Absinthin is a natural product that is isolated from wormwood. Extraordinarily bitter, it is the chief bitter component of absinthe, an intoxicating beverage that was quite popular in France in the late 19th century, especially in the artist community of that period, e.g. van Gogh and Toulouse-Lautrec.

It is quite possible that the final step in the biosynthesis of absinthin involves a Diels-Alder cycloaddition reaction of two identical cyclopentadiene-containing molecules, as shown in the reaction above.

Reading Assignments  
McMurry, Chapter 14 (pp. 464-497)  
(Also review McMurry, Chapter 15, pp. 498-527)

Recommended Problems:  

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..."


**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**.