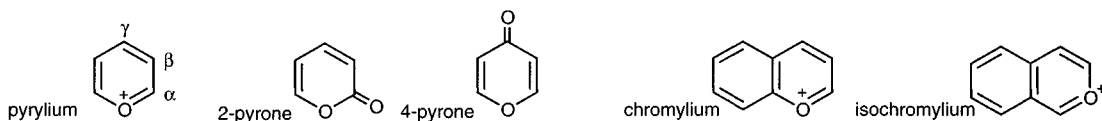
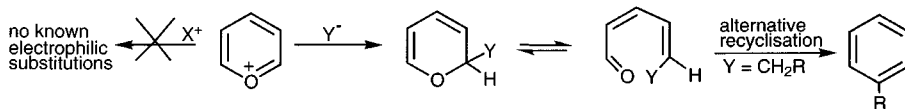


# 7 Typical reactivity of pyrylium and benzopyrylium ions, pyrones and benzopyrones



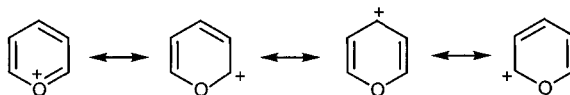
The pyrylium cation presents an intriguing dichotomy – it is both ‘aromatic’, and therefore, the beginning student would be tempted to understand, ‘stable’, yet it is very reactive – the tropylium cation and the cyclopentadienyl anion can also be described in this way. However, all is relative, and that pyrylium cations react rapidly with nucleophiles to produce adducts which are not aromatic, is merely an expression of their relative stability – if they were not ‘aromatic’ it is doubtful whether such cations could exist at all. Pyrylium perchlorate is surprisingly stable – it does not decompose below 275 °C but, nonetheless, it will react with water, even at room temperature, producing a non-aromatic product.

Typical pyrylium reactivities



The properties of pyrylium cations are best compared with those of pyridinium cations: the system does not undergo electrophilic substitution nor, indeed, are benzopyrylium cations substituted in the benzene ring. This is a considerable contrast with the chemistry of quinolinium and isoquinolinium cations and is a comment on the stronger deactivating effect of the positively charged oxygen.

Pyrylium ions readily add nucleophilic reagents, at an  $\alpha$ -position, generating 1,2-dihydropyrans which then often ring open. Virtually all the known reactions of pyrylium salts fall into this general category. Often, the initial product of ring opening also subsequently and spontaneously takes part in an alternative ring closure, generating a benzenoid aromatic system (if Y contains active hydrogen attached to carbon) or a pyridine (if Y is an amine nitrogen).

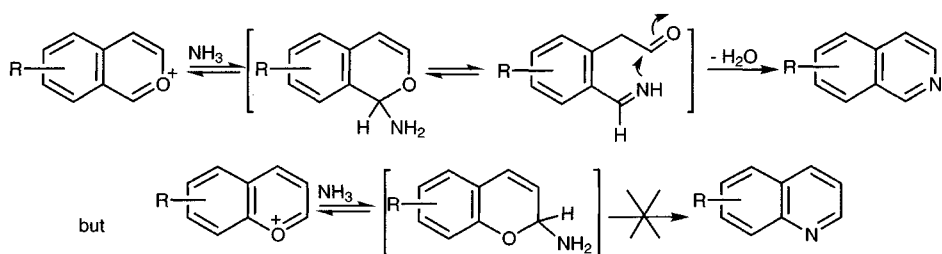


Resonance contributors to the pyrylium cation show that there is greater positive charge at the  $\alpha$ - and  $\gamma$ -positions, but nearly all of the known nucleophilic additions take place at an  $\alpha$ -position. It is relevant to recall here the greater influence of the heteroatom positive charge on pyridine  $\alpha$ -positions versus the  $\gamma$ -position. Pyrylium is more reactive in such nucleophilic additions than pyridinium – oxygen tolerates a positive charge less well than nitrogen. It is worth pointing out again the analogy with carbonyl chemistry – the nucleophilic additions which characterise pyrylium

systems are nothing more nor less than those which occur frequently in acid-catalysed (*O*-protonated) chemistry of carbonyl groups.

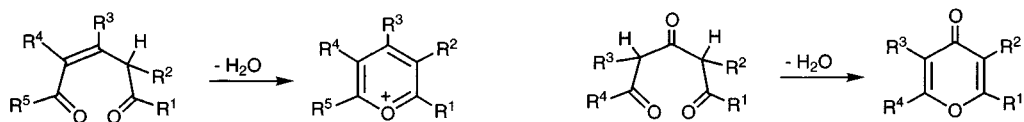


Turning to benzopyrylium systems, one finds exactly comparable behaviour – a readiness to add nucleophiles, adjacent to the positively charged oxygen, in the heterocyclic ring. The interaction of the two isomeric bicycles with ammonia is instructive: one can be converted into an isoquinoline, the other cannot be converted into a quinoline for, although in the last case the addition can and does take place, in the subsequent ring-opened species, no low energy mechanism is available to allow the nitrogen to become attached to the benzene ring.



Pyrones, which are the oxygen equivalent of pyridones, are simply  $\alpha$ - and  $\gamma$ -hydroxypyrylium salts from which an *O*-proton has been removed. There is little to recommend that 2- and 4-pyrones be viewed as aromatic: they are perhaps best seen as cyclic unsaturated lactones and cyclic  $\beta$ -oxy- $\alpha,\beta$ -unsaturated ketones, respectively, for example 2-pyrones are hydrolysed by alkali just like simpler esters (lactones). It is instructive that whereas the pyrones are converted into pyridones by reaction with amines or ammonia, the reverse is not the case – pyridones are not transformed into pyrones by water, or hydroxide. Some electrophilic *C*-substitutions are known for pyrones and benzopyrones, the carbonyl oxygen guiding the electrophile *ortho* or *para*, however there is a tendency for electrophilic addition to a double bond of the heterocyclic ring, again reflecting their non-aromatic nature. Easy Diels-Alder additions to 2-pyrones are further evidence for diene, rather than aromatic, character.

The cyclisation of an unsaturated 1,5-dicarbonyl compound produces pyrylium salts, providing of course that the acidic medium chosen is suitable – it must not contain nucleophilic species which would add to the salt, once formed. Acid-catalysed ring closure of 1,3,5-triketones produces 4-pyrones.



Benzopyrylium salts are formed when phenols react with 1,3-dicarbonyl compounds under acidic, dehydrating conditions. The comparable use of 1,3-ketoesters leads benzopyrones.

