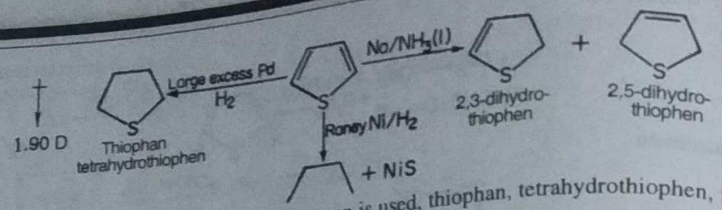


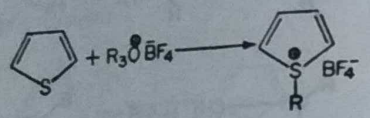
When a large excess of palladium and hydrogen is used, thiophan, tetrahydrothiophen, is formed; since S poisons Pd, the catalyst is used in large excess.

(iii) By Raney nickel and hydrogen :

Raney nickel desulphurises thiophen and *n*-butane is obtained when thiophen is reduced with Ni/H_2.

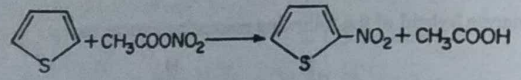
(b) S-alkylation :

When 3° oxonium compounds, such as $R_3\overset{\oplus}{O}\bar{B}F_4$, are treated with thiophen, S-alkylthiophen salts are obtained.



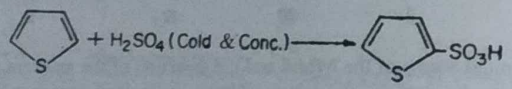
(c) Nitration :

Thiophen is stable in aqueous acids and it does not form salts with them; but it can however be oxidatively decomposed by nitric acid. It is, therefore, nitrated by acetyl nitrate at 2-position.



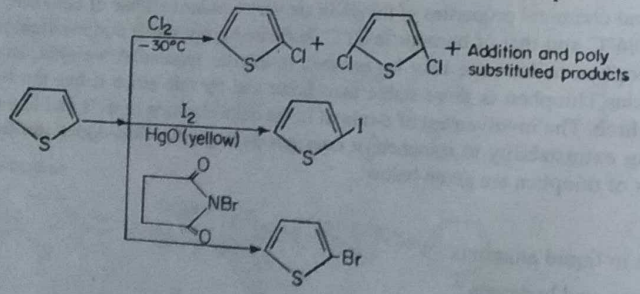
(d) Sulphonation :

In contrast to benzene, it is readily sulphonated by cold concentrated sulphuric acid.



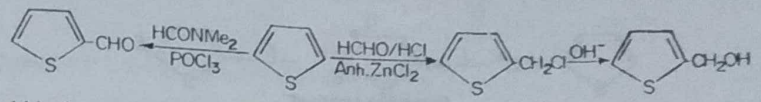
(e) Halogenation :

When thiophen is treated with chlorine at –30°C, 2-chloro- and 2, 5-dichlorothiophens are formed as the main products. However, thiophen can be brominated at 2-position by N-bromosuccinimide (NBS). Whereas 2-iodo-derivative may be prepared by treating it with iodine in the presence of yellow mercuric oxide.



(f) Choromethylation and formylation :

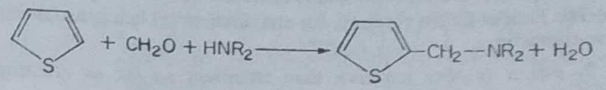
Thiophen can be chloromethylated by formaldehyde and hydrogen chloride in the presence of anhydrous zinc chloride. This can also be formylated by the Vilsmeier-Haak method.



2-Formylthiophen undergoes the Cannizzaro reaction and the benzoin condensation.

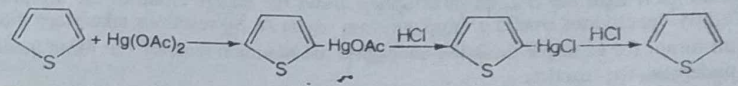
(g) The Mannich reaction :

Thiophen undergoes the Mannich reaction.



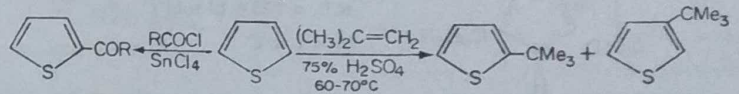
(h) Mercuration :

Thiophen, like furan, undergoes the mercuration reaction with murcuric acetate even in the cold but benzene does not.



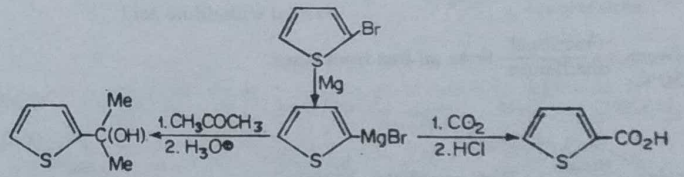
(i) Acylation and alkylation :

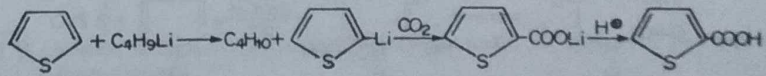
Thiophen can be acylated at 2-position by the Friedel-Crafts method using stannic chloride as catalyst; but when thiophen is alkylated with isobutylene, a mixture of 2- and 3-t-butyl-thiophens is obtained.



(j) Formation of 2-thienylmagnesium bromide :

When 2-bromothiophen is treated with magnesium, 2-thienylmagnesium bromide is formed which can be converted to 2-thiophencarboxylic acid and other thiophen derivatives.



(k) Reaction with butyllithium :

Thiophen reacts with butyllithium to form 2-thienyllithium which can also be converted to 2-thiophencarboxylic acid.