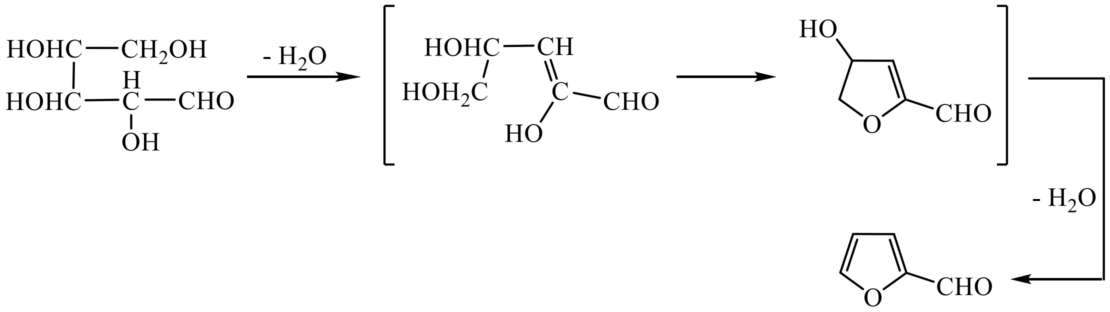
6) Furan:

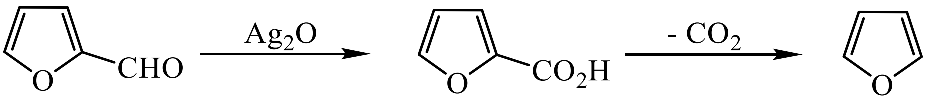
Furan is a colorless, volatile, with pleasant odor (like chloroform). Its boiling point is 31°C, and it is slightly soluble in water but soluble in common organic solvents including alcohol, ether and acetone.

Furan commercial importance is mainly due to its role as the precursor of the very widely used solvent tetrahydrofuran (THF). Furan ring exist in a large number of natural products as the main component; one of these compounds is furfural which manufactured from corn cobs and oat hulls; furthermore acid hydrolysis of polysaccharide produce the pentoses which on loss of water molecule give the furfural that used in the synthesis of polymers, pesticides, fungicides …….. etc.



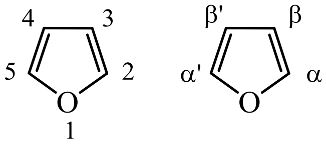
Furfural

In 1877, Baeyer convert furfural to furan via oxidation by silver oxide (Ag_2O).

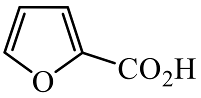


Furfural 2-Furoic acid Furan

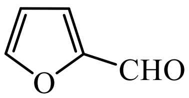
Numbering of the ring proceed with the same manner that used in pyrrole in which the oxygen atom will take number one, furthermore Latin letters α or β have been also used as the following:



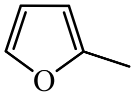
Furan



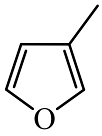
2-Furoic acid



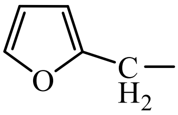
Furfural



2-Furyl



3-Furyl



2-Furfuryl

Since the electronegativity of oxygen atom is higher than nitrogen, thus the contribution of its lone pair of electrons will decrease, so the aromatic character will be less than pyrrole.

6.1) Chemical properties and reactions:

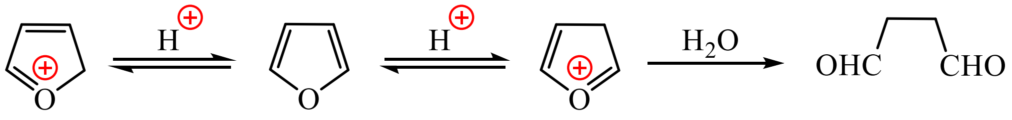
Furan ring is sensitive acidic conditions like enol ether, furthermore they undergoes addition under certain conditions at 2&5 positions like 1,3-conjugated diene. Finally they react with electrophilic reagents at 2&5 positions as in pyrrole.

6.1.1) Effect of acid on furan:

Furan and alkylated furan is more stable than enol ethers toward diluted acids since the lone pair of electrons is delocalized by resonance with π – electrons of the ring.

On the other hand furan ring when treated with concentrated sulfuric acid or Lewis acids will cause ring opening to give succinaldehyde or its substituents.

Note: Lewis acid is a chemical species that has an empty orbital which is capable to accept an electron pair from Lewis base to form Lewis adduct (like $AlCl_3$).

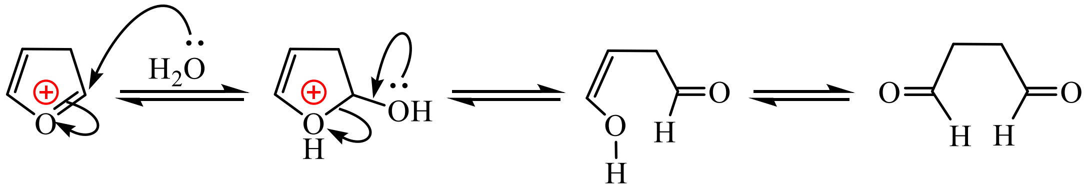


more stable (I)
(α)

less stable (II)
(β)

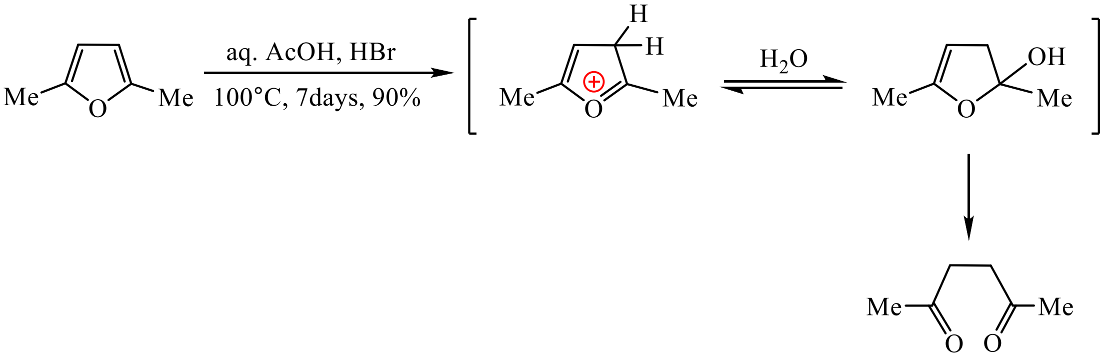
succinaldehyde

The formation of succinaldehyde will proceed as the following:

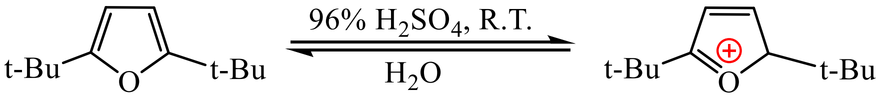


enol succinaldehyde

The following example explains the effect of acids in furan ring:

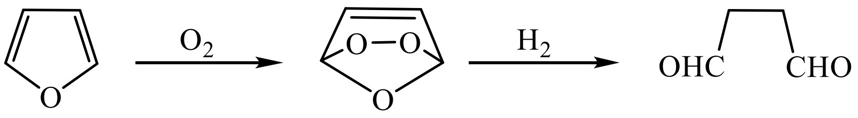


Cation (I) is more stable than (II), and this was proved from (NMR) measurement for the product that formed from the addition of sulfuric acid to 2,5-di-tert-butylfuran, the formed cation is stable at room temperature for 20 days.
Addition of water to the cation will give the starting material.



7.1.2) Addition reactions:

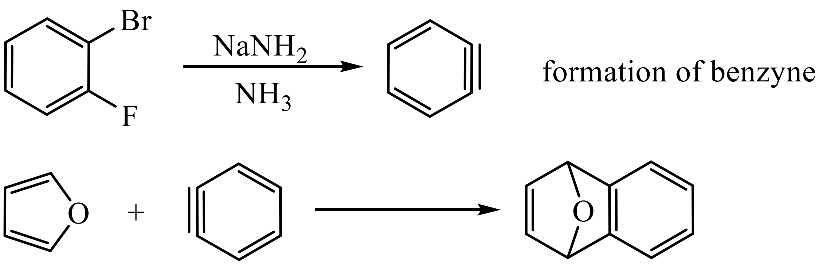
Furan exposure to air will oxidize it to give the peroxides (2,5-addition of oxygen to the ring). These peroxides have been isolated, and their hydrogenation produce succinaldehyde, thus furan is stabilized with small amount of hydroquinone to inhibit the formation of peroxides.



peroxide succinaldehyde

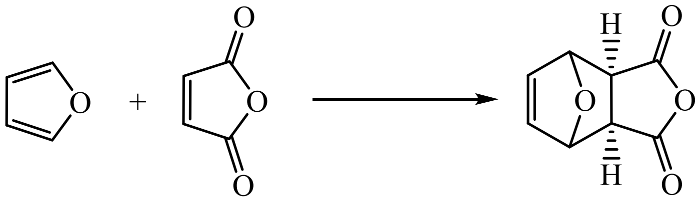
Furthermore furan react as a diene with strong dienophiles like maleic anhydride or benzyne to give Diels – Alder adduct as the following:

1)

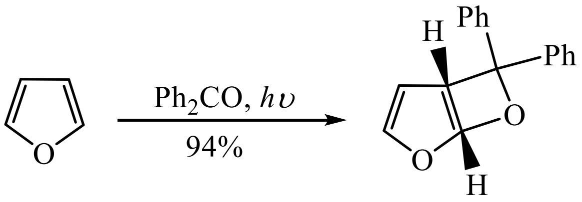


formation of benzyne

2)



Finally the photochemical reaction of furan with di-arylketones (and some aldehydes) afford the cycloaddition product, since the reaction proceeds regeoselectively to give oxetano-dihydrofurans.

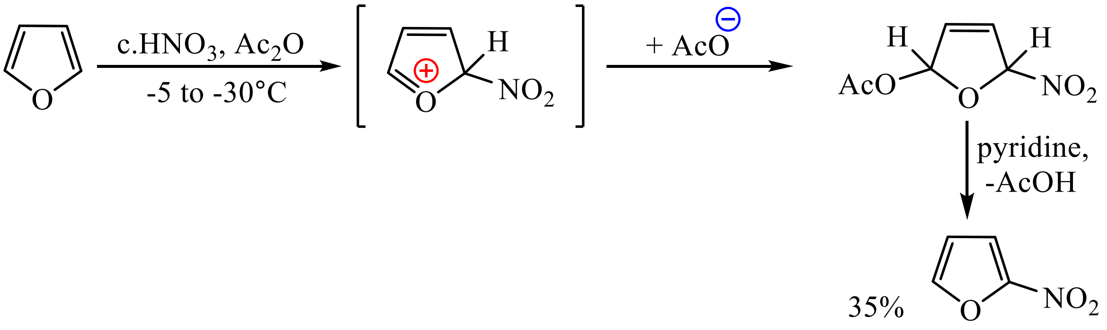


6.1.3) Substitution reaction of furan:

Furan undergoes substitution reaction in the same manner in pyrrole, in which mild conditions have been used, compared with benzene or its derivatives due to the sensitivity of the heterocyclic system toward strong acids or reagents. And here again substitution occurs at C2 or C5 atoms or both of them as the following:

6.1.3.1) Nitration:

Reaction of furan with acetyl nitrate (as a nitrating agent) give 2-nitrofuran as the following:

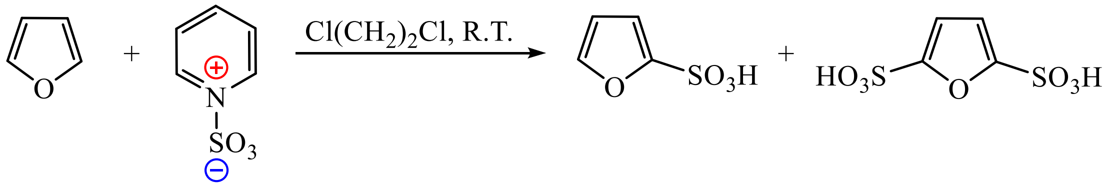


The reaction proceed to give non-aromatic adduct which followed by nucleophilic addition of acetate to the cationic intermediate at C5 atom, followed by loss of acetic acid to give the final substitution product.

Note: Reaction of fuming nitric acid with acetic anhydride at low temperature give acetyl nitrate $AcONO_2$ as a nitrating agent.

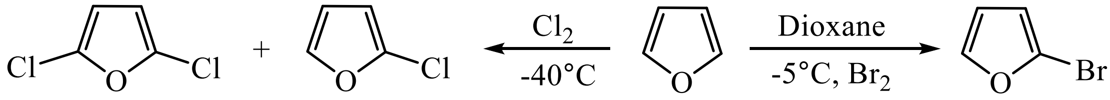
6.1.3.2) Sulfonation:

Furan and its simple alkyl derivatives are decomposed by the usual strong acids (like conc. H_2SO_4), but pyridine sulfurtrioxide (pyridinium sulfonate) complex can be used in the presence of ethylene chloride as a solvent:

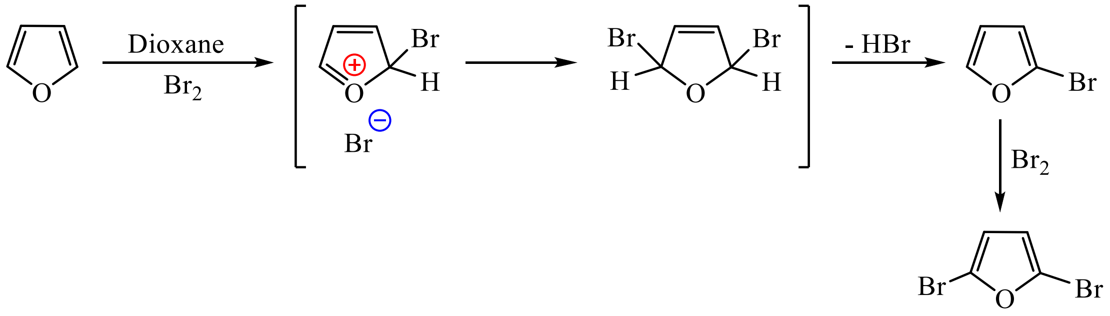


6.1.3.3) Halogenation:

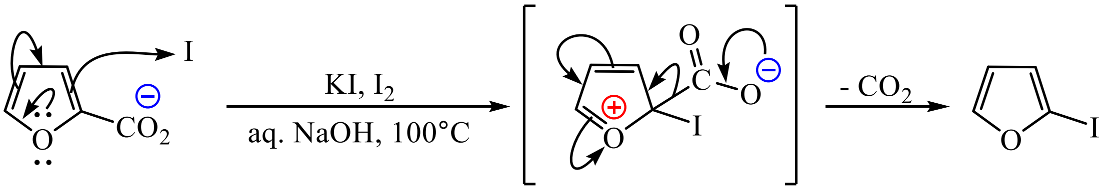
Furan react vigorously with chlorine and bromine but not iodine at room temperature resulting in polymerization due to the evolution of acids (hydrogen halides HX), thus controlled conditions should be used at low temperature (e.g. 0°C , -40°C) to give mono- or di- halo furans.



Bromination reaction proceeds as the following:



On the other hand iodine can be introduced to furan ring by reaction of substituted furan with a mixture of potassium iodide (KI) and iodine (I_2) in which the carboxyl group substituted with iodine.



6.1.3.4) Friedel – Crafts acylation and alkylation:

Traditional Friedel – Crafts acylation or alkylation is not practicable for furan, due to the evolution of hydrogen halides that lead to polymerization. Thus olefins or acetic anhydride have been used for alkylation or acylation respectively instead of alkyl halides or acyl halides.

In these reactions Lewis acids have been used (often boron trifluoride BF_3 or zinc chloride $ZnCl_2$).

e.g.