

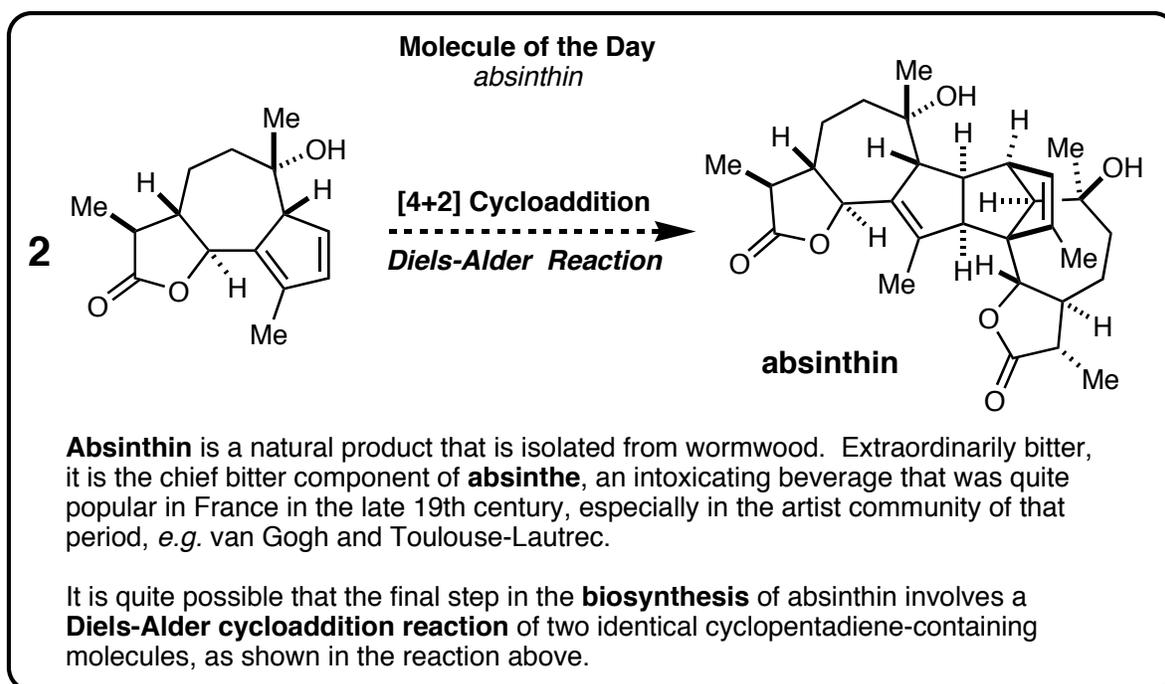
# Massachusetts Institute of Technology

## Organic Chemistry 5.13

October 11, 2006  
Prof. Timothy F. Jamison

### Assignment and Study Guide for Unit III

*Molecular Orbital Theory, Pericyclic Reactions,  
and the Woodward-Hoffmann Rules*



#### Reading Assignments

McMurry, Chapter 14 (pp. 464-497)

(Also review McMurry, Chapter 15, pp. 498-527)

#### Recommended Problems:

Chapter 14: 2-4, 7-10, 18-19, 22, 28, 33-34, 36, 39-40,  
44-45, 51, 55-57.

#### Problem Set #4

*Will be posted on website – Due Friday, October 20.*

"...in the synthesis of vitamin B-12, **R. B. Woodward** hit on a puzzle whose analysis became the point of departure for the discovery of the Woodward-Hoffmann rules concerning the role of orbital symmetry in chemical reactions. This development ushered in a new era in the theory of organic chemistry, and it is particularly fitting that it was the protagonist of modern natural product synthesis who triggered the final breakthrough of the use of the quantum mechanical model of structure and reactivity in organic chemistry, an advance that parallels the establishment of the classical structural theory, the tetrahedral model of carbon, the octet rule, and conformational analysis."

**Albert Eschenmoser** *Science* **1977**, 196, 1410.

"Violations? There are none. Nor can violations be expected of so fundamental a principle..."

**R. B. Woodward and R. Hoffmann**, "The Conservation of Orbital Symmetry" (1970).

## Study Guide

### General Aims of this Unit:

1. We will learn to recognize **pericyclic reactions** and to classify them as being **electrocyclic processes, cycloadditions, or sigmatropic rearrangements**.
2. We will develop a general understanding of the theoretical basis of the **Woodward-Hoffmann Rules** based on the **Frontier Molecular Orbital Theory** of Fukui.
3. We will learn how to apply the **Woodward-Hoffmann Rules** to predict the stereochemical outcome of pericyclic reactions.
4. We will study several pericyclic reactions in detail, learning how to predict the products of these reactions and how to employ them in synthesis. Specifically, we will focus our attention on the **Diels-Alder reaction**, the **Cope rearrangement**, the **Claisen rearrangement**, and **ketene [2+2] cycloadditions**.