**Organic Chemistry 5.13** 

October 8, 2003 Prof. Timothy F. Jamison

## Notes for Lecture #13

Cycloaddition Reactions – The Diels-Alder Reaction

## Molecule of the Day cantharidin



**Cantharidin** is a powerful **irritant** isolated from Cantharis vesicatoria, a.k.a. the "blistering beetle" or "Spanish fly", and is found in the eponymous, alleged aphrodisiac. Several chemistry research groups have prepared cantharidin by total synthesis, and in many of these a **Diels-Alder reaction** was a key step.

**Cycloaddition:** A pericyclic reaction in which 2 **separate** conjugated, overlapping arrays of orbitals **combine**. Cycloadditions proceed by way of a **cyclic transition state**, and **2 sigma bonds** are formed during the course of the reaction.

A **suprafacial** process ("s" in the table below) is one in which the bonds made or broken lie on the **same face** of the orbital array undergoing reaction. In an **antarafacial** process ("a"), the newly formed or broken bonds lie on **opposite faces** of the reacting orbital array.

Woodward-Hoffmann Rules for Cycloadditions		
	Stereochemical Course	
# Electrons	Thermal Mode	Photochemical Mode
4n + 2	[s + s]	[s + a]
4n	[s + a]	[S + S]

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