19 2.3 Structure, reactivity and orientation; see p. 167 (sec. 4.7) and p. 810 (sec. 17.4.4.c).

19.2.4 Chemical properties

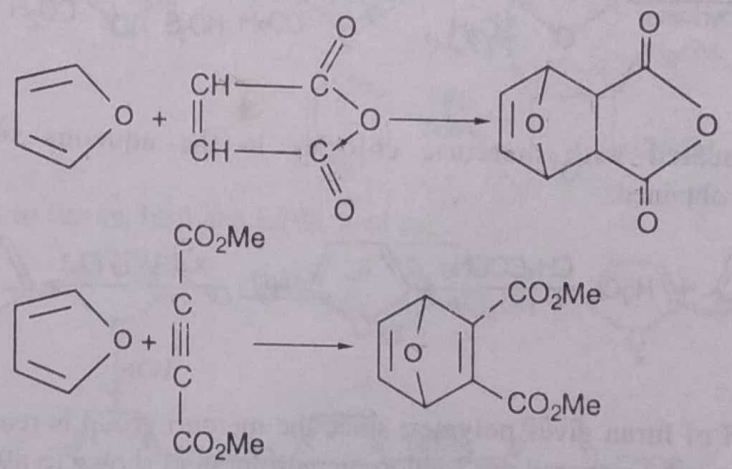
Though furan is an aromatic compound yet it shows a few properties of conjugated dienes. It is also less aromatic than thiophen and pyrrole; perhaps the strong electro-negative character of the O atom makes it draw the π-cloud much towards itself and thus makes furan less aromatic than the other two compounds. This is also supported by their resonance energy order as given below :

$$\text{Furan} < \text{pyrrole} \approx \text{thiophen}$$

Of course the resonance energy of furan is much higher than that of a conjugated diene. However, the following reactions will show its aromatic as well as diene characters. Furan is very weakly basic; it forms oxonium salts with acids; because of this oxonium ion, it polymerises in the acid medium.

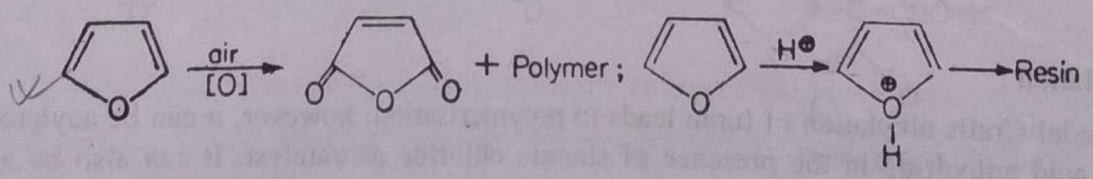
(a) The Diels-Alder reaction :

Among furan, pyrrole and thiophen, only furan undergoes the Diels-Alder reaction, a typical character shown by the conjugated dienes.



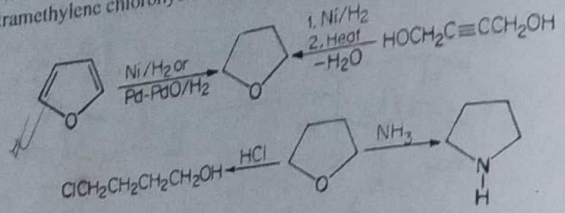
(b) Oxidation and resinification :

Furan is readily oxidized and resinified by the action of acids. The oxidation of furan by air is accompanied by polymerisation. The resinification of furan occurs when any mineral acid is added to it. It is needless to mention that polymerisation is also a typical character of 1, 3-dienes.



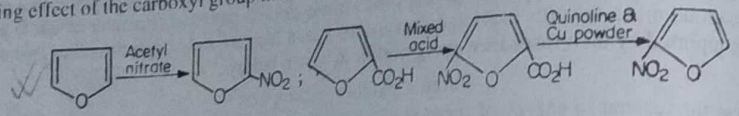
(c) Reduction :

Furan can be reduced to tetrahydrofuran (THF) by Raney Ni or Pd-PdO catalyst and hydrogen. THF is good solvent—it is used to prepare Grignard reagent, adipic acid and nylon. THF can be converted to pyrrolidine and tetramethylene chlorohydrin by the action of ammonia and hydrochloric acid respectively.



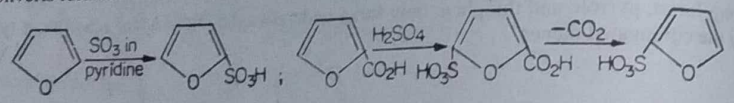
(d) Nitration :

Since furan polymerises in the presence of mineral acids, it cannot be nitrated by the mixed acid. 2-nitrofuran may be prepared by nitrating furan with acetylnitrate. On the other hand, 2-nitrofuran may also be prepared by nitrating furoic acid to 5-nitrofuroic acid and then decarboxylating it; the electron withdrawing effect of the carboxyl group makes furoic acid less suceptible to oxidation than furan.



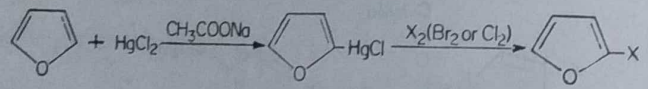
(e) Sulphonation :

For the same reason as given for nitration it cannot be sulphonated by sulphuric acid; sulphur trioxide in pyridine converts furan to 2-furansulphonic acid.



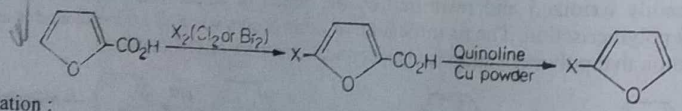
(f) Mercuration :

When furan is heated with mercuric chloride in the aqueous sodium acetate medium 2-chloromercurofuran is obtained.



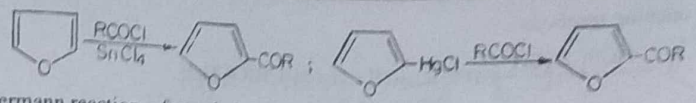
(g) Halogenation :

Direct halogenation of furan gives polymer; since the mercuri group is readily replaced by Br and I, 2-bromo or 2-iodofuran can be prepared via 2-chloromercurofuran as shown (p 897). However 2-chloro- and 2-bromoderivatives can also be prepared from furoic acid.

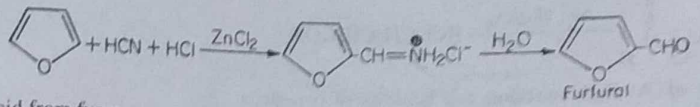


(h) Acylation :

The Friedel-Crafts alkylation of furan leads to polymerisation; however, it can be acylated with acyl chloride or acid anhydride in the presence of stannic chloride as catalyst. It can also be acylated via mercuration.

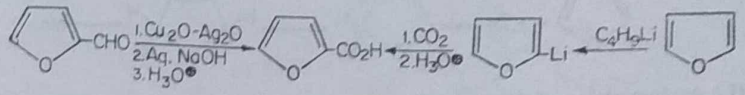


(i) The Gattermann reaction—formylation :



(j) Furoic acid from furan :

When furfural is oxidised with Cu_2O—Ag_2O in aqueous NaOH, it forms furoic acid; this may also be prepared via 2-lithiumfuran.

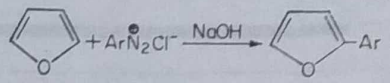


(k) Metalation :

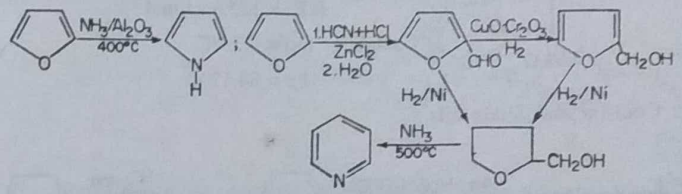
When furan is treated with *n*-butyllithium, 2-lithiumfuran is obtained.

(l) Gomberg reaction :

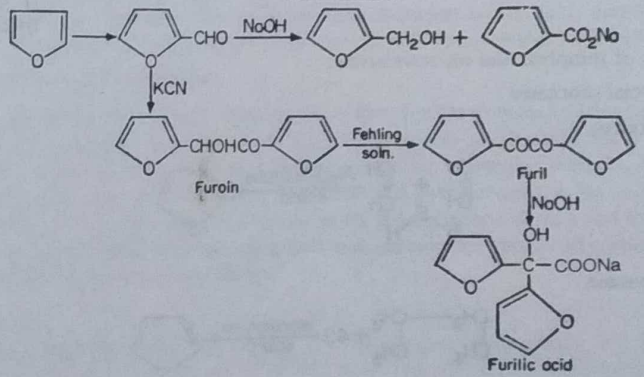
When an alkaline solution of furan is treated with arenediazonium salt, 2-arylfuran is obtained.



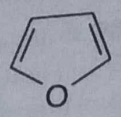
(m) Conversion of furan to pyrrole and pyridine :

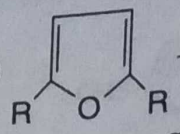


(n) Conversion of furan to furoin, furil and furilic acid etc :



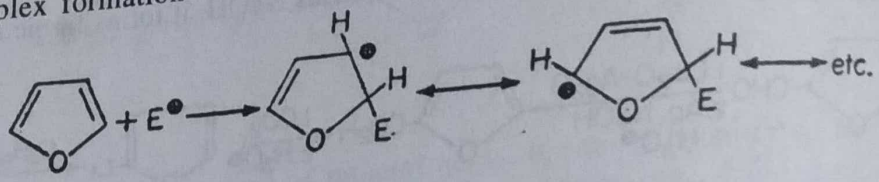
(o) Ring opening reactions :

(i)  $\xrightarrow{HCl/CH_3OH}$ $(CH_3O)_2CH{\cdot}CH_2CH_2CH(OCH_3)_2$

(ii)  $\xrightarrow{\text{Aq. } H_2SO_4}$ $RCOCH_2CH_2COR$

Mechanism of Ar.S_E2 reaction : It consists of two steps :

Step I : σ-complex formation



Step II : Aromatisation of the σ-complex