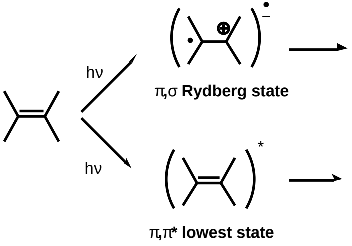
Photochemistry of alkenes:

the short version

The main π,π* absoption of simple alkenes is located at λ < 200 nm, thus limiting the usefulness of most conventional light sources.



carbene leading rearrangements

π,σ **Rydberg state**

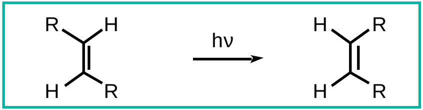
cis-trans isomerizations

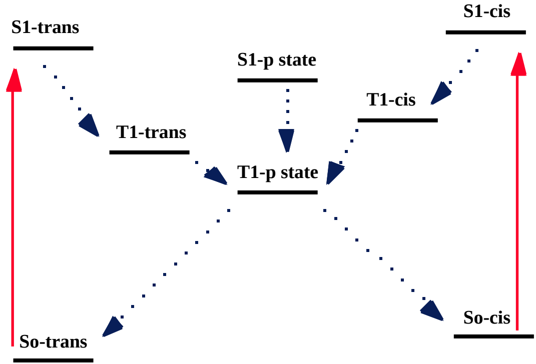
π,π* **lowest state**

Spectroscopy

- **The two lowest absorptions of alkenes involve π,π* and π,3s (Rydberg) states**
- **For ethylene the two transtions are very close and around 170 kcal/mol**
- **For substituted alkenes the Rydberg transition tends to be at lower energies.**
  - **For example for *cis*-2-butene the energies based on the absorption spectra are:**
    - **singlet π,π*	164 kcal mol**
    - **singlet (Rydberg)	141 kcal/mol**
    - **triplet π,π*	97 kcal mol**
- **The lowest triplet state has π,π* character and energies around 94-99 kcal/mol**

The cis-trans (Z-E) isomerization




S1-trans

S1-cis

S1-p state

T1-cis

T1-trans

T1-p state

So-cis

So-trans

Control of the photostationary state

The photostationary state is a wavelength dependent property

$$\left(\frac{[t]}{[c]}\right)_s = \frac{\varepsilon_c \varphi_{ct}}{\varepsilon_t \varphi_{tc}}$$

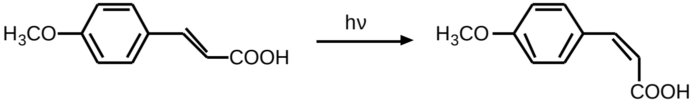
Control of the photostationary ratio

- **excitation ratio**
- **decay ratio**

Synthetic applications:

A convenient way from the more stable (trans) to the less stable (cis) isomer

Example: cinnamic acid



cis isomer produced in 74% yield

Stilbenes: A popular example with photochemists

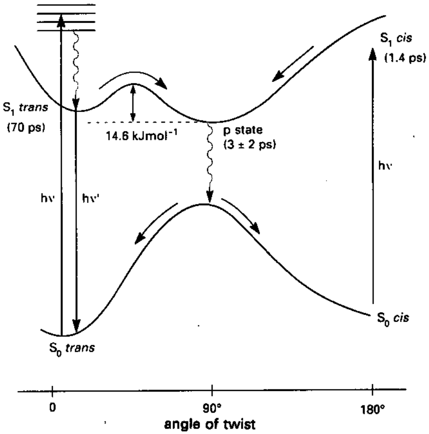
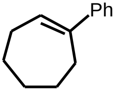
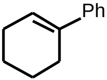
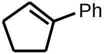
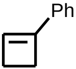


Fig. 6.2. Geometric isomerization of stilbenes (room temperature, hexane solution)[8]

Lifetimes of the S1 state: 70 ps for trans and 1.4 ps for cis stilbene

Fluorescence lifetimes controlled by the ability to rotate the double bond

	$\Phi_{fluorescence}$
	0.016
	0.03
	0.43
	0.27

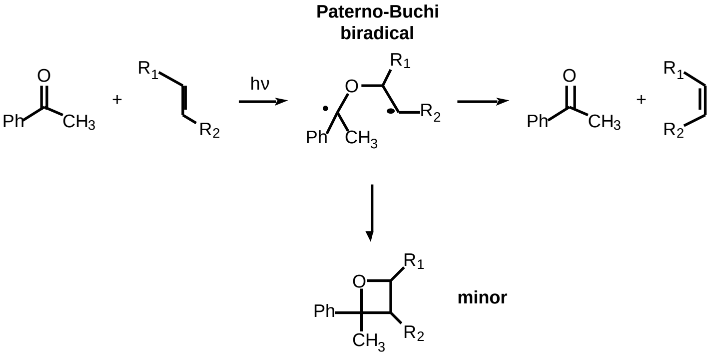
Ketones can promote cis-trans isomerization by two different mechanisms

SENSITIZATION

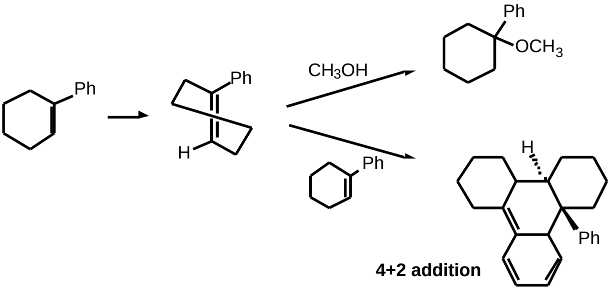
Energy transfer from a triplet ketone (why not a singlet?) can lead to triplet alkene that then follows the normal isomerization pathway, independent of the ketone sensitizer

Ketones can promote cis-trans isomerization by a biradical mechanism

Schenck mechanism



Trans cycloalkenes are highly reactive

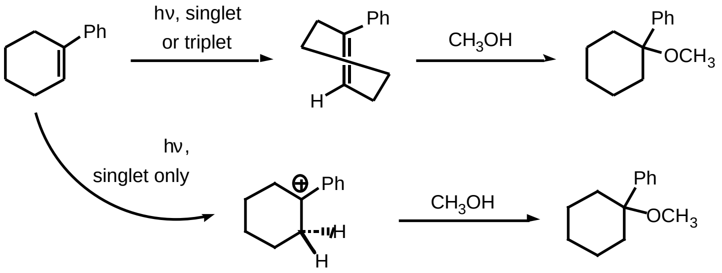


4+2 addition

Followed by hydrogen shift

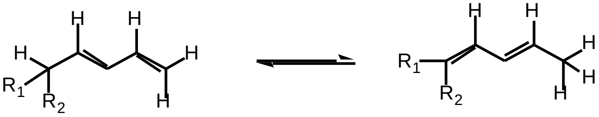
Alcohol addition:

two distinct possible mechanisms



Direct protonation of the triplet state is spin forbidden

Sigmatropic shifts: pericyclic reactions



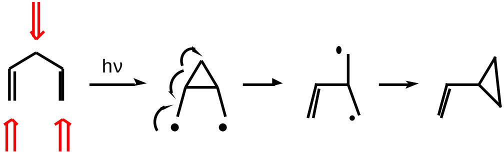
1,5-sigmatropic shift

Questions of antarafacial, suprafacial, etc., for some other opportunity

Di-π-methane rearrangement

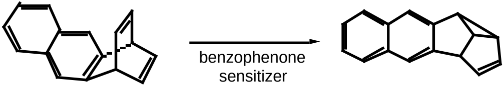
Zimmerman rearrangement

one **sp^3** center



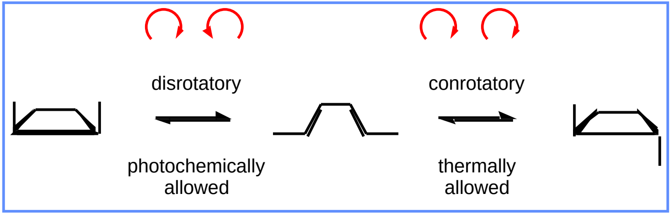
two π systems

Example:



benzophenone
sensitizer

Electrocyclic reactions



disrotatory

photochemically
allowed

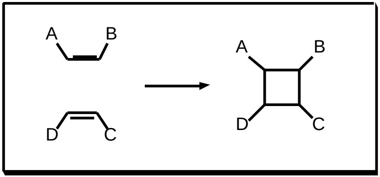
conrotatory

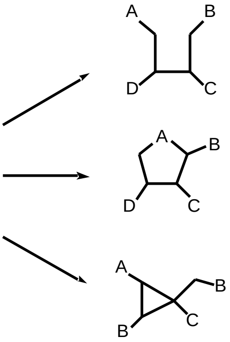
thermally
allowed

Woodward and Hoffmann rules

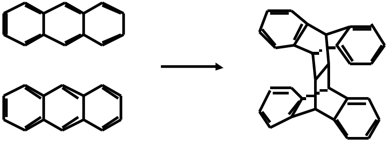
Alkene cyclizations

Simple cyclizations open the door for a variety of synthetic routes

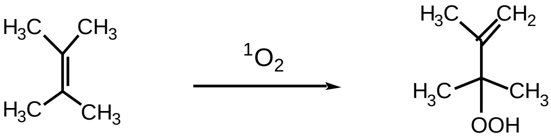




Aromatic analogue



The Schenck or *ene* reaction revisited



(A)