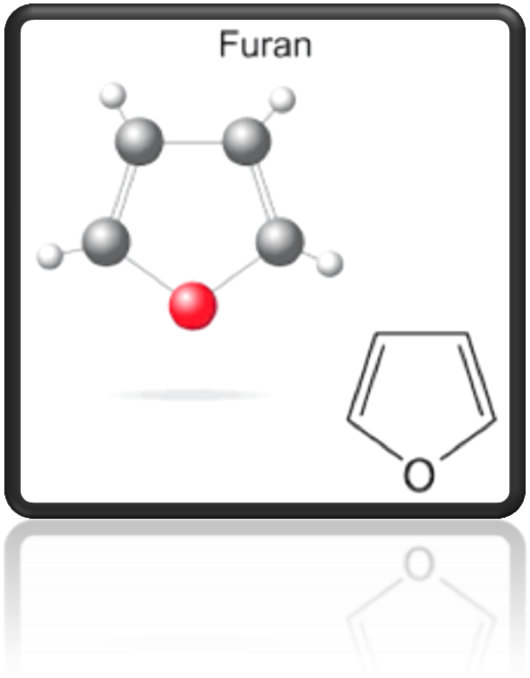
Fayoum Univesity

Heterocyclic Compounds

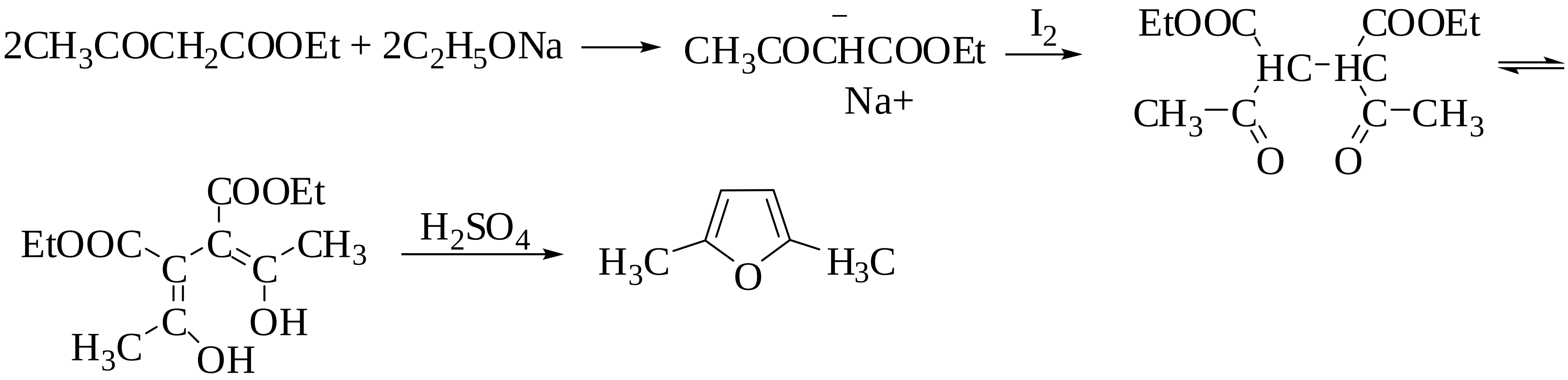


3rd Year Students

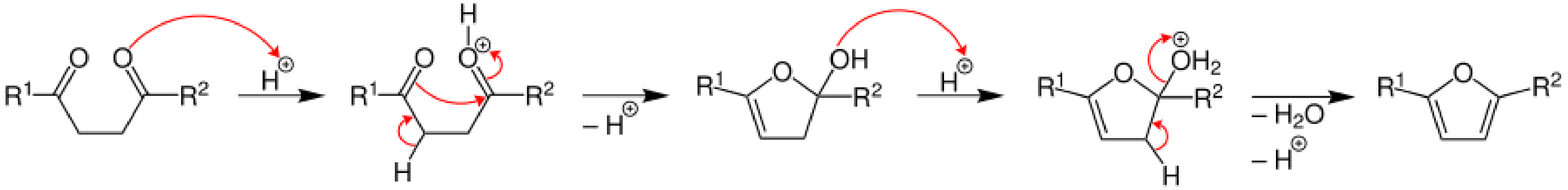
Special Chem, Chem-Phys, Geo-chem, Zoo-Chem, Bot-Chem,

Synthesis Of Furan

1. From cyclodehydration of 1, 4-diketones by acidic reagents, e.g., H_2SO_4, $ZnCl_2$, Ac_2O and P_2O_3

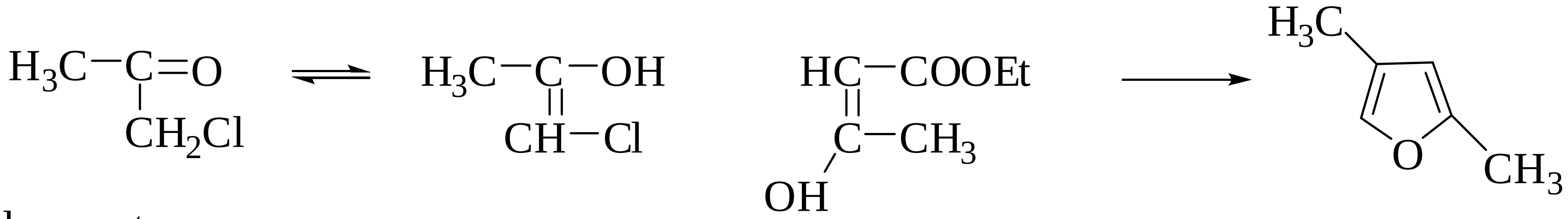


2. From knorr-pyrrole synthesis



Synthesis Of Furan

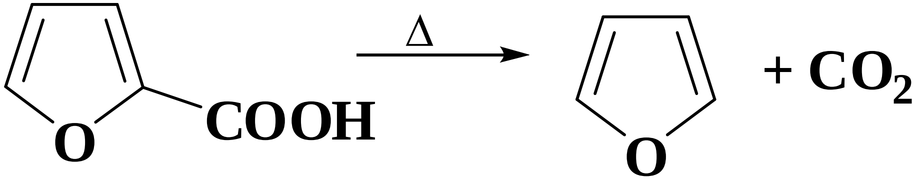
3. Feist's synthesis



Chloroacetone

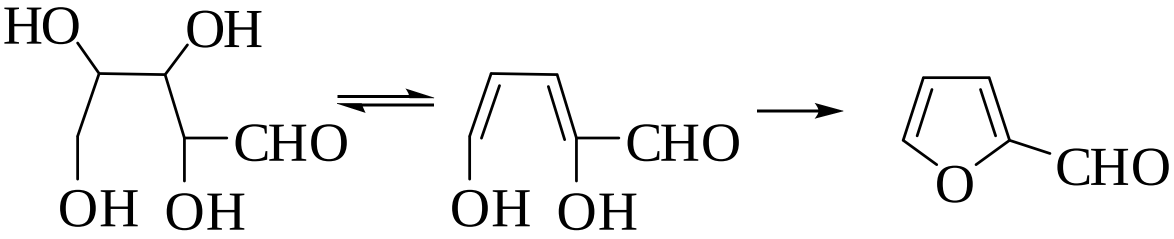
E.A.A

4. From decarboxylation of furoic acid.

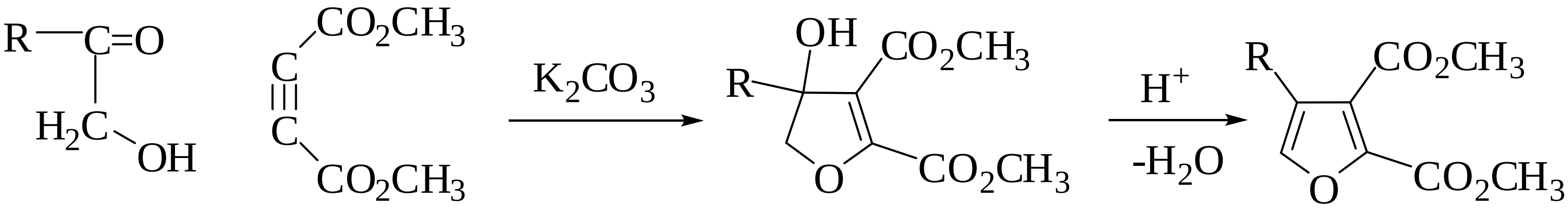


5. Furfural (furan 2-carboxaldehyde)

Furfural is commercially obtained from pentose (occurred in oat hulls) by stream distillation



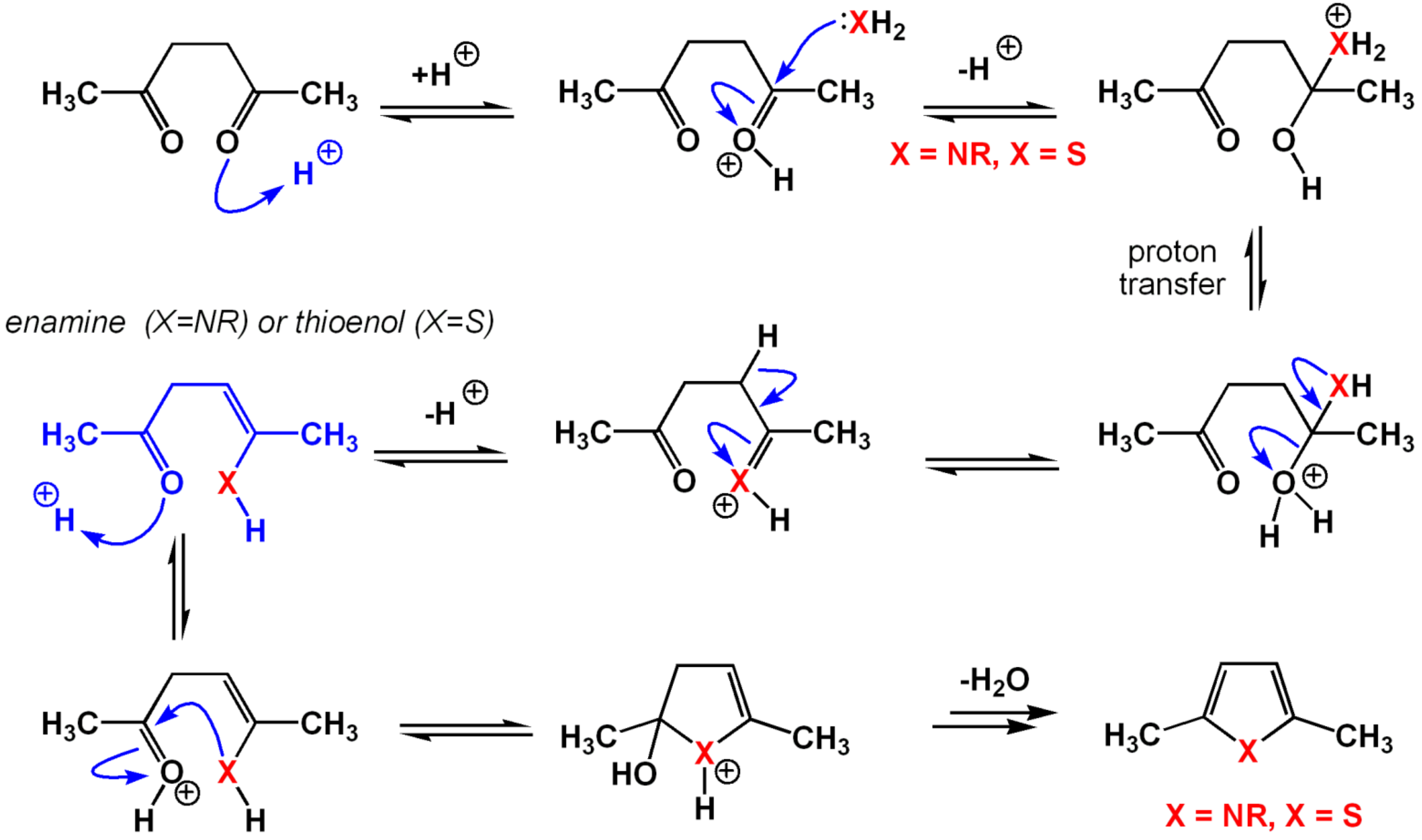
6. By treatment of α-hydroxyketones and acetylenic compounds



Synthesis Of Pyrrole

Paal-Knorr synthesis: pyrroles and thiophenes

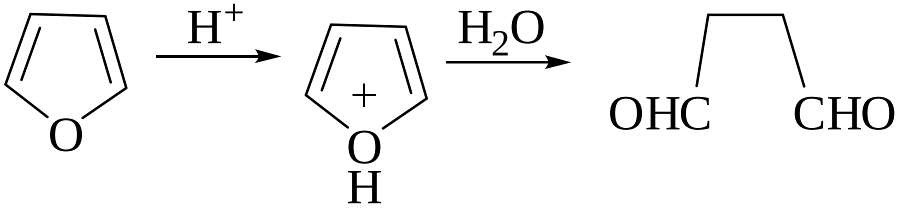
The chemistry involved here is essentially the same as the furan example before, but an enamine or thioenol intermediate is needed.



Reactions Of Furan

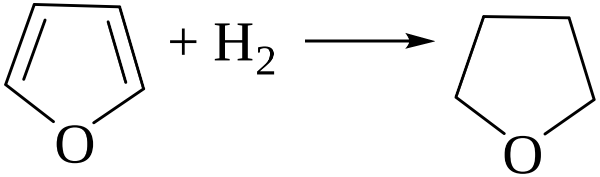
1. Ring opening of furan:

The mildest acidic conditions required to affect the hydrolysis of furan into succinaldehyde to prevent the polymerization



2. Addition reactions of furuan:

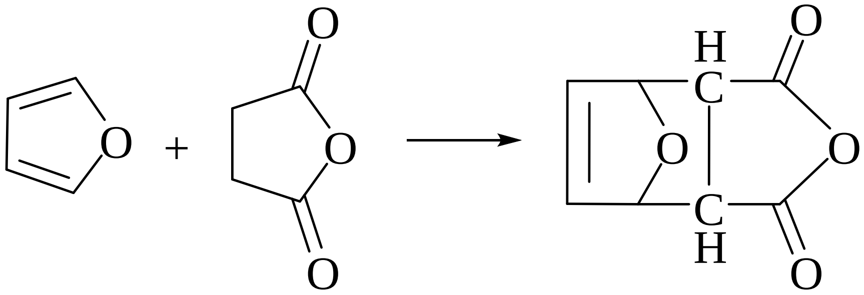
a) Reduction:



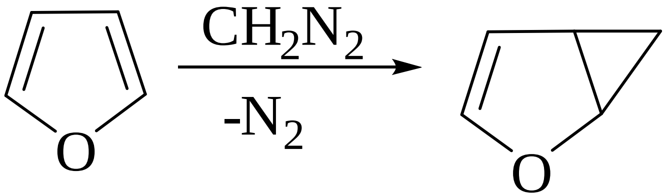
THF

Reactions Of Furan

b) Diels-Alder reaction:

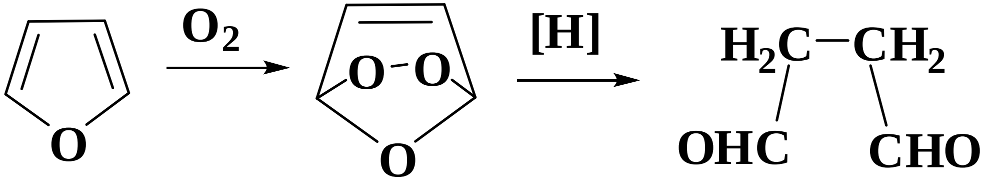


c) Addition of carbenes (with diazomethane):



Reactions Of Furan

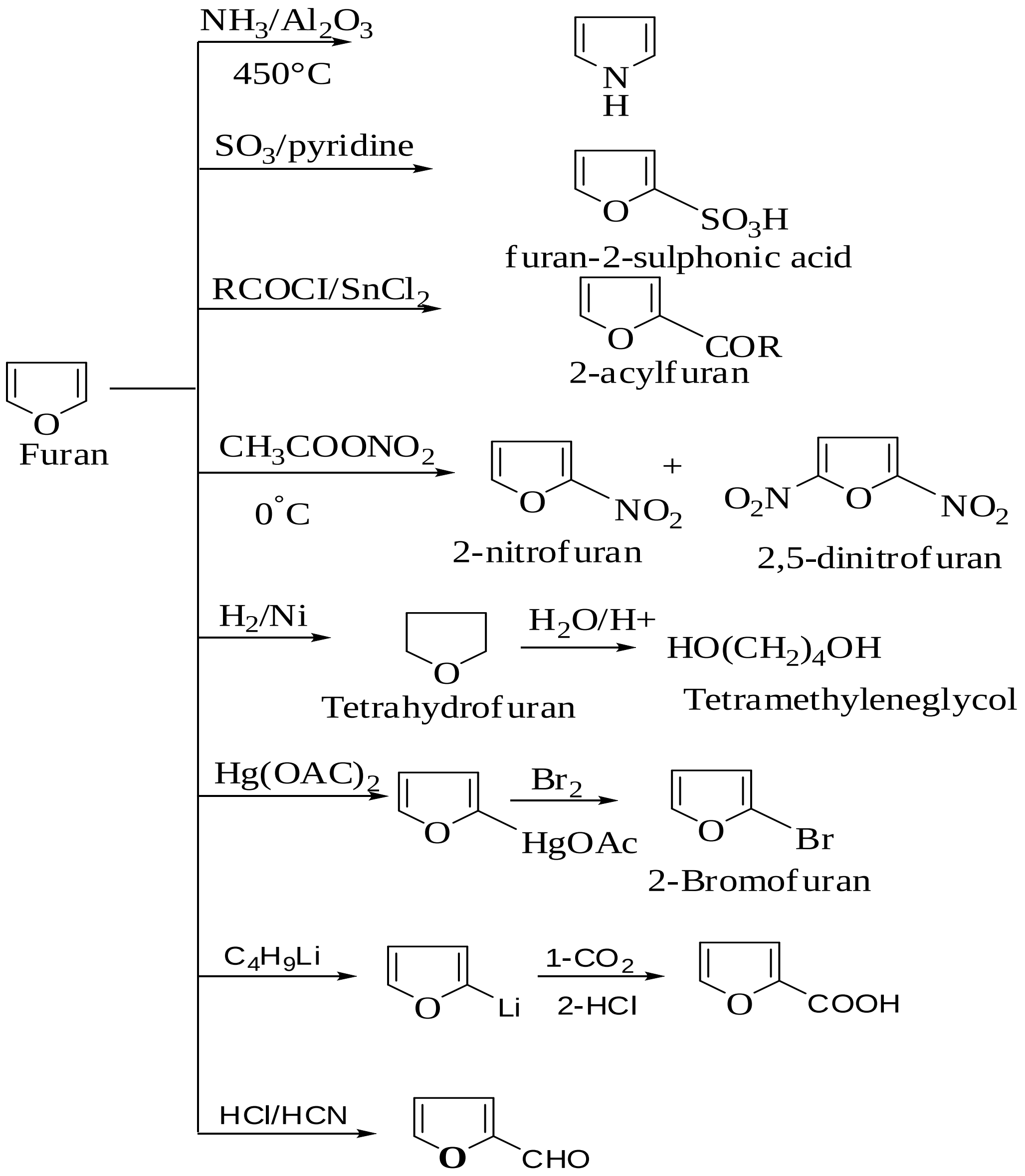
d) Furanis not stable in presence of air and usually stabilized by addition of small amount of hydroquinone. Air oxidation takes place by 2, 5 addition forming peroxide. Hydrogenation of furan peroxide gives succinaldehyde.



3. Electrophilic substitution of furan:

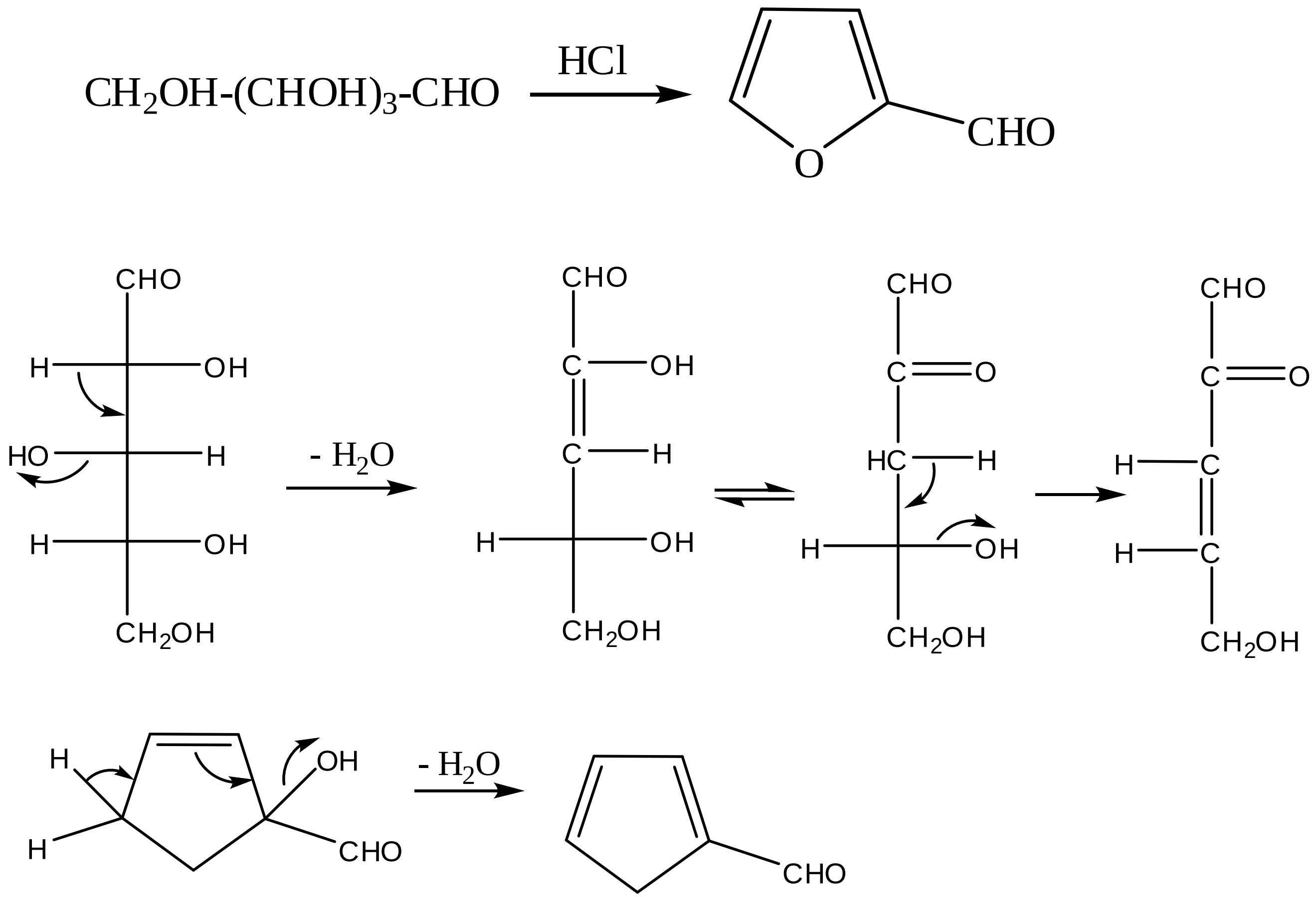
*Furan cannot be directly nitrated with nitric acid (is very readily attack by oxidizing agents). 2-Nitrofuran may be prepared by nitrating furan with acetyl nitrate (CH_3COONO_2). Similarly, furan cannot be directly sulphonated, but 2-sulphonic acid may be prepared by action of SO_3/pyridine on furan.
*If (-I) group is present in the ring, then sulphonation can be carried out directly, e.g., furoic acid gives furoic 5-sulphonic acid.
*Furan reacts readily with halogen, but the liberated (HX) causes polymerization, because of this halogenated furan prepared by indirect method, e.g., by brominating furoic acid and decarboxylating the product, 5-bromofuroic acid to 2-bromofuran by heating in quinolone in the presence of copper bronze. Aluminum chloride attacks furan ring, and Friedel-Crafts is best carried with $SnCl_4$.

Reactions Of Furan



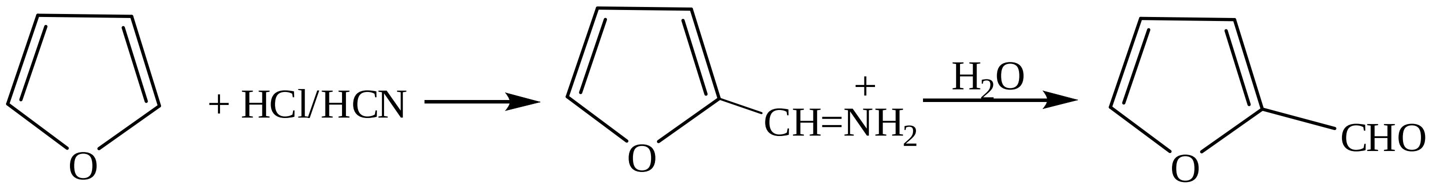
Synthesis Of Furfural

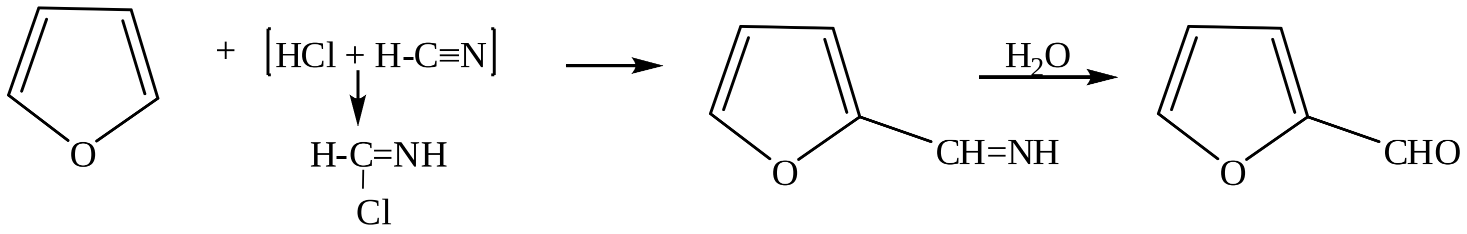
1. From dehydration of aldopentoses



Synthesis Of Furfural

2. From Gattermann’s reaction:

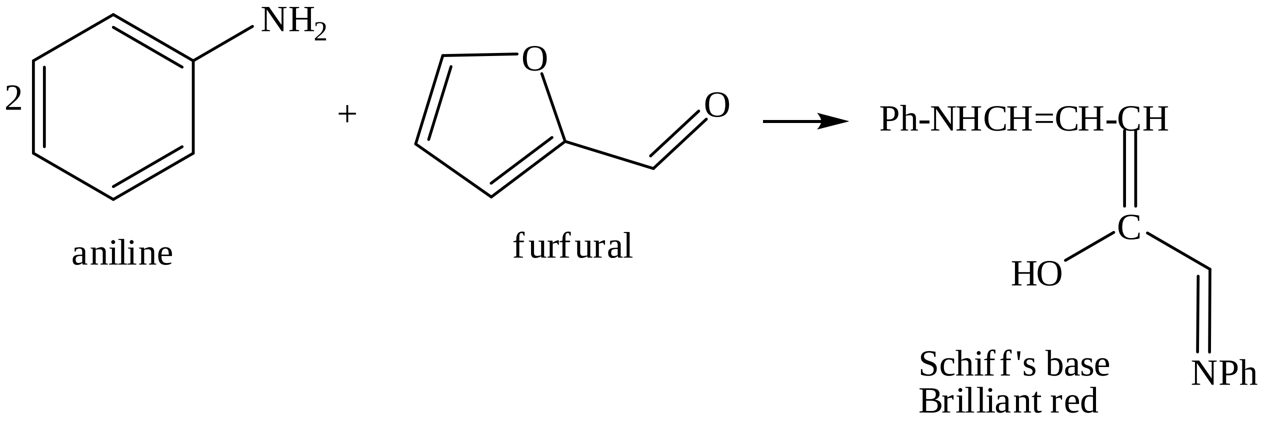




Reactions Of Furfural

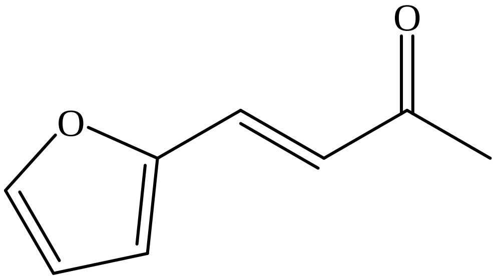
Furfural is chemically very similar to benzaldehyde as the following

1. It undergoes oxidation (KMnO4) to furoic acid.
2. When it was submitted to react with sodium hydroxide it undergoes cannizzaro reaction and gives a mixture from furfuryl alcohol and sodium salt of furoic acid.
3. It under goes benzoin condensation and gives furoin.
4. It reacts with aniline in the presence of acetic acid and gives Schiff's base.



Reactions Of Furfural

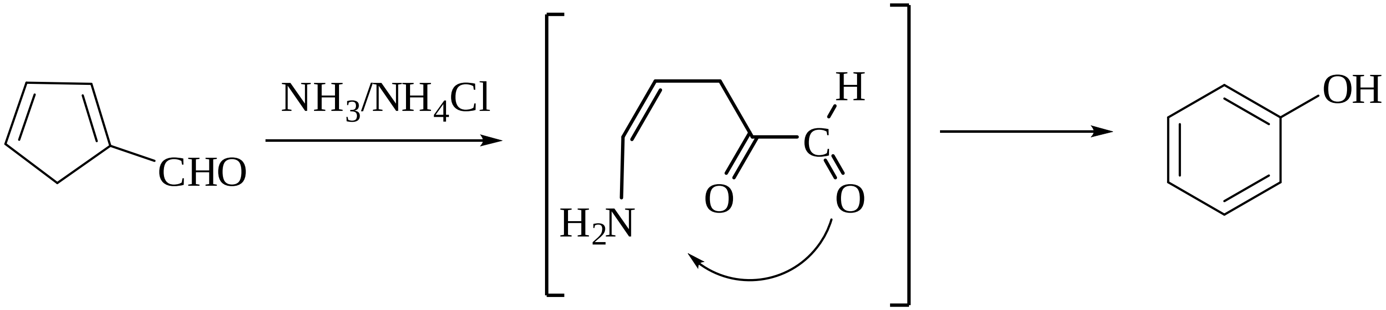
5. It reacts with acetone and yields furfurylidene acetone.



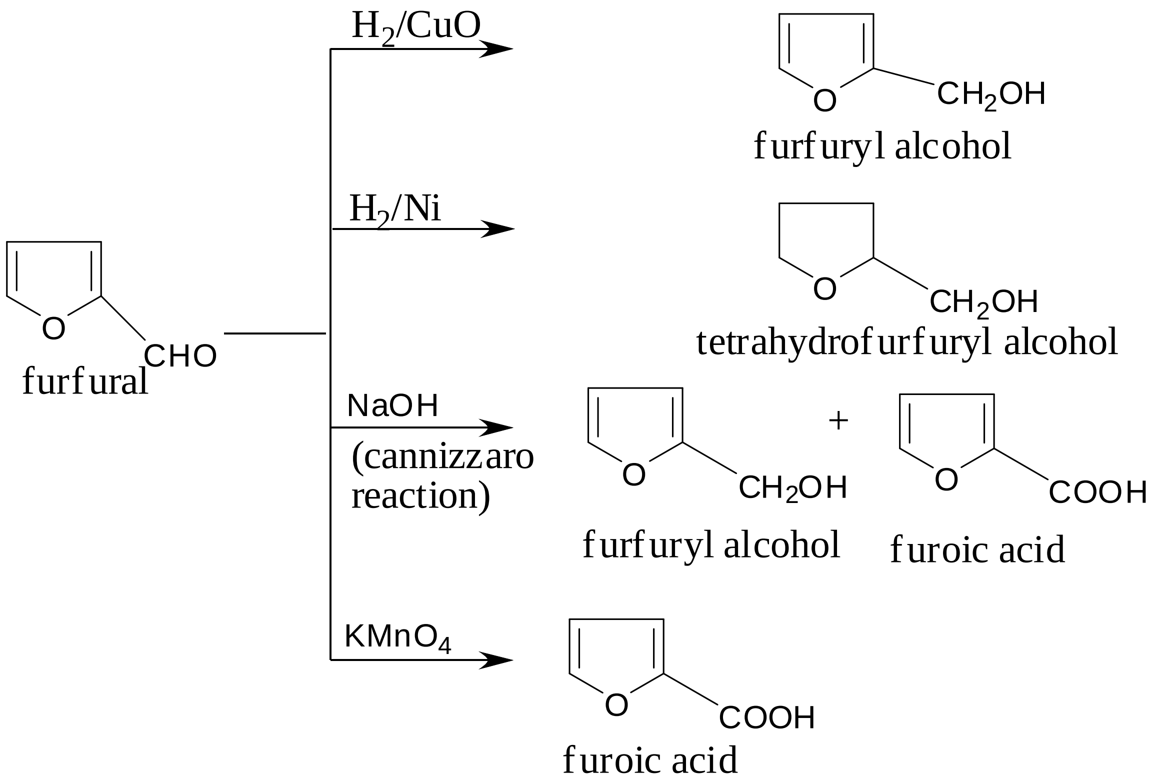
furfurylidene acetone

6. It reacts with CaO/400ºC, it loses carbon monoxide and gives furan by steam decomposition.

7. With ammonia and ammonium chloride gives 3-hydroxypyridine.



Reactions Of Furfural



Reactions Of Furfural