## 2. INTRODUCTION AND PURPOSE

A Diels-Alder reaction of 1,3-butadiene and aleic anhydride will be carried out to produce cyclohexene-cis-1,2dicarboxylic anhydride. The product will then be hydrolyzed to the diacid. Both the anhydride and the diacid will be tested via unsaturation tests and melting point determination.

## 3. MAIN REACTION & MECHANISMS

### **Diels-Alder reaction:**



### 4. TABLE OF REACTANTS & PRODUCTS

### **Table of Reagents Diels-Alder Reaction:**

	Structure	MW	Amou used	unts	Moles theoretic	ally	
Compound	#	(g/ mol)	mL	grams	used	required	Physical properties
petroleum ether	-	-	~5	3.28	-	-	$b.p = 60-80^{\circ}C$ flash point = -30°C, density = 0.656 g/ mL

Xylene		318.501	11	9.48	-	-	$b.p. = 140^{\circ}C$
-							flash point = $25^{\circ}$ C,
							water insoluble,
							solvent for rxn
							density = $0.862$ g/ mL
3-sulfolene, $C_4H_6O_2S$	1	118.150	-	2.47	0.0209	0.0181	white, pale yellow
							crystal
1,3-Butadiene, $C_4H_6$	2	54.0914	-	1.13	0.0209	0.0181	colorless gas
maleic anhydride,	3	98.058	-	1.77	0.0181	0.0181	colorless, white solid
$C_4H_2O_3$							with penetrating odor,
							causes burns.

Limiting reagent = maleic anhydride

## Hydrolysis Reaction:

			Amounts			
	Structure	MW	used	Moles theo	retically	
Compound	#	(g/ mol)	grams	Used	required	Physical properties
cyclohexene-cis-1,2-	4	152.088	1.23	0.00809	0.00809	$m.p. = 103 - 104^{\circ}C$
dicarboxylic anhydride						
H <sub>2</sub> O	-	18.0	excess	-	-	-

Limiting reagent = anhydride

# **Table of Products**

	Structure	MW	Theoretical yield		Theoretical
Compound	#	(g/ mol)	grams	Moles	Physical properties
cyclohexene-cis-1,2-	4	152.088	2.75	0.0181	$m.p. = 103 - 104^{\circ}C$
dicarboxylic anhydride					
4-cyclohexene-cis-1,2-	5	168.088	1.36	0.00809	$m.p. = 164 - 166^{\circ}C$
dicarboxylic acid					
SO <sub>2</sub>	-	64.0	13.38	0.209	gas, noxious odor,
					dissolves in water to
					produce acid

# 5. YIELD DATA

## THEORETICAL CALCULATIONS:

	Butadiene +	maleic anhydride	➔ cyclohexene-cis-1,2-dicarboxylic anhydride
Before	0.0209 mol	0.0181 mol	0
Change	-0.0181 mol	-0.0181 mol	+0.0181 mol
After	0.0028 mol (ER)	0 mol (LR)	0.0181 mol (2.75 g)

	Diels-Alder adduct + (1.23 g of anhydride)	- water -	diacid
Before	0.00809 mol	Excess	0
Change	-0.00809 mol	-	+0.00809 mol
After	0 mol (LR)	ER	0.00809 mol (1.36 g)

<b>OBSERVED YIELD:</b>	
Mass of anhydride (%)	2.46 g (89.5 %)
Mass of diacid (%)	1.05 g (77.2%)

### 6. EXPERIMENTAL PROCEDURE AND RESULTS

### Reaction under gentle reflux

A reaction apparatus was set up as shown in Dailey p. 25. 2.5-g 3-sulfolene and 1.5-g maleic anhydride were separately weighed and placed into 1-mL of xylene in the florence flask. The flask was gently heated to dissolve solids and gently refluxed for 30-minutes, then cooled. 10-mL of xylene and ~5-mL petroleum ether was added, and the solution cooled to induce crystallization. The crystals were collected by vacuum filtration.

### Hydrolysis of the anhydride

~6-mL of distilled water was added to 1.23 g of anhydride and the mixture heated until boiling. The diacid was crystallized in an ice-water bath and collected via vacuum filtration.

### Melting points and test for unsaturations (Bromine and Baeyer test)

Melting points of the dried anhydride and diacid were obtained, and the Bromine and Baeyer tests for unsaturation performed as described in Gilbert and Martin, p. 651-654.

Mass, 3-sulfolene	2.47 g
Mass, maleic anhydride	1.77 g
Mass, filter paper (for anhydride)	0.34 g
Mass, filter paper + anhydride (wet)	2.80 g
Mass, anhydride (% yield)	2.46 g (89.5 %)
Anhydride, m.p.	98°C (fast); 97-100°C (slow)
<b>Observations of Diels-Alder reaction</b>	liquid in flask went from clear to light brown, crystallized
	anhydride was off-white, "fluffy" and crystalline
Bromine test	+, orange color disappears quickly
Baeyer test	+, formation of dark brown MnO <sub>2</sub>

Mass, anhydride to be hydrolyzed	1.23 g
Mass, filter paper (for diacid)	0.15 g
Mass, filter paper + diacid dried	1.20 g
Mass, diacid (% yield)	1.05 g
Diacid, m.p.	165 <sup>°</sup> C (fast); 162-163 <sup>°</sup> C (slow)
Observations of process/ product	liquid in flask was yellowish, crystallized diacid was white,
	waxy solid
Bromine test	+, orange color disappears quickly
Baeyer test (drops for blank: drops for sample)	+, formation of dark brown MnO <sub>2</sub>

7. OBSERVED PHYSICAL PROPERTIES OF PRODUCTS OBTAINED—Please see data tables.

### 8. SIGNIFICANT SIDE REACTIONS

There were no significant side reactions for this experiment since the 1,3-butadiene was produced directly from 3-sulfolene and therefore would not have an opportunity to dimerize.

## 9. METHOD OF PURIFICATION—Please see procedures.

### **10. CONCLUSIONS**

Some product (anhydride and diacid) loss most likely occurred during crystallization; some product may have remained dissolved and was lost in the filtrate. The melting points for both substances are also a few degrees lower than the expected melting points, indicating a slight degree of impurity. The anhydride may have some small amount of diacid

formed by the reaction of the anhydride with moisture in the air, or there may have been an opportunity for contamination as both substances were left to air-dry and were left exposed (albeit in the lab locker) for one week.

11. ANSWERS TO ASSIGNED QUESTIONS 2. a)



5. 3-sulfolene and maleic anhydride should be *completely* dissolved in xylene before heating the mixture to effect reaction because failure to do so will lower the yield of the reaction significantly because the butadiene will distill out of the solution before it has an opportunity to react with the maleic anhydride.

6. The double bond of the anhydride will undergo an *anti*-addition of the  $Br_2$  because of the formation of the 2-step reaction mechanism in which a bromonium ion intermediate sterically prevents addition of the second Br to the same face of the double bond. The Br's will be trans—diequatorial in their position relative to the hexane ring.





12. BIBLIOGRAPHY

Dailey, William. Chemistry 502: Laboratory Manual, Summer 2007. UPenn.

Gilbert and Martin, Experimental Organic Chemistry: A Miniscale and Microscale Approach, Saunders College, 1998.