Ethereal oxygen influences on solvomercuration and hydrogenation reactions
by Steven Ben Glancy

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 the ethereal oxygen on the reactivity of cis-8-oxabicyclo[4.3.0]non-3-ene in solvomercuration and catalytic hydrogenation reactions are examined. The solvomercuration rate enhancement observed for this compound, compared to its carbon analog, is examined using the law of increasing electron demand. The rate decrease observed with the substitution of a vinyl proton with a methyl group is discussed in relation to the present solvomercuration model. The results presented indicate that changes in solvomercuration rate are due to changes in the rate of the solvolysis step and not the stability of the mercurinium ion intermediate.

The influence of the ethereal oxygen on the catalytic hydrogenation of cis-8-oxabicyclo[4.3.0]non-3-ene over 5% Pt on alumina is examined using tetrahydrofuran (THF) as a model. The results presented indicate that the oxygen atom of both compounds inhibits the adsorption of hydrogen.

These results also show that due to the size of cis-8-oxabicyclo[4.3.0]nonane, unlike THF, it inhibits both cyclohexene adsorption as well as hydrogen adsorption.

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APPROVAL

of a thesis submitted by

Steven Ben Glancy

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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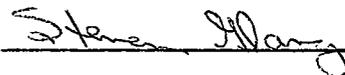
Date ___Nov. 28 1983_____

to

my wife and friend

VITA

Steven Ben Glancy, the only son of Jack and Carleen Glancy, was born on December 15, 1953, in Adrian, Michigan. After living in California until the age of 11, he moved with his family to Jackson, Mississippi. After graduating from Callaway High School in June 1972, he moved to Billings, Montana with his mother and two of his sisters. After receiving a Bachelor of Science degree in chemistry in June 1977 from Eastern Montana College he pursued graduate studies in chemistry at Montana State University. On March 20, 1982 he married Vickie Leigh Nelson.

ACKNOWLEDGEMENT

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ABSTRACT

Influences of the ethereal oxygen on the reactivity of cis-8-oxabicyclo[4.3.0]non-3-ene in solvomercuration and catalytic hydrogenation reactions are examined. The solvomercuration rate enhancement observed for this compound, compared to its carbon analog, is examined using the law of increasing electron demand. The rate decrease observed with the substitution of a vinyl proton with a methyl group is discussed in relation to the present solvomercuration model. The results presented indicate that changes in solvomercuration rate are due to changes in the rate of the solvolysis step and not the stability of the mercurinium ion intermediate.

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INTRODUCTION

Heteroatom Effects in Directing Organic Reactions

Our lab has been, and continues to be, interested in the effects of heteroatoms on the structure and reactivity of molecules. It has been shown that heteroatoms can influence the reactivity of molecules in ionic reactions through inductive and dipolar effects and by participation, when stereochemistry allows. In reactions where the lone pair electrons can interact with the active reagent, heteroatoms can compete with a double bond for the reagent, as in the case of catalytic hydrogenation. Determining the type of interaction a heteroatom is exerting during a reaction is often difficult and of the three heteroatoms, oxygen, nitrogen, and sulfur, of particular interest to our program the effects produced by oxygen appear to be the most subtle.

The most-widely used approach in the elucidation of heteroatom effects has involved the determination of relative and/or absolute reaction kinetics. Investigators have rationalized the effect of a remote oxygen on the solvolysis rate of a molecule in terms of the interaction between the incipient carbonium ion in the transition state and the oxygen induced dipole, and/or oxygen's lone pair

electrons. Oxygen's effect on the rate of solvolysis has been shown to be dependent on its position in the molecule, relative to the carbon on which the positive charge will form, and the stereochemistry of the molecule. These factors have been illustrated by Tarbell and Hazen in the solvolysis of the arenesulfonates of cyclohexane, tetrahydropyran, and tetrahydrofuran.[1] The oxygen-induced dipole was thought to destabilize the incipient carbonium ion in the transition state, resulting in a decrease in the rate of solvolysis beyond the expected decrease for inductive effects alone. The results shown in Table 1 also illustrate that when stereochemistry permits, as in the case of 3-tetrahydropyranyl brosylate, oxygen can participate in the reaction to stabilize the carbonium ion. The proposed participation, shown in figure 1, has been suggested as the reason for the unexpectedly high rate of solvolysis found for this compound.
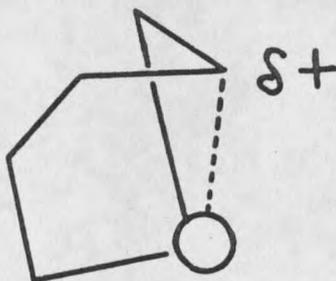
Figure 1.   Oxygen Participation in Carbonium ion Stability.

Table 1
Acetolysis of Arenesulfonates.
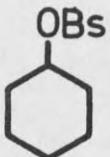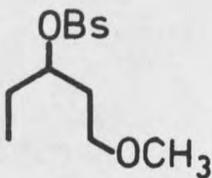
compounds	rate x $10^5 sec^{-1}$
OBs cyclohexyl	45.2
OBs with OCH$_3$	35.1
OBs with H$_3$CO and OCH$_3$	8.20
OBs tetrahydropyran (4-position)	1.40
OBs tetrahydropyran (3-position)	2.47
OBs tetrahydrofuran	0.55

The 24-fold increase in rate of solvolysis of the endo isomer of 9-oxabicyclo[4.2.1]nonan-2-yl compared to the exo isomer was rationalized by Paquette in terms of the oxygen participation shown in Figure 2.[2] The rate increase due to the stabilization of the incipient carbonium ion in the transition state by oxygen participation has been shown to be less than the rate increase due to participation by other heteroatoms. For example, Wilder found the solvolysis rate ratio of t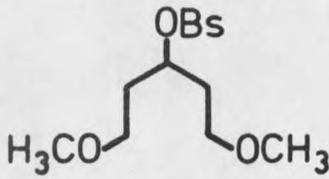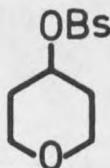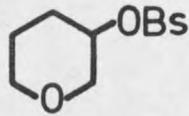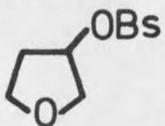he endo/exo isomers of 4-oxatricyclo[5.2.1.0^{2,6}]dec-8-yl brosylates to be 50:1[3] while the ratio for the sulfur analog was 1000:1.[4] Although Wilder felt the rate ratio alone was insufficient evidence for oxygen participation, the rearrangement outlined in Figure 3 gave support to the proposed participation. It was rationalized that the oxygen had stabilized the carbonium ion intermediate long enough for the rearrangement to occur, whereas with the carbon analog the solvolysis of the carbonium ion was too fast for any rearrangements to occur.
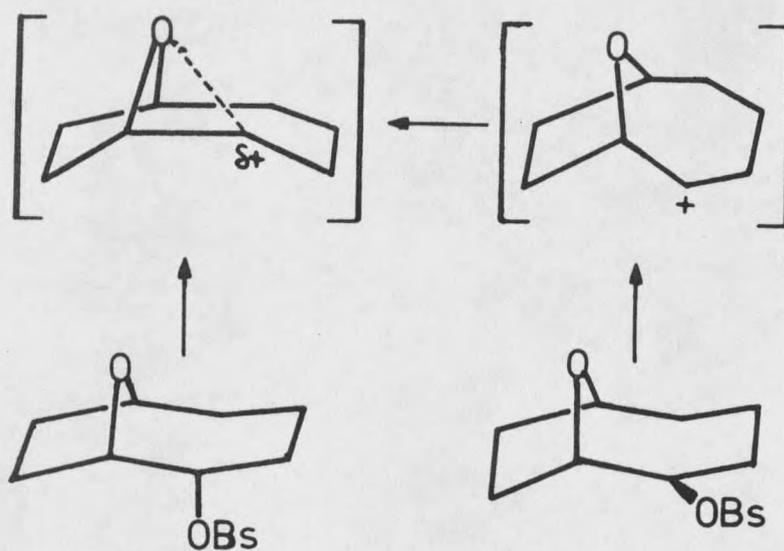
Figure 2. Rationale for the 24-fold increase
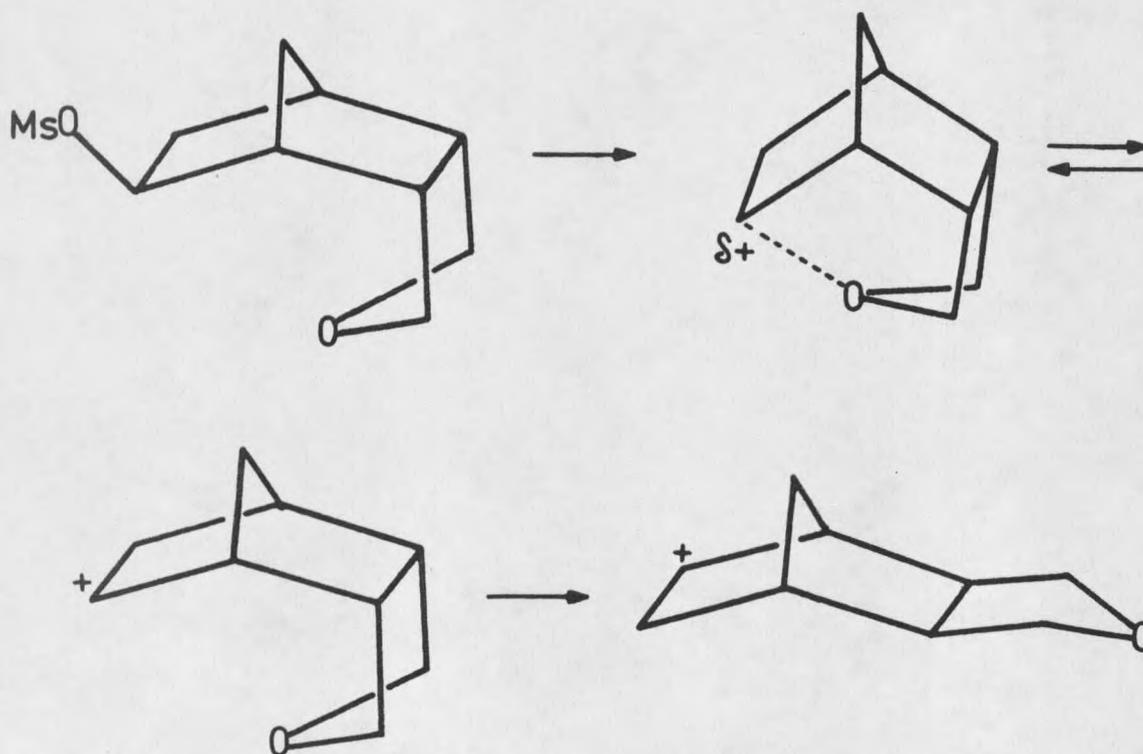in solvolysis rate.

Figure 3. Rearrangement due to oxygen participation.

Some investigators insist that at least an order of
magnitude difference in rates is required before heteroatom
participation can be considered a contributing factor in the
rate increase. Since the heteroatom electronic effects may
not be identical for the stereoisomers used in the test for
heteroatom participation, it would be difficult to isolate
participation from electronic differences for small rate
enhancements. In the investigation of the effects of remote
substituents on the addition of 2,4-dinitrobenzenesulfenyl
chloride to norbornene, Kwart and Miller observed that the
electronic effects of substituents are not the same for the
exo and endo isomers of norbornene, as the results shown in
Table 2 indicate.[5] Likewise, Kwart found the electronic
effects of substituents in the axial position to be
different from those at the equatorial position of mono- and
disubstituted cyclohexenes.

Gassman used the method of "increasing electron demand"
to determine the relative ability of the carbon-carbon bond
of an epoxide, a cyclopropyl group, and a pi-bond to
stabilize the carbonium ion formed during the solvolysis of
the compounds shown in Table 3.[6] 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 substituents on the carbon
atom, then a remote functional group will not participate in

Table 2
Addition of 2,4-Dinitrobenzenesulfenyl chloride to
Norbornenes.
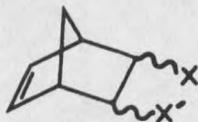
	X		X'		Relative rates
exo		$CH_2CH_2CH_2$		(cis)	139
	H		H		100
exo	CH_3		H		98.3
endo	CH_3		H		66.5
exo	COOH		COOH	(cis)	0.637
endo	COOH		COOH	(cis)	1.50
exo		$-\overset{\text{C}}{\underset{\text{O}}{\|}}-O-\overset{\text{C}}{\underset{\text{O}}{\|}}-$		(cis)	0.0501
endo		$-\overset{\text{C}}{\underset{\text{O}}{\|}}-O-\overset{\text{C}}{\underset{\text{O}}{\|}}-$		(cis)	0.000893

the reaction. The relative ability of a functional group to participate in a reaction was determined by comparing the ratio of the rate when the electron demand was satisfied by substituents on the carbon atom to the ratio when the electron demand was satisfied by a remote functional group participation. Gassman found that the electron demand of a tertiary carbonium ion was low enough that the functional group under investigation did not participate, while a secondary carbonium ion possessed a high enough electron demand to promote participation. By examining the "alpha-methyl/hydrogen" ratio the problem of changing electronic effects with changes in the stereochemistry of the molecule was avoided.

Peterson found that inductive effects from a methoxy group influenced the rate of addition of trifluoroacetic acid to a double bond over a span of eleven methylene carbons.[7] The inductive effects were found to decrease linearly with the number of methylene groups at a rate of 0.64 per methylene carbon. Table 4 shows the relative rates of addition of trifluoroacetic acid found by Peterson for three compounds related to our work. In a related study, investigating the electron withdrawing effects of an ether linkage and acetal groups on the oxidation of alkene with permanganate ion and osmium tetroxide, Henbest[8] observed the results shown in Table 5.

Table 3
Oxygen's inductive effects
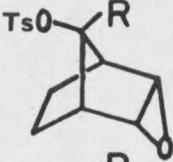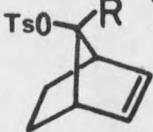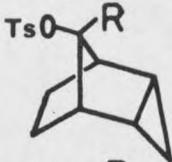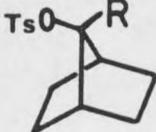on carbon-carbon bond participation.

compound	relative (Me/H) ratio

TsO R

10^8

TsO R

10^{11}

TsO R

10^{14}

TsO R

1

Table 4
Addition of Trifluoroacetic Acid.

compound	relative rate
	1.0
	122
	30
	152