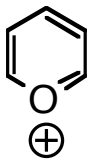
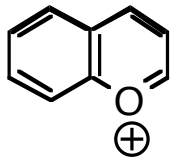
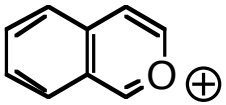
PYRYLIUM IONS AND PYRONES
(chapt 7-9)



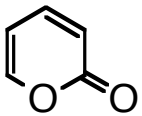
Pyrilium



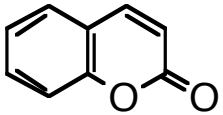
Chromylium



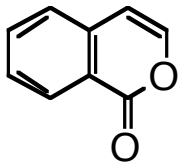
Isochromylium



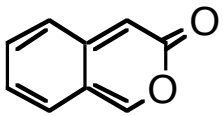
2-Pyrone

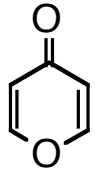


Coumarin

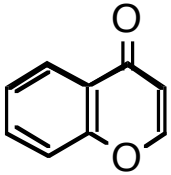


Isocoumarin



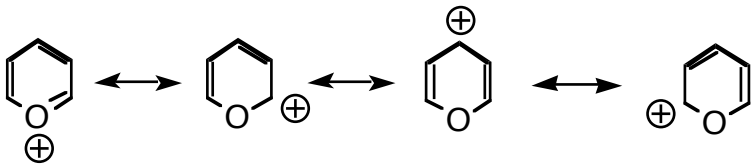


4-Pyrone



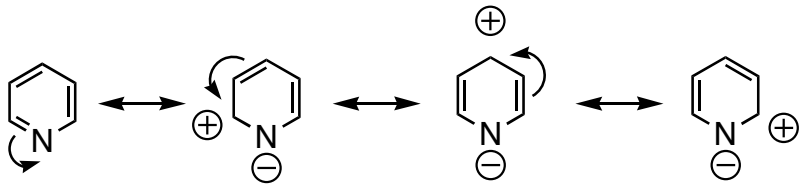
Chromone

PYRYLIUM IONS



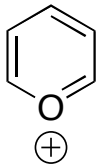
Aromatic - Reactive
Counter ion often ClO_4^-

c.f.:



Electron deficient ring:

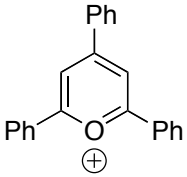
- **No react. with electrophiles**
- **No react. with radicals**
- **Reaction with nucleophiles**
- **(Reacts in cycloadditions)**



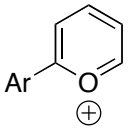
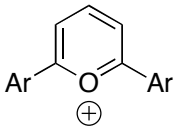
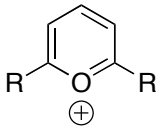
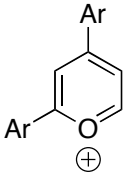
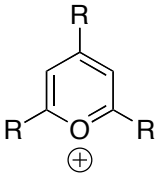
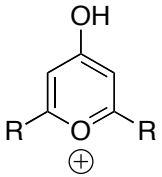
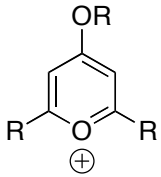
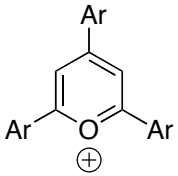
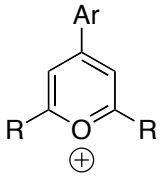
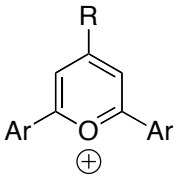
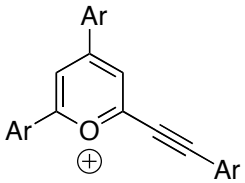
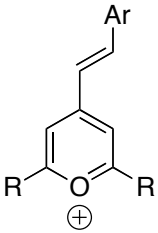
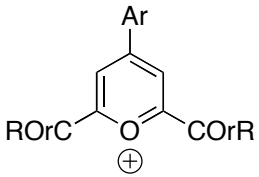
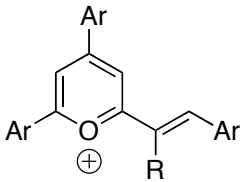
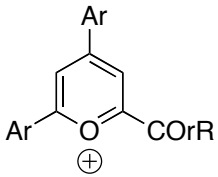
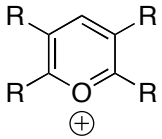
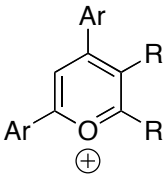
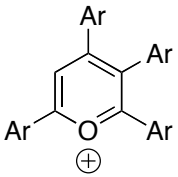
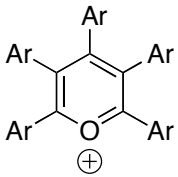
$X^{\ominus}$

X=ClO_4: 36 refs in SciFinder
X=BF_4: 16 refs in SciFinder

Com. avail. (SciFinder) ca 170

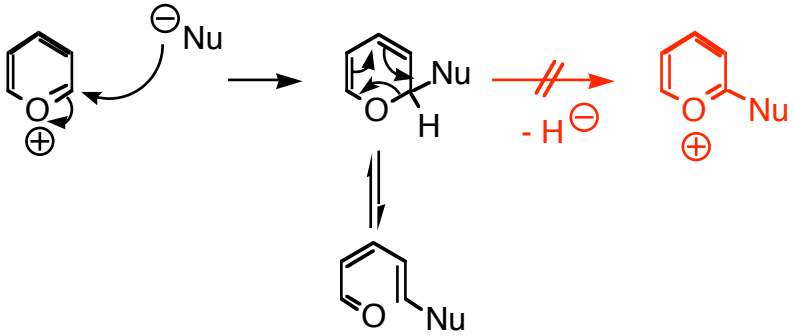


Com. avail. with 12 diff. anoins

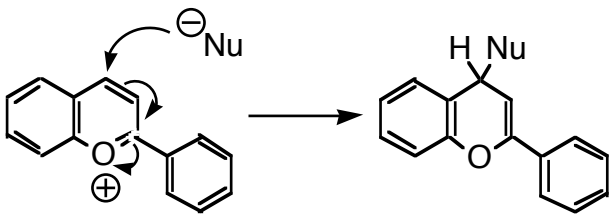
Reactions with nucleophiles

1,2-Add. - Ring opening!



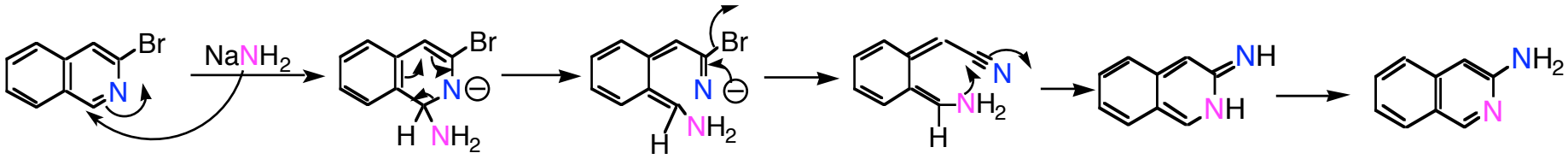
Nu: Water, alcohols, ammonia, amines, organometallics / carbanions, Wittig reagents hydrides

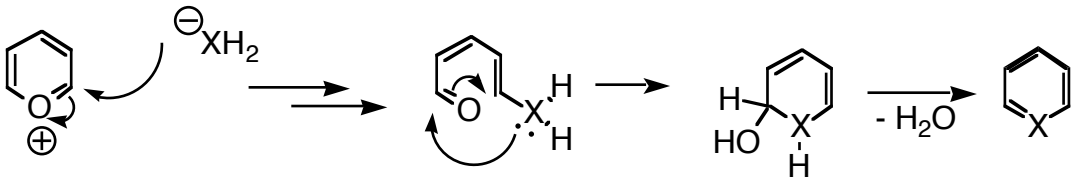
1,4-add. common on flavylium



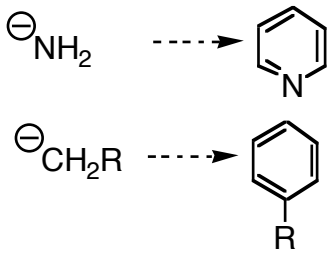
Reactions with nucleophiles

ANRORC (add. of Nu., Ring Opening and Ring Closure)





Nu = -XH_2 (-NH_2, -CH_2R)



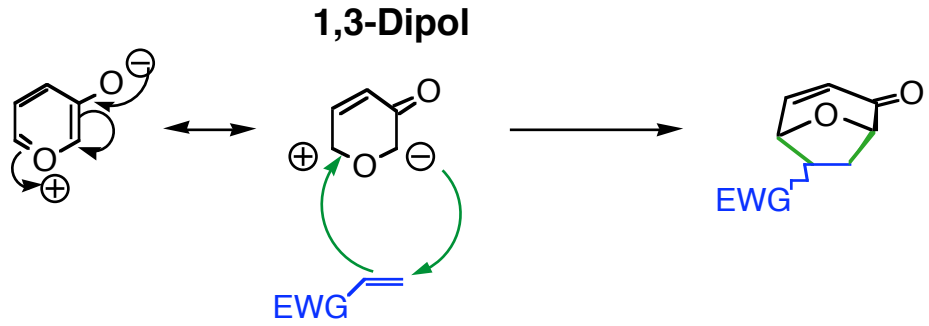
More stable aromatic rings

Good yields

Availability starting material

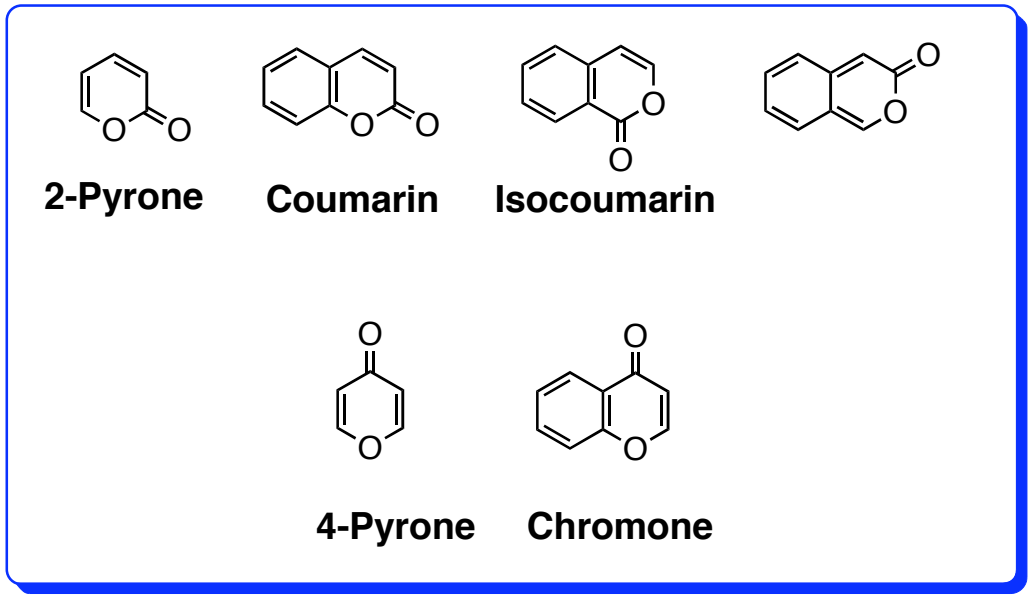
Cycloadditions

3-oxidopyryliums

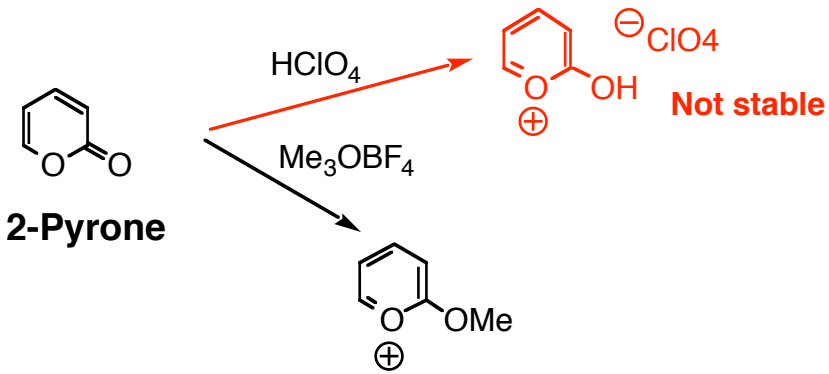


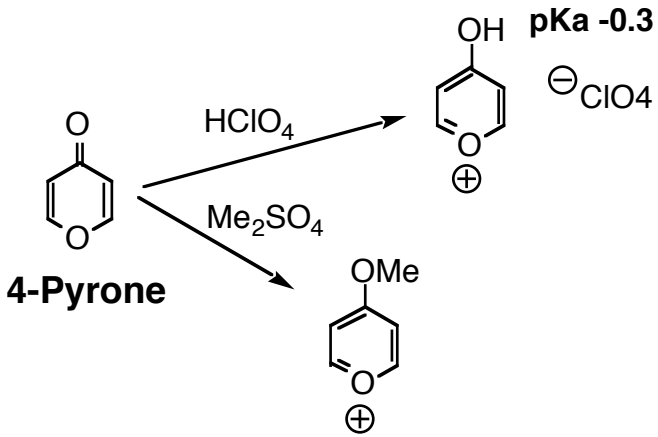
Further transformations to 7-membered rings

Pyrones



Reactions with Electrophiles

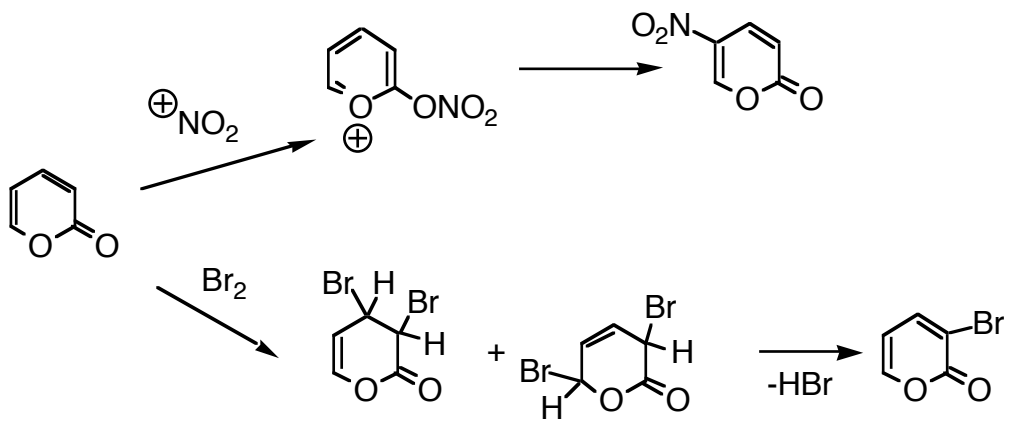




No E-fil Ar Subst

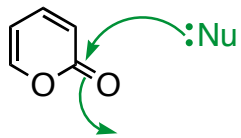
Reactions with Electrophiles

E-fil Aromatic Substitution like products, but by other mechanisms

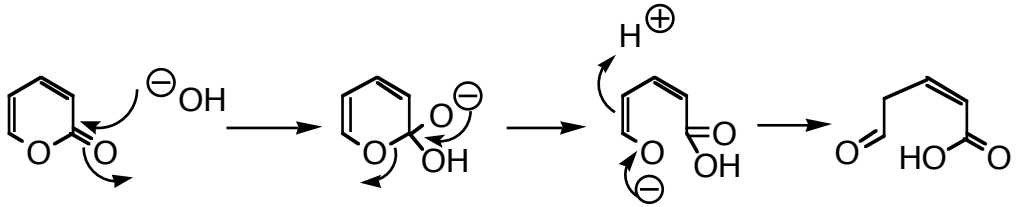


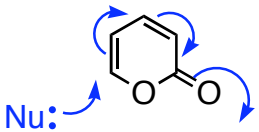
Reactions with Nucleophiles

lactone

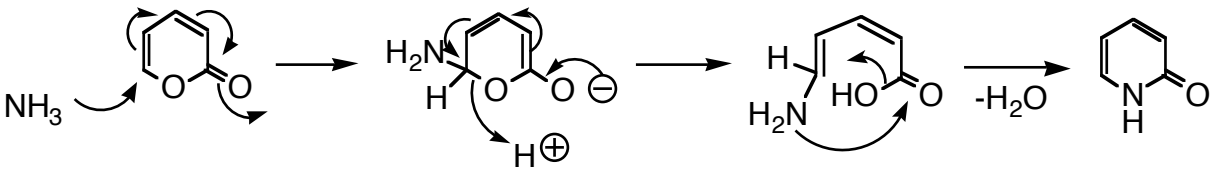


OH^-, RMgX

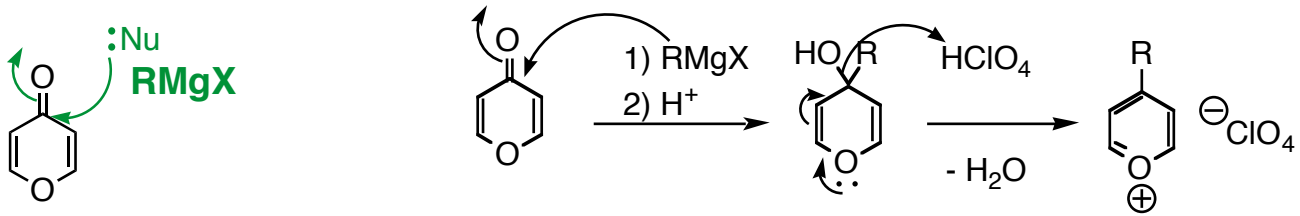


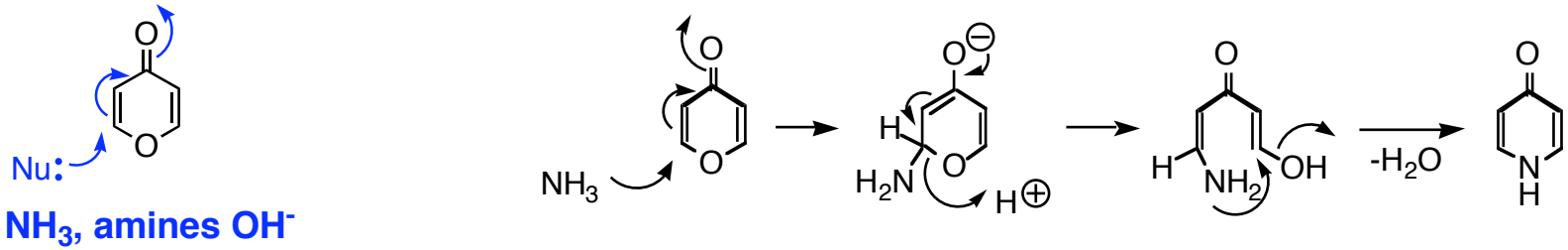


NH_3, amines CN^-



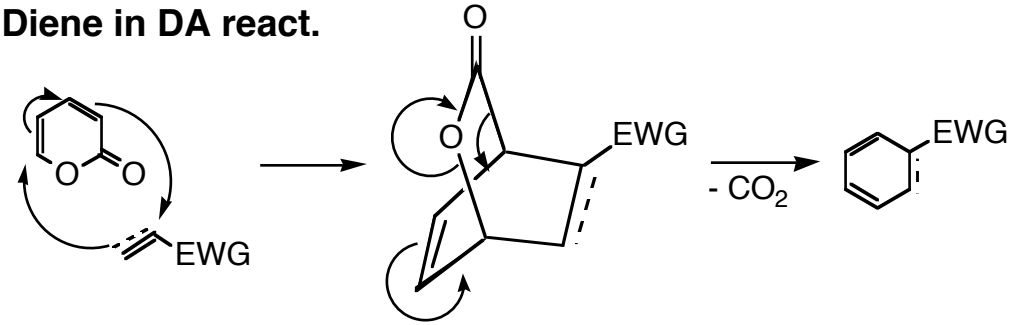
Reactions with Nucleophiles



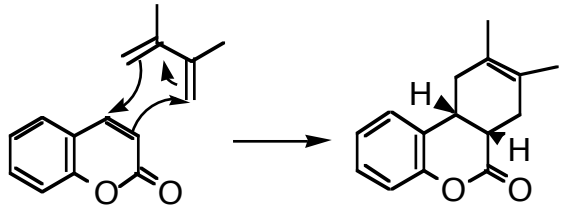


Cycloadditions

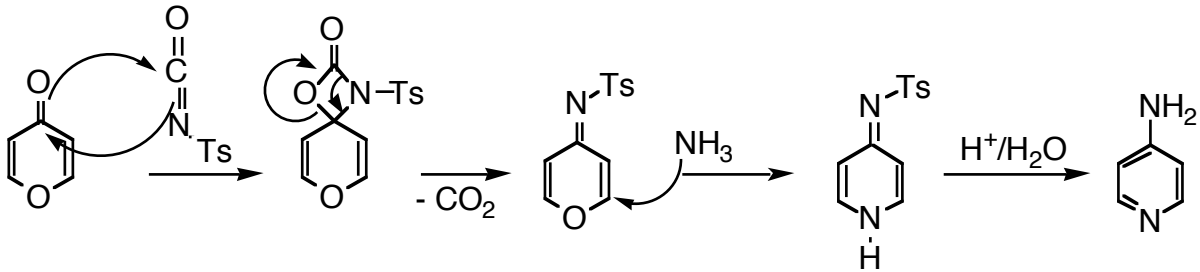
Diene in DA react.



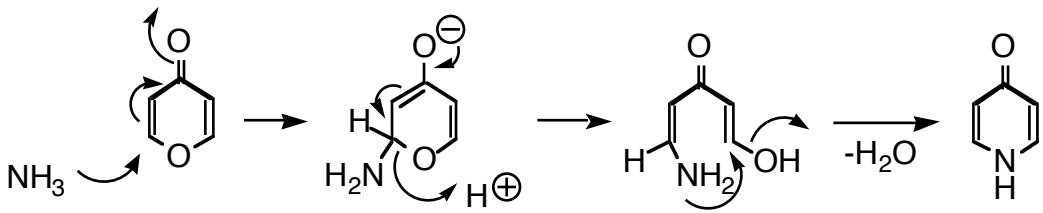
Dienophile in DA



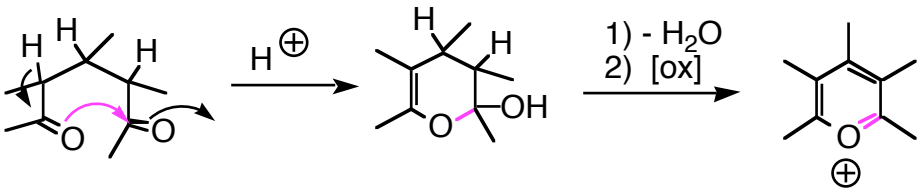
[2+2] with tosyl isocyanate

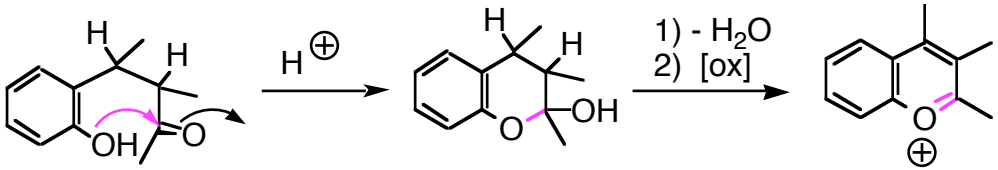


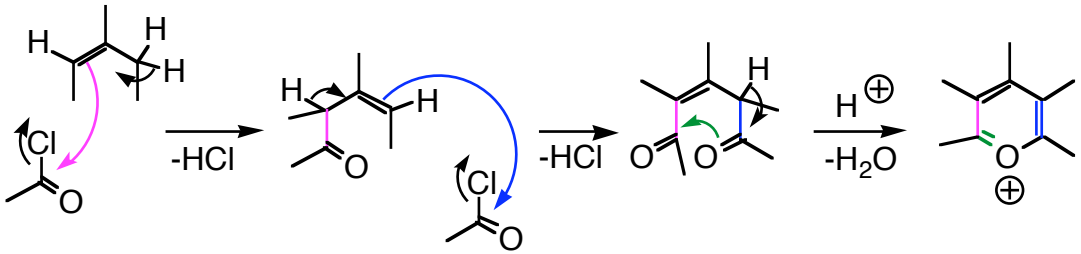
c.f. NH_3 add to 4-pyrones



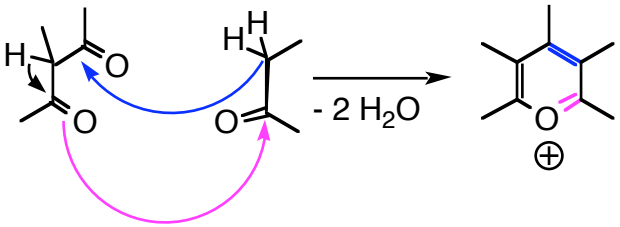
Synthesis - Pyrylium

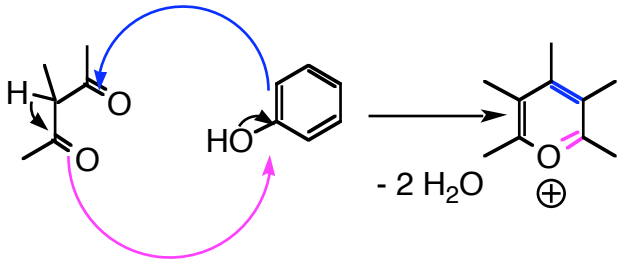




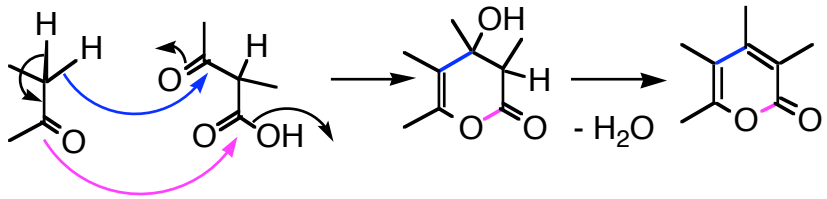


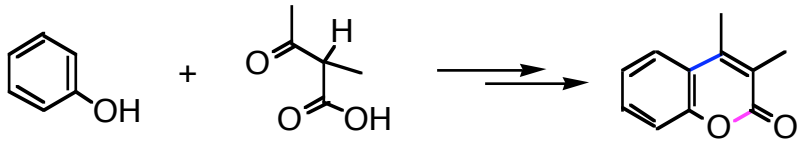
Synthesis - Pyrylium

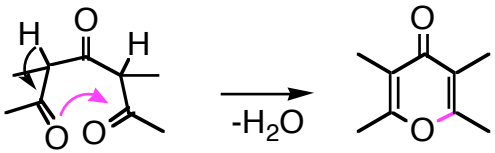


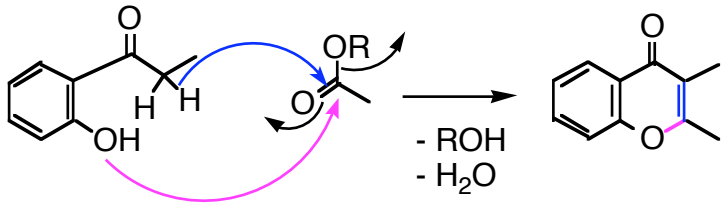


Synthesis - Pyrones

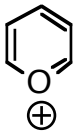




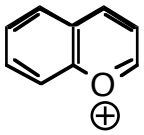




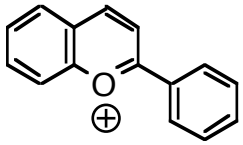
Natural products etc.



Pyrilium



Chromylium



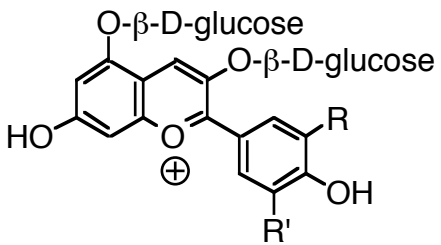
Flavylium

Anthocyanines:

- Gycosides of polyhydroxyflavylium (Aglycon = anthocyanidin)

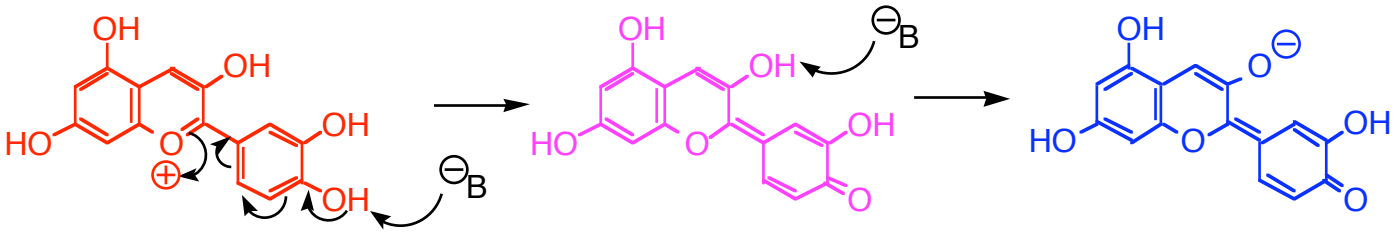
- Colored (red / violet / blue) pigments, red / blue flowers, blueberries, grapes (red wine) etc.

- Antioxidants - Polyphenols - Radical scavengers

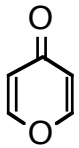


R=OH, R'=H: cyanin
R=R'=OMe: Malvin

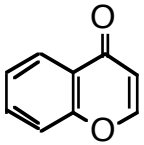
Cyanidine / Cyanidol



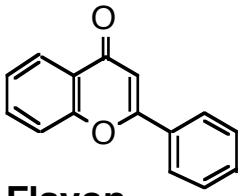
Natural products etc.



4-Pyrone



Chromone

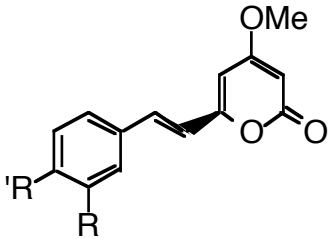


Flavon

Kawapyrones:

- Isolated from Káwa

- Relaxing drug used in Polynesia

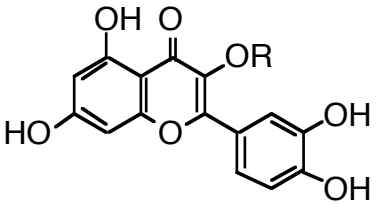


Flavonoids:

- Gycosides of polyhydroxyflavon

- Colored (yellow) pigments in plants

- Antioxidants Polyphenols - Radical scavengers

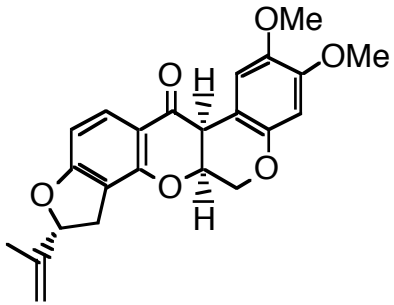


R=H: Quercetin
R= L-Rhamnose: Quercetrin
R= D-Glucose-L-Rhamsone: Rutin

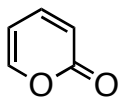
Rothenone

-Insecticide

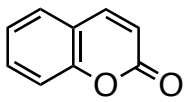
-Parasites in rivers



Natural products etc.

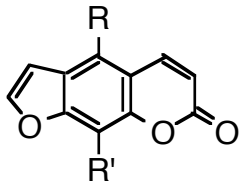


2-Pyrone

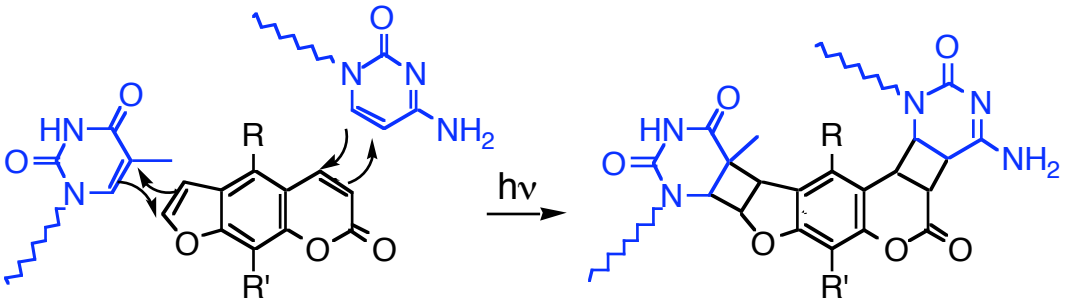


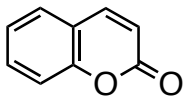
Coumarin

Psoralenes
-Isolated from various plants
-Photochemotherapy against psoriasis
-[2+2] cycloadd. with cytosin / thymin in DNA



R=R'=H: Psoralen
R=H, R'=OMe: Xantotoxin (8-MOP) - Metoksalen - Geroxalen$^{(R)}$

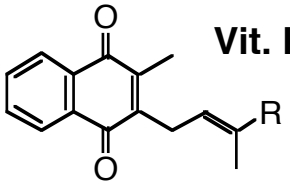




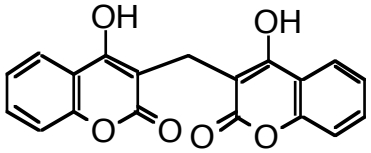
Coumarin

Dicoumarol
-Anticoagulant - Vit K antagonist
-Sweet clower disease

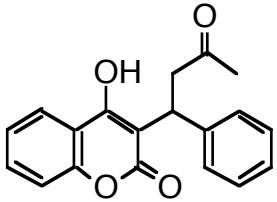
Sweet clover (*Melilotus officinalis*)

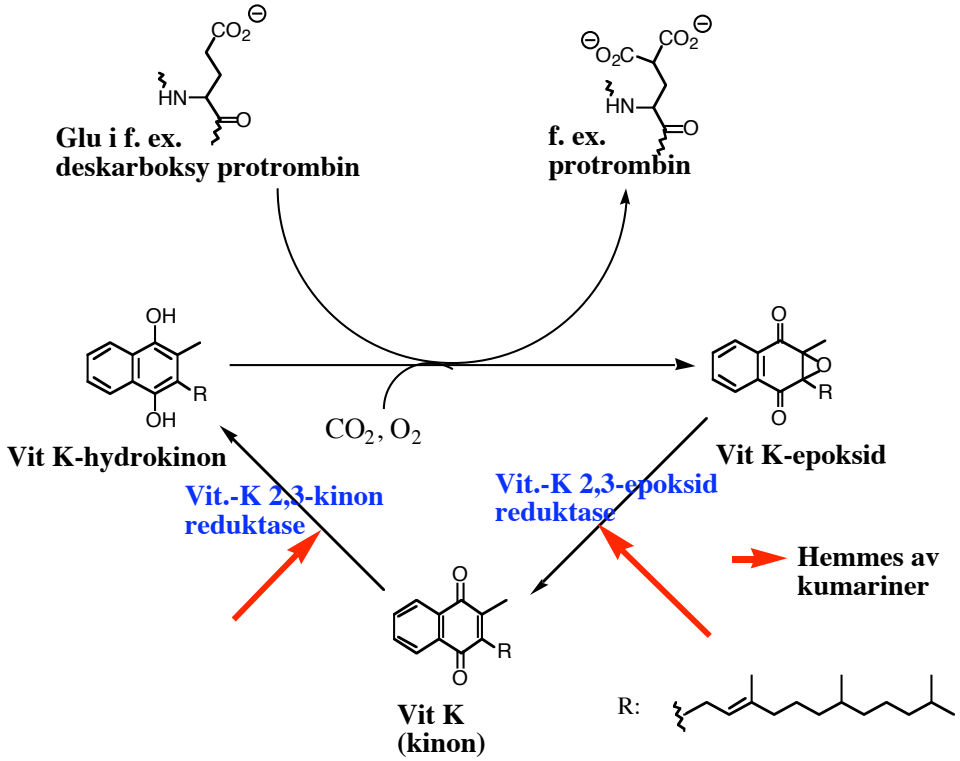


Vit. K

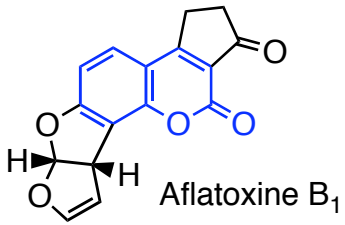


Warfarin - Marevan®





Aflatoxines
-From *Aspergillus flavus* (fungus)
-Attacks nuts etc.
-Carcinogenic



Aflatoxine B_1