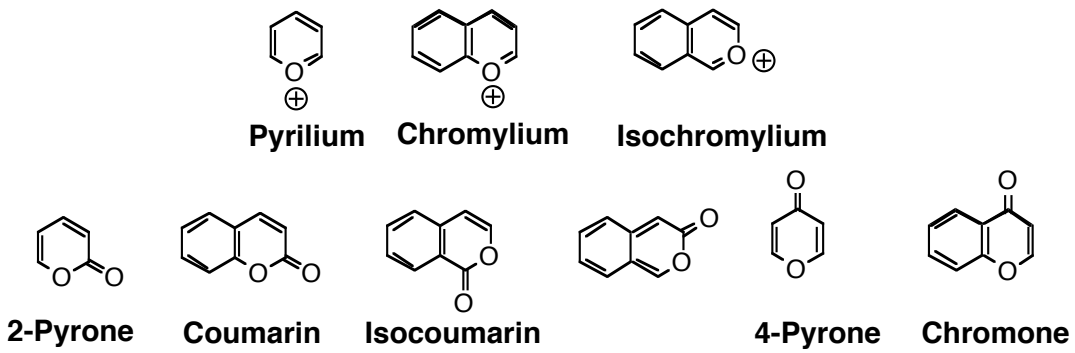
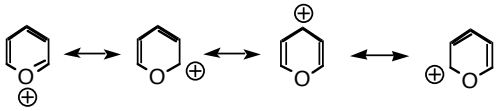
PYRYLIUM IONS AND PYRONES
(chapt 7-9)

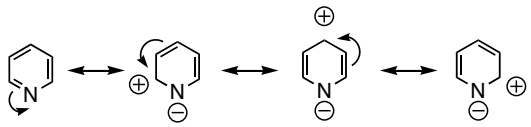


PYRYLIUM IONS



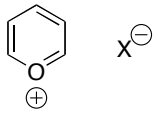
Aromatic - Reactive
Counter ion often ClO_4^-

c.f.:



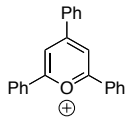
Electron deficient ring:

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

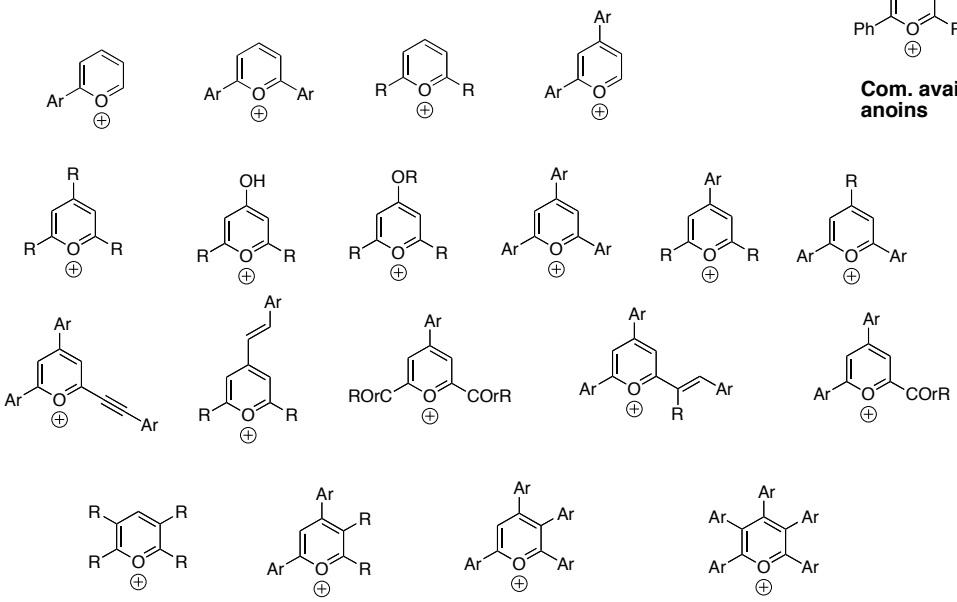


X=ClO_4: 36 refs in SciFinder
X=BF_4: 16 refs in SciFinder

Com. avail. (SciFinder) ca 170 in 2007



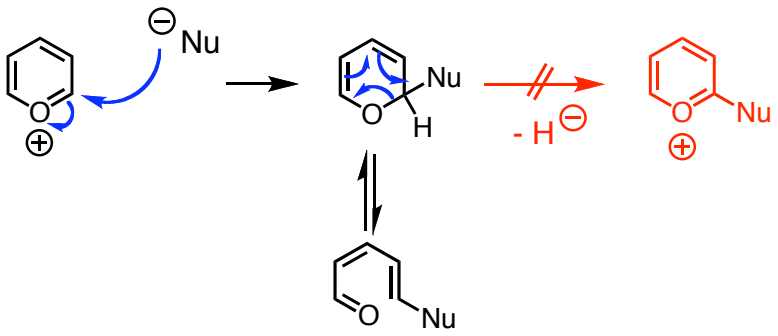
Com. avail. with 12 diff. anoins



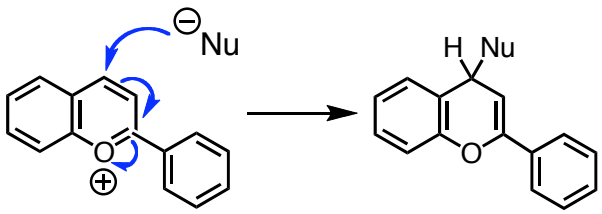
Reactions with nucleophiles

1,2-Add. - Ring opening!

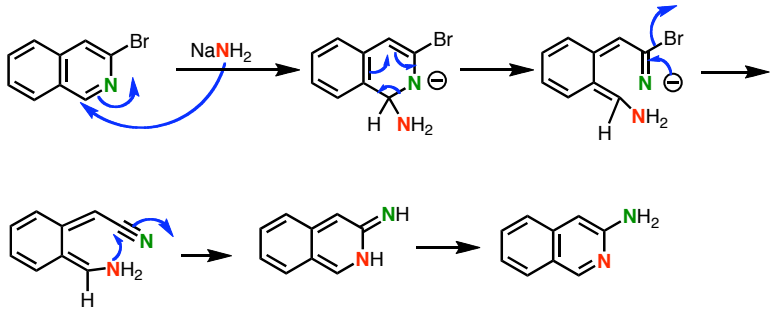
Nu: Water, alcohols, ammonia, amines, organometallics / carbanions, Wittig reagents hydrides



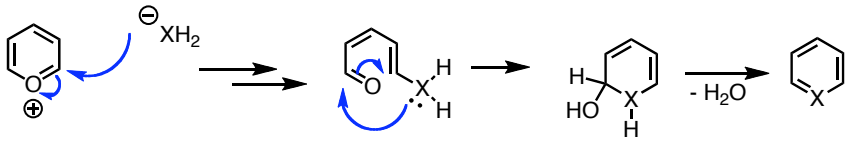
1,4-add. common on flavylium

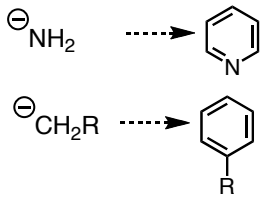


ANRORC (add. of Nu., Ring Opening and Ring Closure)



Nu = -XH$_2$ (-NH$_2$, -CH$_2$R)





More stable aromatic rings

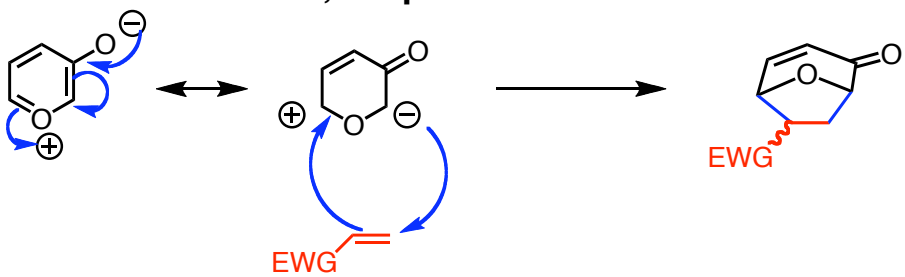
Good yields

Availability starting material

Cycloadditions

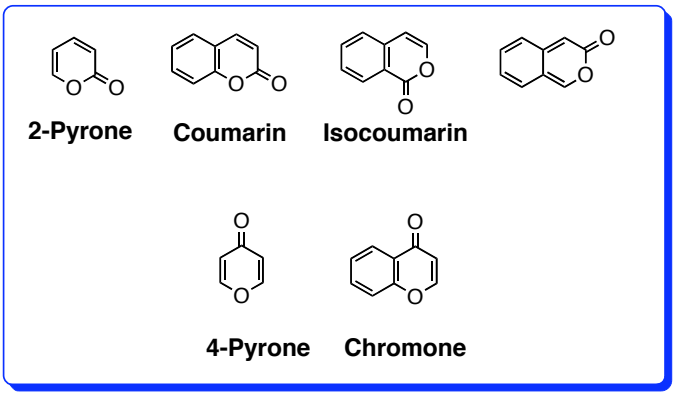
3-oxidopyryliums

1,3-Dipol

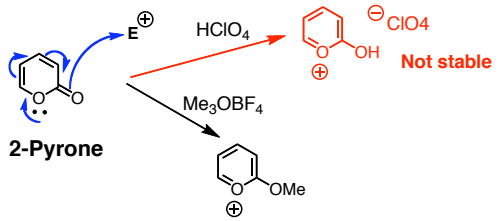


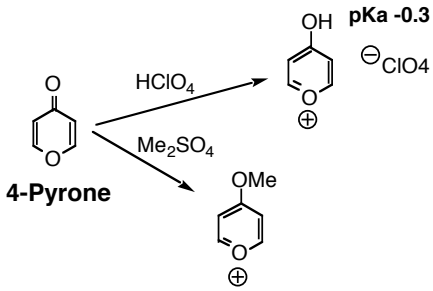
Further transformations to 7-membered rings

Pyrones



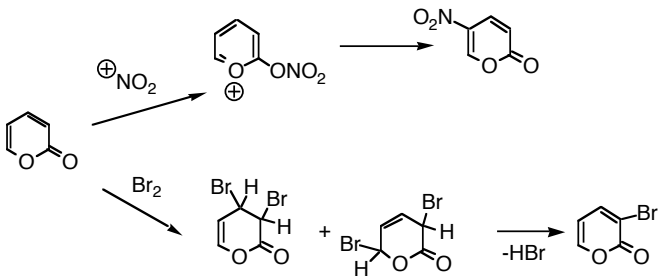
Reactions with Electrophiles





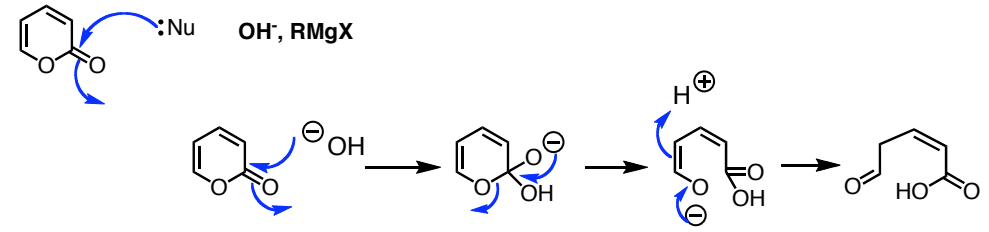
No E-fil Ar Subst

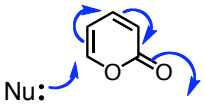
E-fil Aromatic Substitution like products, but by other mechanisms



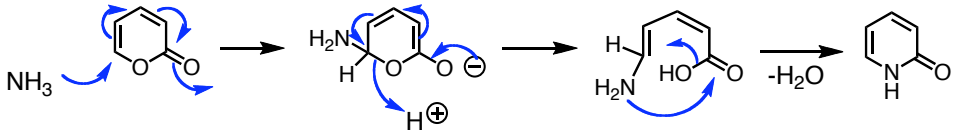
Reactions with Nucleophiles

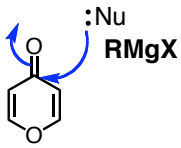
lactone

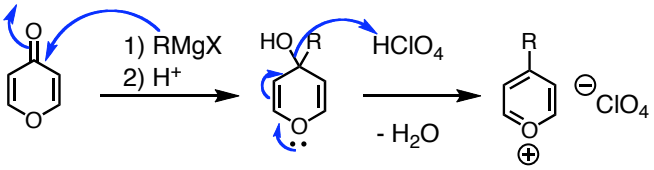


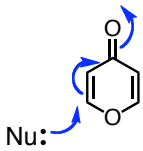


NH_3, amines, CN^-

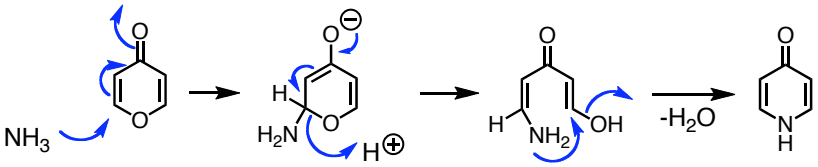






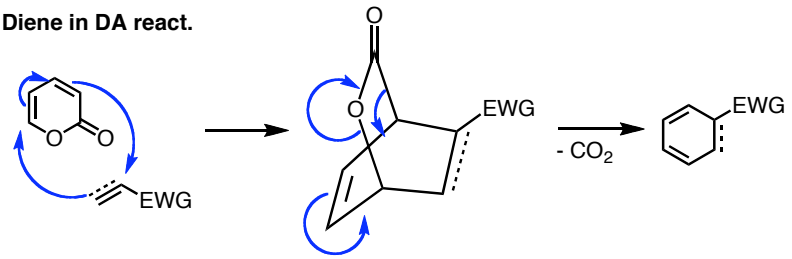


NH_3, amines OH^-

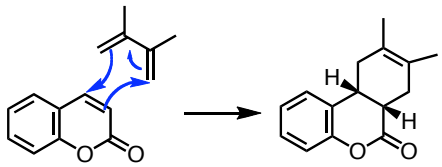


Cycloadditions

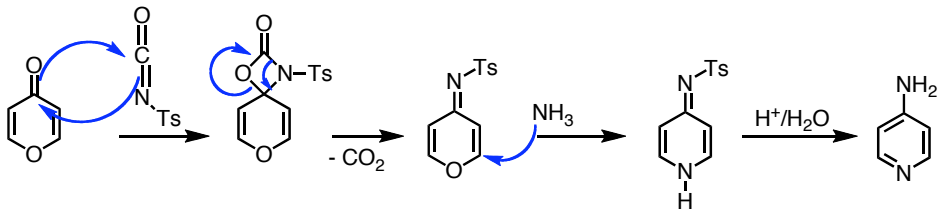
Diene in DA react.



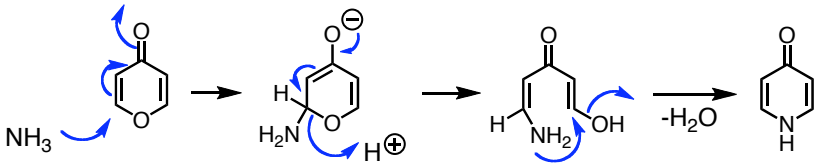
Dienophile in DA



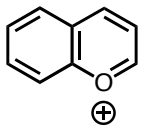
[2+2] with tosyl isocyanate



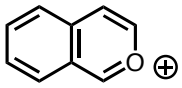
c.f. NH_3 add to 4-pyrones



Benzopyrilium

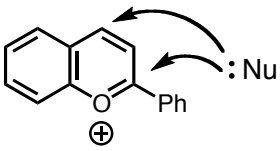


Chromylium



Isochromylium

No E-fil Ar subst in benzene ring (in contrast to (iso)quinolines)

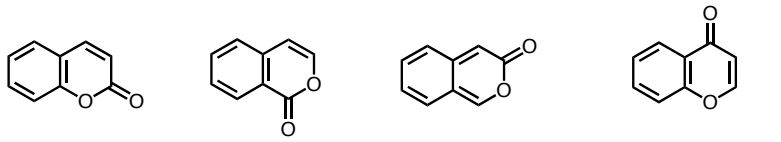


Flavylium

Selectivity?

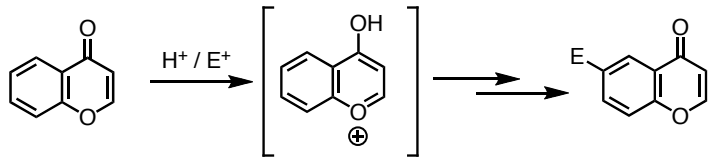
- **ROH at C-4 u. mild cond**
- **Ammonia / amines mixt**
- **Soft carbanions at C-4**
- **NB! C-2 attack leads to ring opening**

Benzopyrones



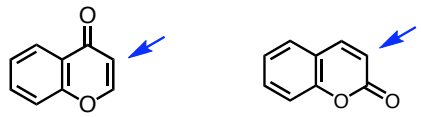
Coumarin **Isocoumarin** **Chromone**

React with E-files



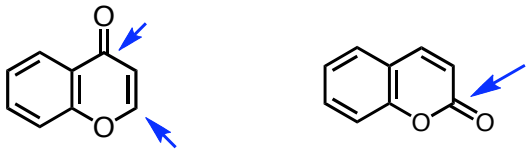
intermed. strongly acidic cond.

(also subst. in benzene ring for coumarines u. acidic cond)



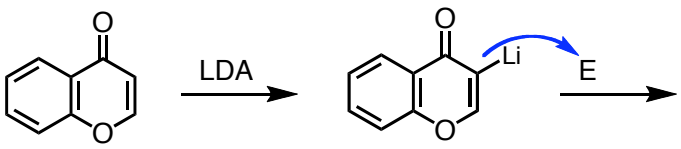
Reacts with E-files u neutral conditions

React with Nu-files

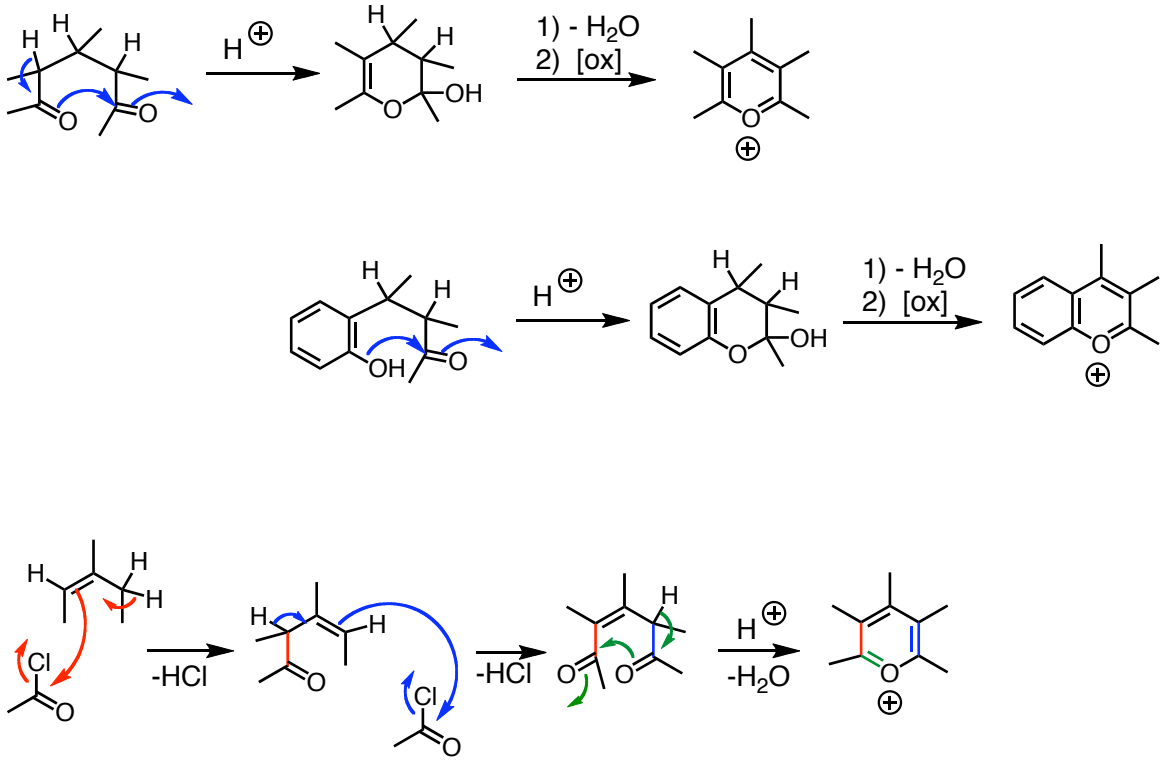


Reacts with Nu-files (ring openings)

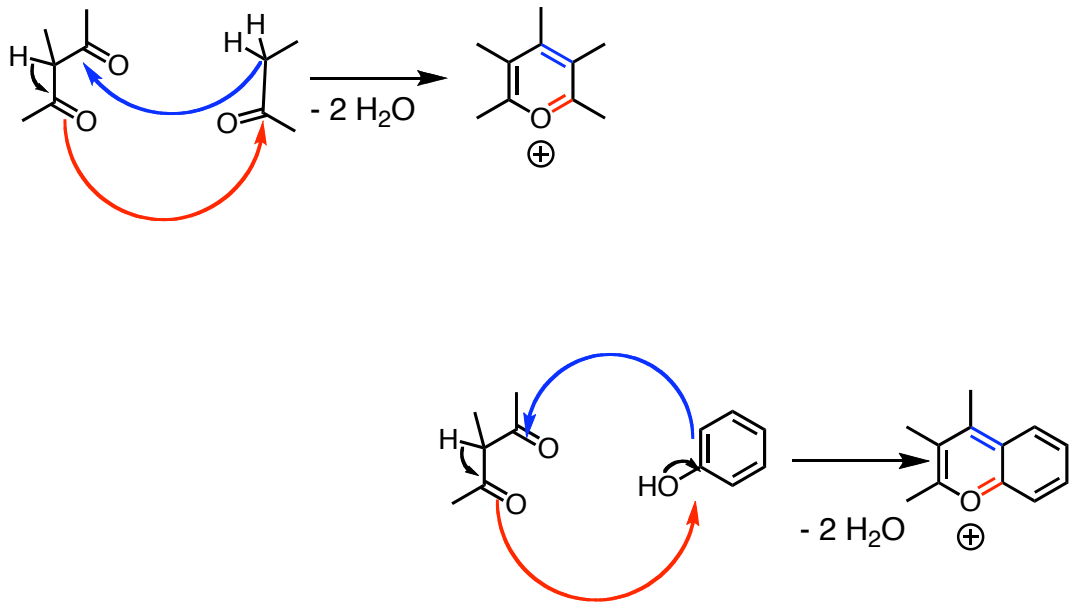
Metallation



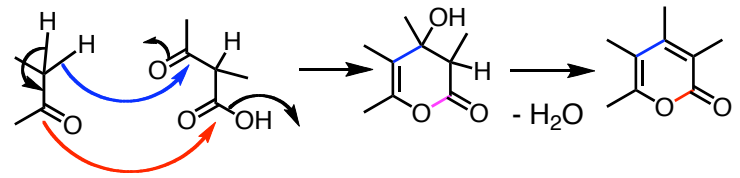
Synthesis - Pyrylium

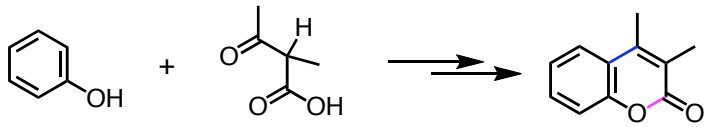


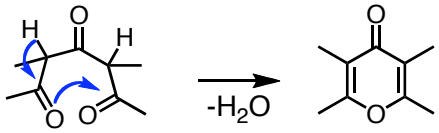
Synthesis - Pyrylium

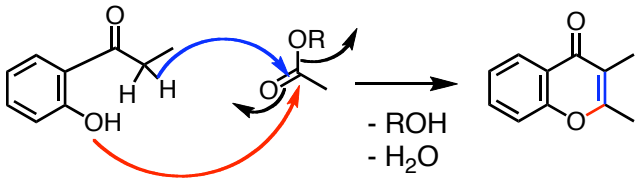


Synthesis - Pyrones

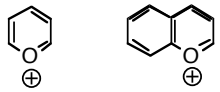




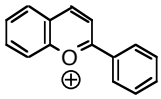




Natural products etc.



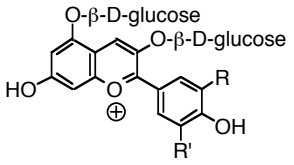
Pyrilium **Chromylium**



Flavylium

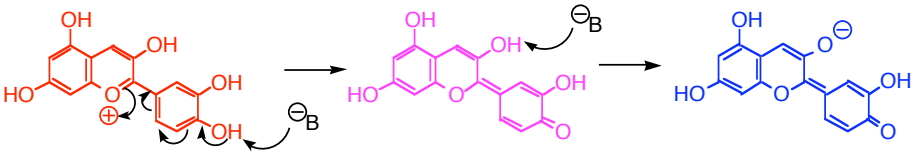
Anthocyanines:

- **Gycosides of polyhydroxyflavylium (Aglycon = anthocyanidin)**
- **Colored (red / violet / blue) pigments, red / blue flowers, blueberries, grapes (red wine) etc.**
- **Antioxidants - Polyphenols - Radical scavengers**

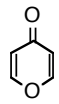


R=OH, R'=H: cyanin
R=R'=OMe: Malvin

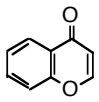
Cyanidine / Cyanidol



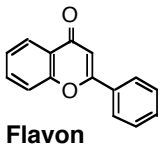
Natural products etc.



4-Pyrone

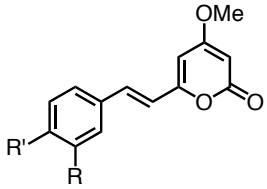


Chromone

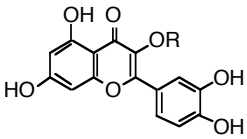


Flavon

Kawapyrones:
- **Isolated from Káwa**
- **Relaxing drug used in Polynesia**

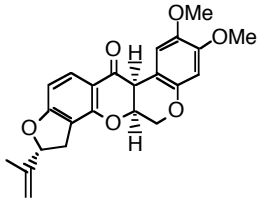


Flavonoids:
- **Gycosides of polyhydroxyflavon**
- **Colored (yellow) pigments in plants**
- **Antioxidants Polyphenols - Radical scavengers**



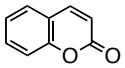
R=H: Quercetin
R= L-Rhamnose: Quercetrin
R= D-Glucose-L-Rhamsone: Rutin

Rothenone
-Insecticide
-Parasites in rivers



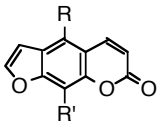
Natural products etc.

2-Pyrone

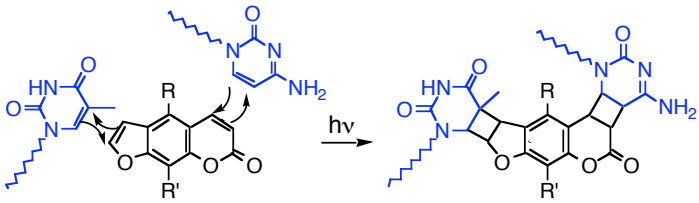


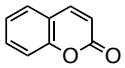
Coumarin

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

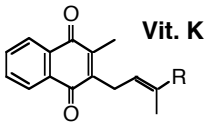


R=R'=H: Psoralen
R=H, R'=OMe: Xantotoxin (8-MOP) - Metoksalen - Geroxalen(R)



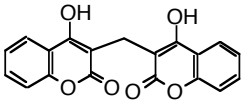


Coumarin



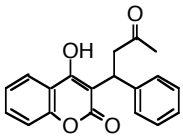
Vit. K

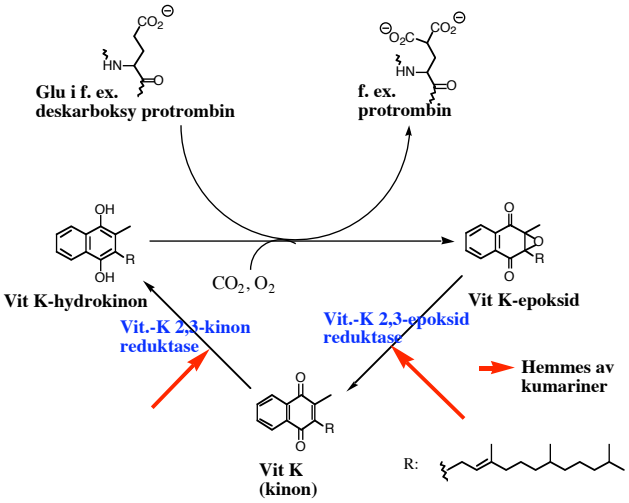
Dicoumarol
-Anticoagulant - Vit K antagonist
-Sweet clower disease



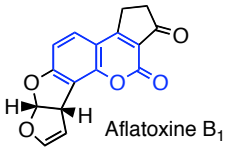
Sweet clover (*Melilotus officinalis*)

Warfarin - Marevan®





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



Aflatoxine B_1