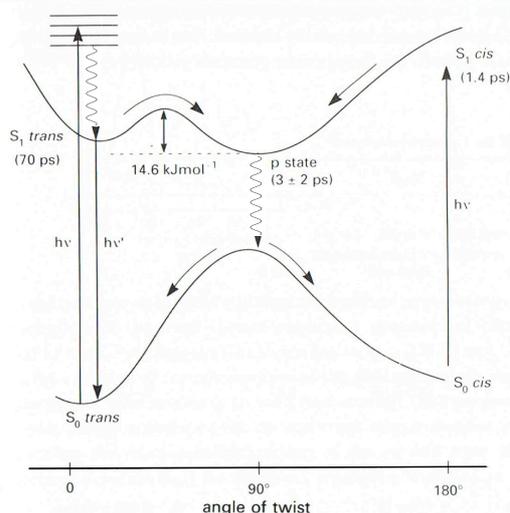
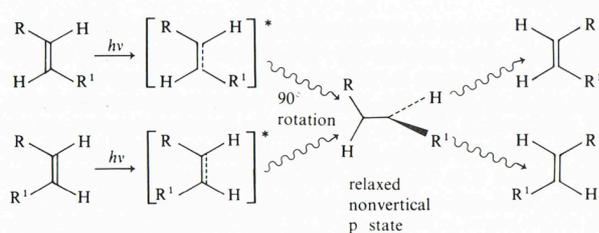


4. Organic photosynthetic reactions

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4.1 Reactions of ethenes and aromatic compounds

Photoreactivity of ethenes



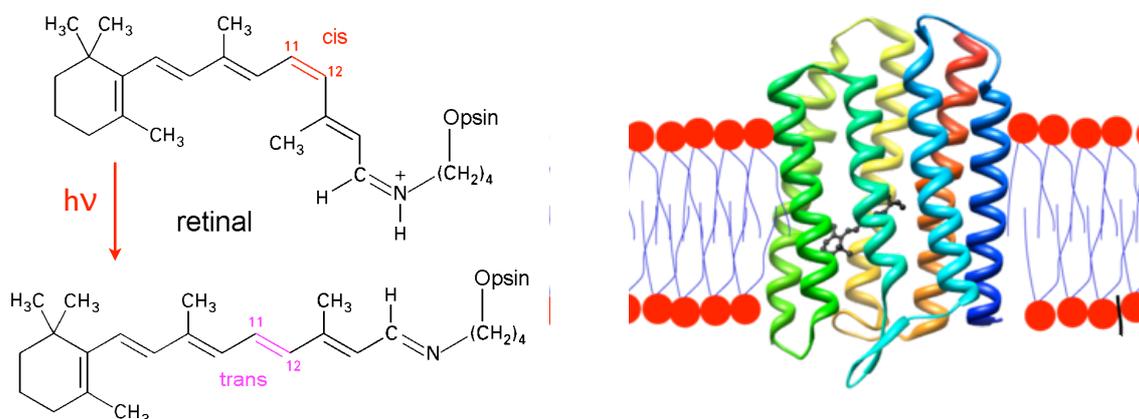
Geometrical isomerization

In π - π^* excited states, there is effectively no π bond and so the central σ bond may rotate to yield the lowest energy conformation. Rapid radiationless decay can take place from a relaxed nonvertical state ("p-state") and lead to either geometrical isomer.

Cis-trans (Z-E) photoinduced interconversion of 1,2-disubstituted ethenes and other doubled-bonded systems, such as azo compounds (N=N) and oximes (N=C) is thus a very general process. The isomerization reaction occurs from both the singlet and the triplet excited states, and in appropriate cases can be initiated by electron transfer sensitizers.

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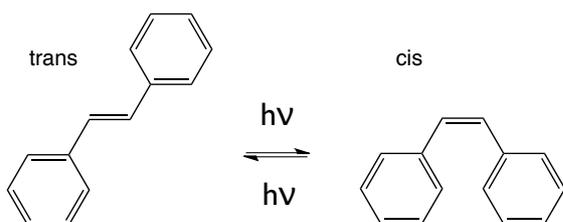
Cis-trans photoisomerisation and vision



Retinal (or vitamin A aldehyde) is a polyene chromophore. Bond to the proteins opsins, it is the photochemical basis of animal vision. The mechanism of vision begins with the photoisomerization of retinal. When the 11-*cis*-retinal chromophore absorbs a photon it isomerizes to the all-*trans* state. This isomerization induces the folding of the entire surrounding protein, which switches from the metarhodopsin (yellow colored) form to the rhodopsin (red-purple) form. This folding causes the opening of an ion channel through the cell membrane, triggering nerve signaling.

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Cis-trans interconversion



$$\frac{[cis]}{[trans]} = \frac{\epsilon(trans)}{\epsilon(cis)} \cdot \frac{\Phi(trans \rightarrow cis)}{\Phi(cis \rightarrow trans)}$$

Stilbene	<i>cis</i>	<i>trans</i>
$\epsilon^{313 \text{ nm}} / \text{mol}^{-1} \text{ l cm}^{-1}$	2,400	16,200
$\Phi_{\text{isomerization}}$	0.35	0.50

Under continuous irradiation by light, whose wavelength is absorbed by both isomers, a photostationary state is obtained, corresponding to a defined *cis* : *trans* isomer ratio.

In the case of stilbene *cis-trans* interconversion, about 96 % of the *cis* isomer is obtained at the photostationary state under 313 nm irradiation.

Intersystem crossing in ethene is very inefficient. Triplet excited state population can however be obtained through photosensitization. In this case, the extinction coefficients of the respective isomers do not control the final *cis* : *trans* ratio obtained in stationary conditions.

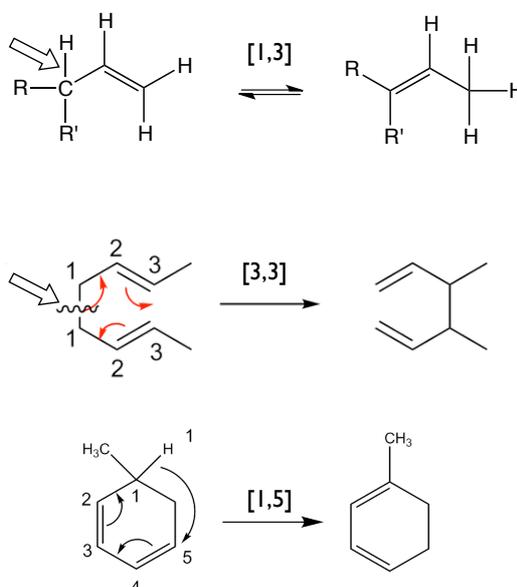
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Photoreactivity of ethenes

Sigmatropic shifts are rearrangements that can be induced both thermally and photochemically. It involves the migration of a σ bond across an adjacent π system, with a consequent switching of the double bond-single bond arrangement in the molecule.

The process occurs in a concerted manner and is a member of a class of reactions known as **pericyclic reactions** since the reorganization of the electrons is accomplished in a cyclic array.

The reaction can proceed in both directions and usually yields a mixture of isomers. The ratio of isomers in the photostationary state depends upon the absorption properties of both isomers and the quantum yields of the forward and back reactions as in *cis-trans* interconversion.



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Pericyclic reactions

General rules, called after Woodward and Hoffmann, govern the mechanism of pericyclic reactions and are based on the symmetries of the electronic orbitals involved:

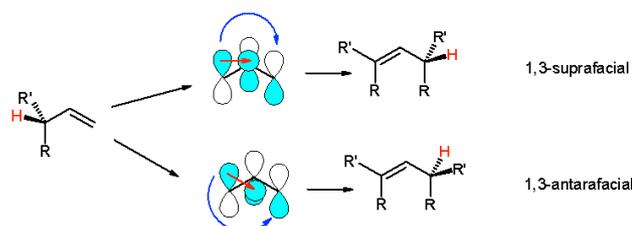
- In an open chain containing $4n$ electrons (where $n \in \mathbb{N}$) a bonding interaction between the termini must involve overlap between orbital envelopes on opposite faces of the system (antarafacial) and this can only be achieved in a conrotatory process.
- In systems containing $4n + 2$ electrons, terminal bonding interaction within ground-state molecules requires overlap of orbital envelopes on the same face of the system (suprafacial), attainable only by disrotatory displacements.
- Photochemical reactions lead to a reversal of terminal symmetry relationships and reversal of stereospecificity.



Robert B. Woodward
(1917-1979)



Roald Hoffmann
(1937-)
Nobel prize 1981

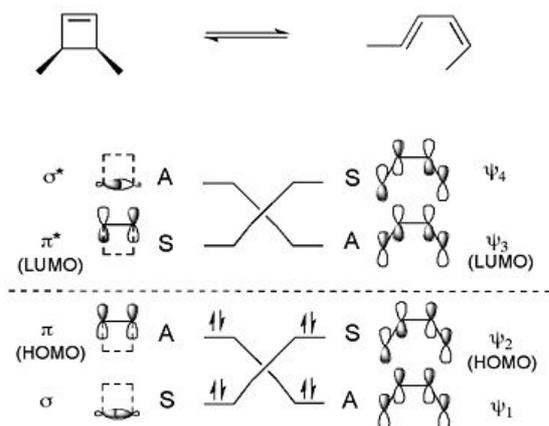


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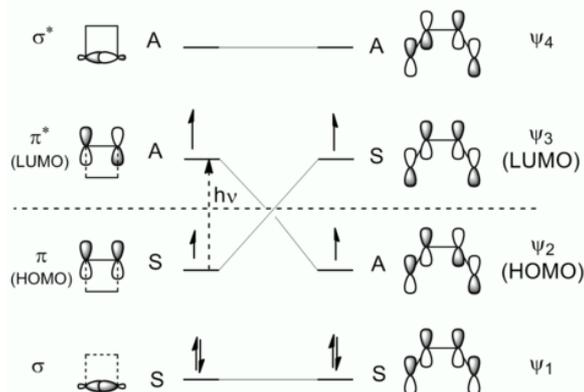
Electrocyclic reactions

An electrocyclic reaction is a type of pericyclic rearrangement where the net result is one π -bond being converted into one σ -bond or vice-versa.

Correlation diagrams, which connect the molecular orbitals of the reactant to those of the product having the same symmetry, can be constructed. These show in a 4-electron system that the conrotatory process is allowed for a thermally induced reaction (left), while the disrotatory process is allowed for the photoinduced reaction (right).

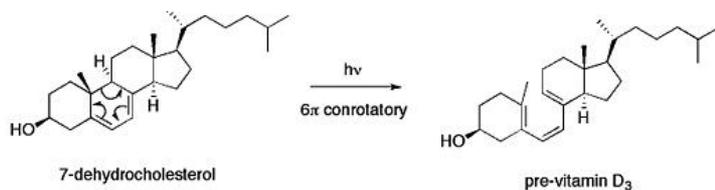
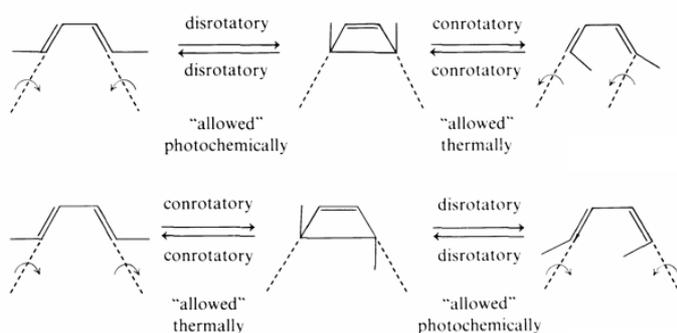


Frontier orbitals are symmetric (S) or antisymmetric (A) with respect to conserved symmetry element



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Electrocyclic reactions



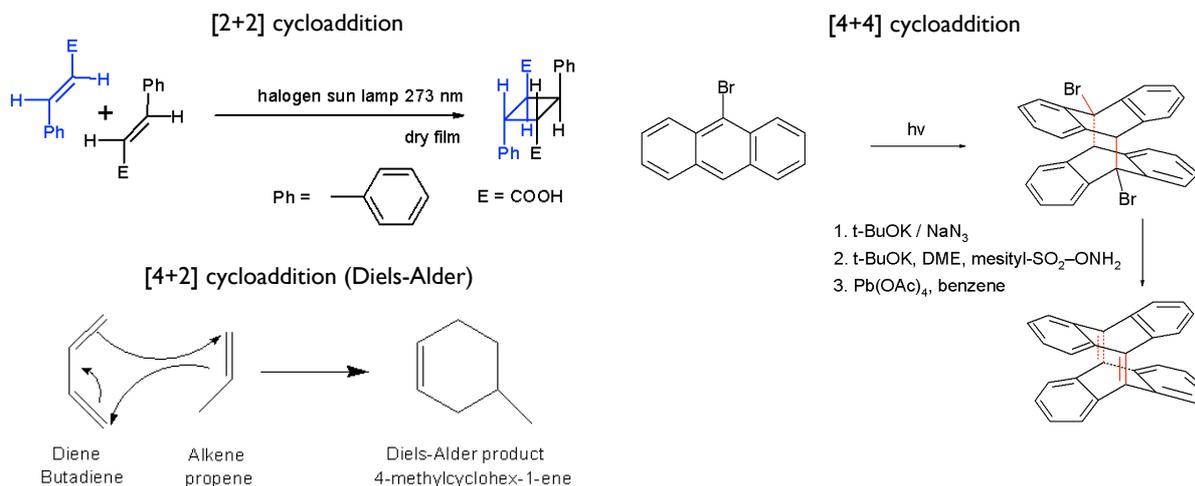
Application of Woodward-Hoffmann's rules imply that the stereospecificity obtained by a thermally activated reaction is inverted in the case of a photochemically activated process. Isomers that are impossible to prepare normally by thermal reactions become then accessible photochemically.

Electrocyclic reactions occur frequently in Nature. One example is provided by the biosynthesis of vitamin D₃. In this 6 electrons ($4n+2$) system, the first step involves a photochemically induced conrotatory ring opening of 7-dehydrocholesterol to form pre-vitamin D₃.

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Cycloaddition reactions

Cycloaddition is a pericyclic chemical reaction, in which two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic adduct in which there is a net reduction of the bond multiplicity. The resulting reaction is a cyclization reaction. Cycloadditions are usually described by the backbone size of the participants. A Diels-Alder reaction between an ethene and a diene is thus a [4+2] cycloaddition.



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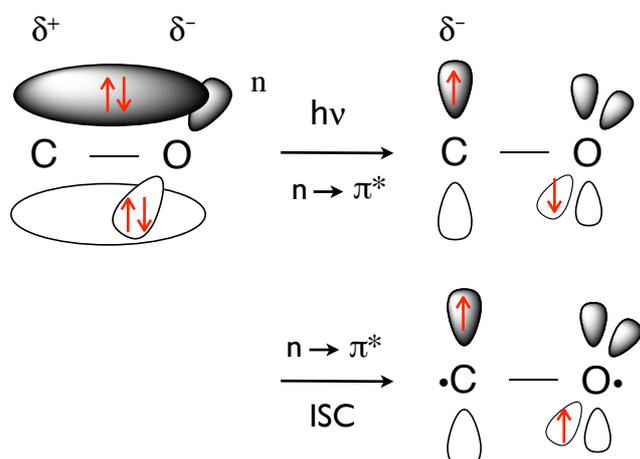
4.2 Photochemistry of carbonyl chromophore

Photoreactivity of carbonyls

$n \rightarrow \pi^*$ transition: $\lambda_{\max} = 280\text{-}300\text{ nm}$

Symmetry-forbidden transition:

$\epsilon = 15\text{-}60\text{ mol}^{-1}\text{ l cm}^{-1}$



In the ground state, the C=O functional group is polarized, with the electronic density being mainly carried by the oxygen atom. Carbon in this case is electrophilic and is thus subjected to nucleophilic attack.

(n, π^*) excited state is much less polar. The electronic density gained by the carbon atom makes it essentially nucleophilic.

In the triplet excited state, the transition dipole moment of the carbonyl group tends to increase due to spin correlation effect. Unpaired electrons in n and π^* orbitals tend then to separate as much as possible. The (n, π^*) excited state can in that case be seen as a di-radical and will be involved in homolytic reactions.

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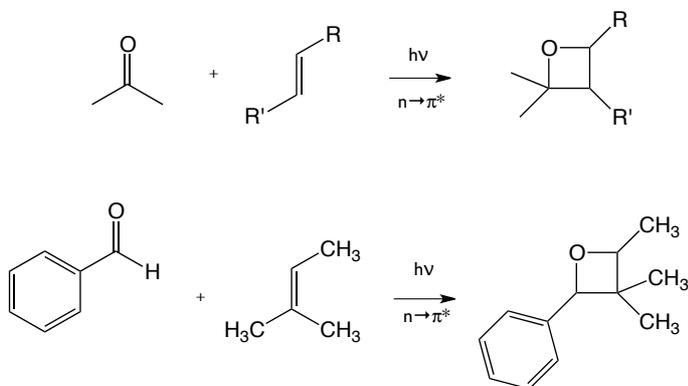
Photoreactivity of carbonyls

Cycloaddition to ethenes, dienes and ethynes

The oxygen atom in the (n, π^*) excited state of a ketone has electrophilic character (compare with alkoxy radicals) and can attack ground state ethenes $>C=C<$ or ethynes $-C\equiv C-$ to yield oxetanes through ($2\pi+2\pi$) cycloaddition.

The reaction of benzaldehyde with 2-methylbut-2-ene is one of the earliest reported photo-reaction and is widely known as the *Paterno-Büchi reaction*.

Reaction of enones and aromatic carbonyl compounds with ethenes occurs almost exclusively from the triplet.

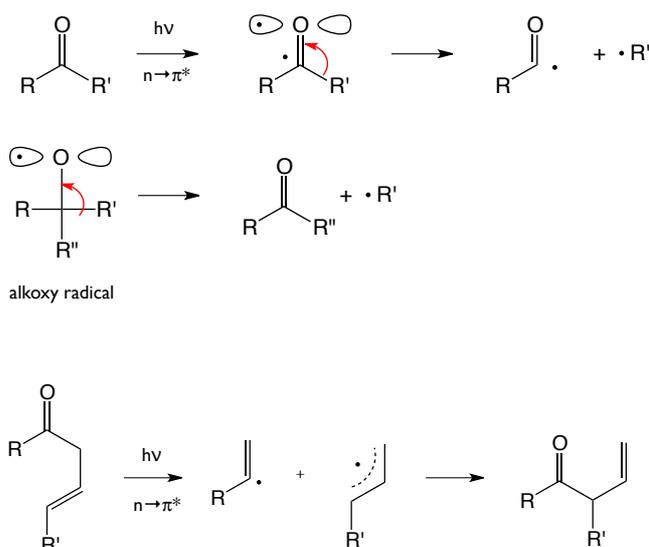


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Homolytic cleavage in α -position

A simple model of the (n, π^*) excited state of a ketone shows the nonbonding electron on the oxygen-centered p-type n orbital and the unpaired electron in the antibonding π^* orbital leads to α -bond cleavage and the formation of acyl and alkyl radicals (or homolytic C-H bond cleavage for aldehydes) on irradiation. The homolytic cleavage of neighbouring single bond is called *Norrish type 1* reaction.

β, γ unsaturation of ketones aids α -cleavage as a result of resonance stabilization in the allyl radical. But in this case, recombination of the acyl and allyl radicals is favored, giving the products of a 1,3-sigmatropic shift.



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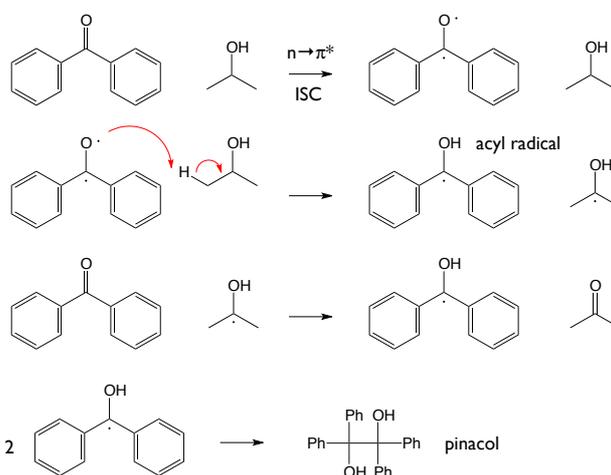
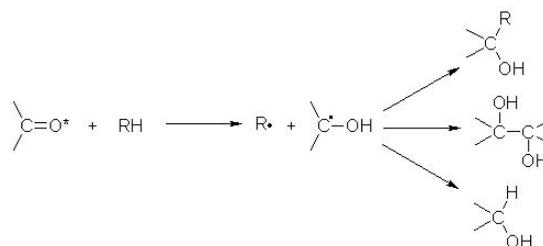
Hydrogen abstraction by carbonyl excited state

Intermolecular hydrogen abstraction

The (n, π^*) excited states of ketones, particularly in the triplet state, resemble alkoxy radicals and they can abstract a hydrogen atom from a suitable donor.

The three products of the above reaction scheme show that the initial pair of radicals formed can combine to give a photoaddition product, or the radical coming from the ketone can dimerize, or abstract another hydrogen atom.

Suitable donors RH are primary or secondary alcohols (such as isopropanol), ethers, alkylbenzenes or some alkenes, rather than alkanes, where the C–H bond is generally too strong.



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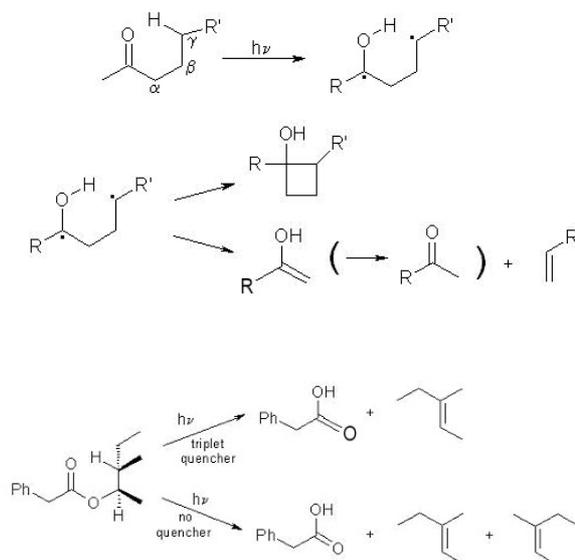
Hydrogen abstraction by carbonyl excited state

Intramolecular hydrogen abstraction leading to cleavage or cyclization

This is the predominant photochemical reaction (*Norrish type 2* reaction) for many acyclic, dialkyl or alkyl aryl ketones having at least 3 carbon atoms in one of the groups attached to C=O.

Hydrogen abstraction can occur from a position within the ketone molecule, forming a biradical that may cyclize. In an unconstrained system a ketone (n, π^*) excited state shows a preference for abstraction from the γ -position.

Aryl ketones generally react via a triplet (n, π^*) excited state, but dialkyl ketones react through both singlet and triplet states. The singlet state reaction (performed by using excess triplet quencher) is stereoselective, but the triplet state reaction is not.



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Hydrogen abstraction by carbonyls - Photoenolization

When the reactive carbonyl function and a γ -hydrogen are conjugated via an aromatic ring or double bond, the 1,4-diradical created by hydrogen abstraction quickly relaxes to a conjugated enol tautomer. If an aromatic ring has been disrupted by the photoenolization, the enol tautomer is unstable and rapidly reverts to the initial aromatic carbonyl compound. This transformation finds practical application in UV filters. The three compounds on the left are examples of current sunscreen components.

