Chemistry 408: Research in Dr. Adcock's Lab

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Chemistry 408

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Project Overview:

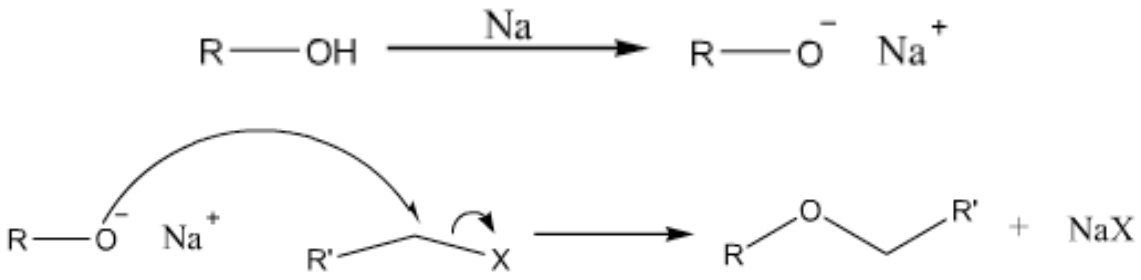
Should be kept away from acid to prevent racemization, exists as 50-50 enantiomers

Drip in

Will be 5-carbon chiral, very volatile & easily moved to the vacuum line
High boiling from 60-70 degrees C
Will retain stereochemistry and be characterized by NMR

Will be chiral

The reaction will proceed via a Williamson Ether Synthesis Reaction Mechanism.



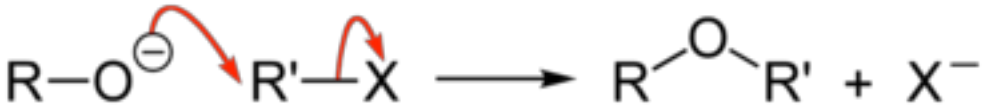
The reaction mechanism first involves the reaction of the alcohol with the sodium metal. This forms the conjugate base of the alcohol (the alkoxide). At this point, hydrogen gas is formed as a byproduct after which the alkoxide is reacted with the alkyl halide. This reacts via a SN2 mechanism.

This reaction converts alcohols into ethers and usually forms hydrogen gas as a byproduct. Alexander Williamson formulated the synthesis in 1850. The reaction helped to prove the structure of ethers and is currently used for lab and industrial synthesis.

The reaction remains the simplest and most popular method for preparing ethers. Since the reaction is incredibly forceful, usually protecting groups are used.

It is conducted at temperatures between 50 to 100 degrees C and usually runs from 1 to 8 hours. Side reactions are common but the complete disappearance of starting materials is rare. Usually, the addition of a catalytic quantity of a soluble iodide salt will speed up the reaction and there can exist a 50-90% yield.[1]

The general reaction mechanism is as follows:



[1] "Williamson Ether Synthesis,"
16 Apr. 2009 <http://www.chemhelper.com/williamsonether.html>.

Reactant & Product Information:

Name:	FW: (g/mol)	MP: (C)	BP: (C)	d: (g/mL)
2-butanol (sec-butyl alcohol)	74.12	-115	98	0.808
Diglyme (2-bis-methoxyethyl ether)	134.18	-68	162	0.937
Triglyme (triethylene glycol dimethyl ether)	178.13	-45	216	0.986
2-methoxybutane	88.15		62.6	0.742
Na (metal)	22.989	97.82	83	0.927
CH3I	141.94	-66.45	42.43	2.2789

Further, Acetone might appear w/a FW of 58.08 g/mol. Sec butyl methyl ether is noted to have a boiling point of 75 degrees C.[2]

Measurements:

The reaction begins with 8.08 g of butanol, 2.53121 g of Na at 1% access, 7.06131 mL CH3I, and about 40 mL of solvent (2-methoxyethylether).

[2] "Sigma-Aldrich." 17 Apr. 2009 http://www.sigmaaldrich.com/chemistry/chemical-synthesis/chemical-synthesis-catalog.html.

Procedure:

Part 1:

The entire procedure was conducted under nitrogen gas. Nitrogen gas kept a dead space to keep atmospheric oxygen or moisture outside of the reaction mixture. A 100 mL round bottom flask was placed in a crystallizing dish on a heater. The RBF was connected to the nitrogen gas. A stir bar was placed inside the RBF and 40 mL of 3-methoxyethylether was added.

10 mL of butanol was accurately poured over the edge. 2.7 g total of small cubic pieces of sodium were prepared. The pieces were added to the reaction, which was stirring, one at a time to gauge actions of the reaction. Oil was poured into the crystallizing dish and the thematic stirrer was left stirring at 350 rpm and 60 degrees C overnight.

Figure 1: Part 1 Apparatus

Part 2:

After allowing the mixture to mix over night, it appeared frothy. It was left at 60 degrees C and 350 rpm. The RBF was moved out of the oil and allowed to cool. The bottom of the RBF was rinsed with PE.

CH3I was taken out of the freezer and allowed to cool to room temperature to remove moisture and prevent the subsequent creation of NaH. A total of 7.06131 mL CH3I was added at a constant slow steady rate.

Figure 2: Part 2 Apparatus

Part 3:

The heat was turned off and the compound was allowed to stir. A fractional distillation was set-up. The RBF was stirring at 150 rpm. There are three compounds to be recovered: the product, recovered diglyme, and the volatiles pulled in the vacuum trap.

Figure 3: Part 3 Apparatus

A second trial was conducted where it should be noted that for the first part, an oil bath was not used. For the second part, an excess amount of CH3I was not utilized. Only 6.78 mL was added.

Direct fluorination was also conducted and the compound was bombarded with F_2 gas to exchange the hydrogen molecules with fluorine.

IR Spectrum of GLC Purified 2-methoxybutane at 30 torr:

Infrared spectroscopy (IR spectroscopy) is a smaller category of spectroscopy that covers the infrared region of the electromagnetic spectrum. It usually spans frequencies between 4000 and 400 cm-1. The most commonly used technique is that of absorption spectroscopy. IR spectroscopy is useful because it allows for compound identification. It also allows one to determine product composition. Radiation in this region is absorbed by inter-atomic bonds in organic compounds.

Tables can be found in the literature that list the usual peaks for certain functional groups and trends. Each chemical bond has its own specific peak based on its frequency. These different environments absorb varying intensities and varying frequencies. One must observe the bond order and the type of atom to determine where the chemical bond will most likely absorb. These are the most important factors. It should be noted that the mass of the attached atoms holds great importance. IR frequency is lowest for those atoms that have the greatest mass.

The IR spectrum contains a peak that spans from about 3000 to 2850 cm-1, which indicates that, a C–H stretch is present and that the compound in question is an alkane. Since there are bands present to the right of 3000, this means an alkyl

group is present. There is also an obvious band in the 12600-1000 (s) area, which corresponds to an ether. Gaps in the spectrum correspond to solvent absorption.[3]

[3] "Introduction to IR Spectra,"
16 Apr. 2009 <http://www.chem.ucla.edu/~webspectra/irintro.html>.

GC Mass Spectrum Product Distillation 1st Run

The procedure for GC Mass Spectrum attainment involves a mass spectrometer that creates charged particles from molecules. The ions are analyzed to provide information about the compound. From this information, one can gauge the molecular weight of the compound and its chemical structure.

The compound to be analyzed is injected into the GC and vaporized. The compound moves through the column. The varying parts of the compound become separated as they travel through. The compound flows through to the ionizer, the ion analyzer, and the detector.

When analyzing the spectrum, it is important to search for the molecular ion. This peak will be the highest mass in the spectrum and is the result of removing one electron. This peak is equivalent to the molecular weight of the compound.

The product, in our case, is the 2-methoxybutane and its formula weight is approximately 88. The molecular ion peak is visible in the entire spectrum. The other peaks present represent the fractured parts of this compound and are referred to as daughter peaks. By working with formula weights, one can determine what they correspond to. Solvent peaks might be present as well as acetone, which is used to clean the needle for injection. [4]

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[4] "Introduction to Mass Spectrometry,"
16 Apr. 2009 <http://www.chem.arizona.edu/massspec/intro_html/intro.html>.

GC Mass Spectrum Product Distillation 2nd Run

2-methoxybutane NMR Spectrum

Nuclear Magnetic Resonance (NMR) is a spectroscopic technique, which provides information about the structural and chemical properties of molecules. It is an analytical technique used to determine the purity and content of a compound. NMR is most useful since it can aid in determining physical properties of compounds at a molecular level.

Chemical shift is an important concept to understand when analyzing NMR Spectrum. This relates to the effective magnetic field at the nucleus. Electron shielding affects this field. The electrons cause a shielding field, which opposes the external magnetic field. An atomic nucleus whose shift is reduced is shielded and the nucleus that is increased is considered de-shielded. Resonant frequency is the highest when the nucleus is the most electronegative.

Spin-spin coupling can affect the effective magnetic field. The orientations of neighboring nuclei are important. For each type of nucleus, there is a splitting of the signal. This is where the N+1 splitting rule is the most useful in analysis.

A coupling constant, denoted as J, can be determined as the frequency difference between two multiplet lines. This value does not depend on the magnetic field strength.[5]

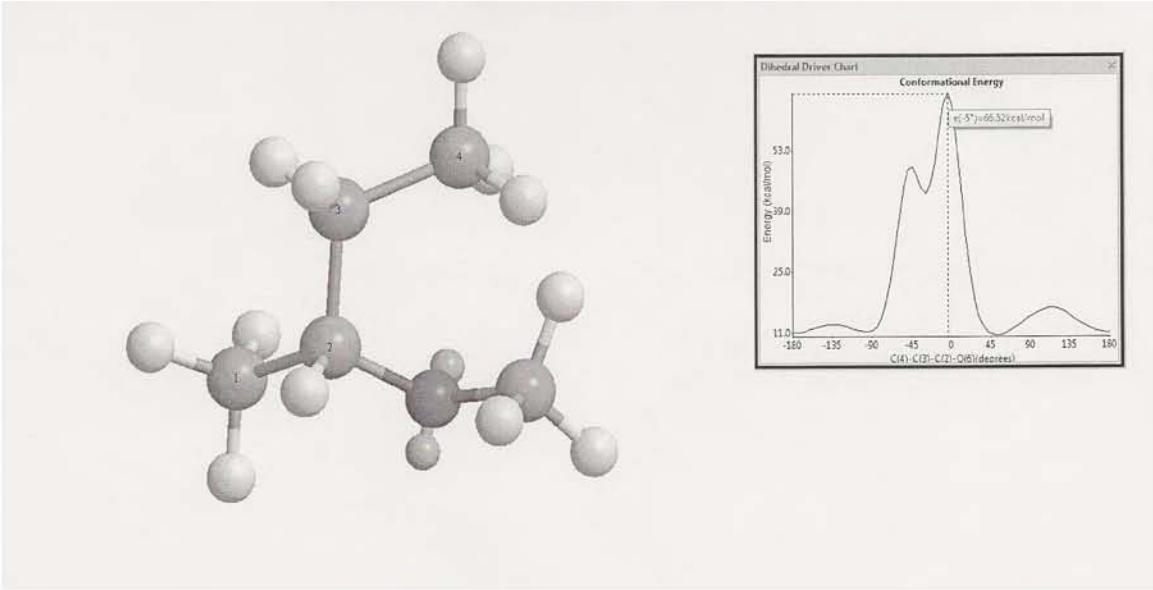
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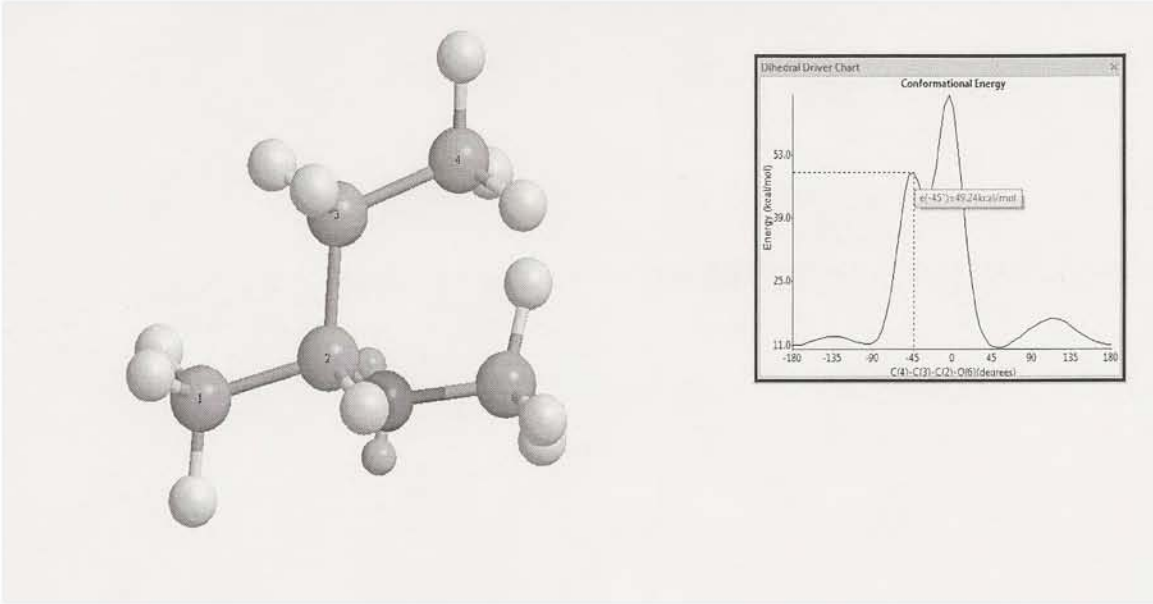
[5] Eberhard Breitmaier, Structure Elucidation by NMR in Organic Chemistry: A Practical Guide (New York: John Wiley & Sons. Ltd., 2002), p. 1-68.

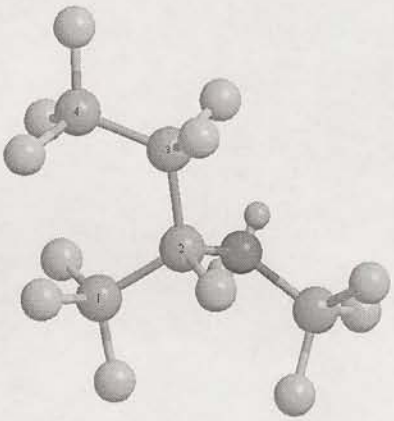
Fluorinated NMR Spectrum

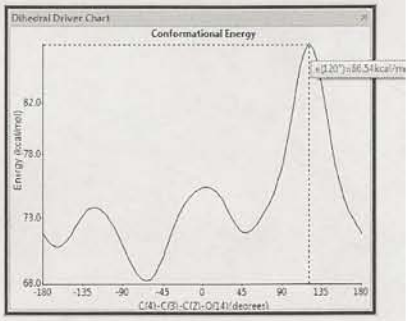
Fluorinated NMR Spectrum (2)

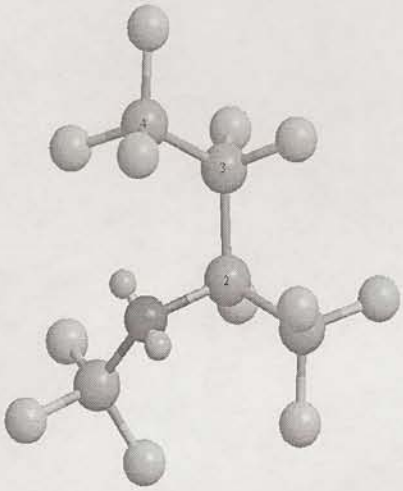
Rotational Barriers about the 2,3 bond in 2-methoxybutane

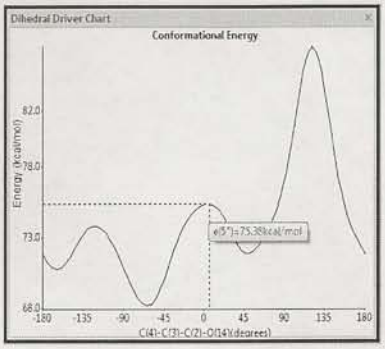


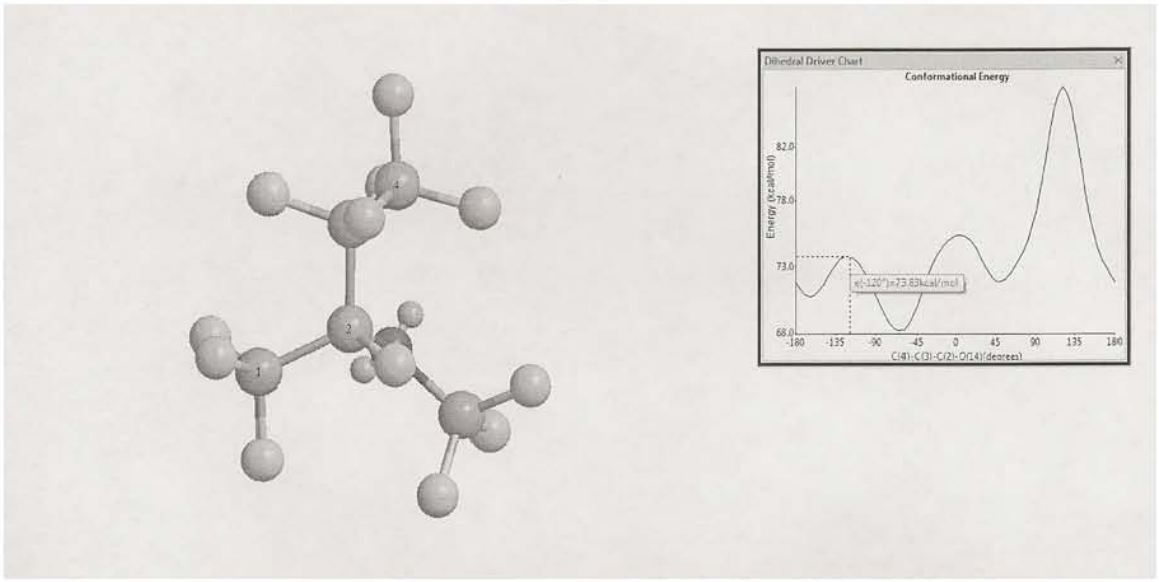





Dihedral Driver Chart
Conformational Energy
Energy (kcal/mol)
82.0
78.0
73.0
68.0
-180
-135
-90
-45
0
45
90
135
180
C(4)-C(3)-C(2)-O(14)(degrees)




Dihedral Driver Chart
Conformational Energy
Energy (kcal/mol)
82.0
78.0
73.0
68.0
e(5°)=75.38kcal/mol
-180
-135
-90
-45
0
45
90
135
180
C(4)-C(3)-C(2)-O(14)(degrees)


Dihedral Driver Chart
Conformational Energy
Energy (kcal/mol)
82.0
78.0
73.0
68.0
-180
-135
-90
-45
0
45
90
135
180
C(4)-C(3)-C(2)-O(14) (degrees)

Complete Simulation of the ABMX3 System

Complete Simulation of the ABX3 System