural effects. An experimental and theoretical analysis is made of the factors influencing the stereochemistry and stability of the sulfoxides formed from the oxidation of cis-8-thiabicyclo[4.3.0]non-3-ene. The utility of lanthanide shift reagents in conformational analysis is examined and a comparison is made between conformations determined by lanthanide induced shift studies and CNDO/2 calculations.

"Flog that man, Mr. Christian!"

"But, Sir, he's dead!"

"Mr. Christian, I said flog that man!"

--Capt. Bligh, Frigate "Bounty" Royal Navy folklore

## INTRODUCTION

Interest in the ways in which heteroatoms influence the reactivity and structure of organic molecules has been, and continues to be, of theoretical and practical concern. Classically, the approach in determining relative and absolute reactivities has involved the investigation of reaction kinetics in an attempt to elucidate reaction mechanisms.<sup>1-3</sup>

In heteroatom containing molecules, the influence of heteroatoms on reactivity has been related to the degree in which heteroatoms can stabilize positive charges, as interpreted through solvolysis reactions.<sup>4,5</sup> Table 1 illustrates the effects of sulfur and oxygen on reactivity. The endo tricyclic sulfide reveals a 752-fold rate enhancement over its carbon analog.<sup>6</sup> Gratz and Wilder have attributed the rate difference to the displacement of the leaving group in the transition state by sulfur's unpaired electrons, resulting in an intermediate with a delocalized positive charge (Figure 1). Whether this, or some other explanation, such as sulfur d orbital participation in stabilizing a classical carbonium is applicable, sulfur has been shown by numerous investigators to exhibit a significant effect on reactivity.<sup>4-21</sup>

In the case of the exo structures, the significance of the relative rate differences could be debated. It is the contention of some investigators that at least an order of magnitude difference in rates

Table 1. Solvolytic rate influences by sulfur and oxygen.

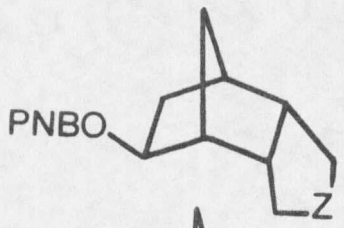
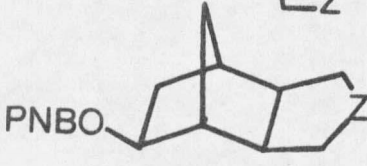
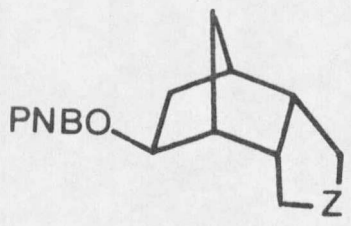
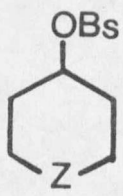

		Rel. Rates	
	Z = S	752	
	CH <sub>2</sub>	1.0	
	S	0.8	
	CH <sub>2</sub>	0.7	
	O	2.53	
	CH <sub>2</sub>	1.00	
	O	0.11	
	CH <sub>2</sub>	1.00	
			

Figure 1. Sulfur stabilization.

is required before the rate differences can be attributed to heteroatom participation. It has been suggested by Schleyer, however, that "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."<sup>22</sup> Since the sulfur in the *exo* structure is positioned relatively distant from the leaving group, appreciable sulfur participation in carbonium ion stabilization would not be expected. Thus the relative rate differences should be small, as confirmed by the experimental results.

Oxygen is a heteroatom which has demonstrated various effects upon reactivity.<sup>23-40</sup> Wilder observed a 2.53-fold rate enhancement of the oxygen containing *endo* tricyclic structure over the carbon analog.<sup>23</sup> The rate difference was interpreted as being due to remote oxygen participation by oxygen's non-bonding electrons. Tarbell, however, has demonstrated an oxygen rate retarding effect in tetrahydropyranyl-4-brosylate relative to cyclohexyl brosylate, attributing the rate difference to a transannular dipolar effect.<sup>24</sup>

Nitrogen, as sulfur, has been shown to exhibit large rate enhancement effects.<sup>41-45</sup> Figure 2 illustrates the magnitude of nitrogen participation when nitrogen is geometrically capable of donating electrons.<sup>41</sup>

Another means by which heteroatom influences have been examined has involved competitive oxymercuration studies.<sup>46,47</sup> The oxymercu-























































































































































































































































































































































































