CHB-401: Heterocyclic Compounds (Section B)

THIOPHENE

Organic Chemistry III

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INTRODUCTION

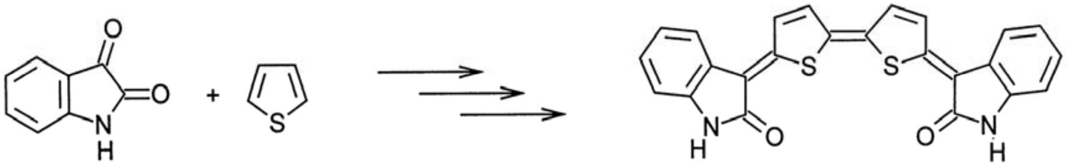
Thiophene is a heterocyclic compound with the formula C_4H_4S. Consisting of a planar five-membered ring, it is aromatic as indicated by its extensive substitution reactions. It is a colorless liquid with a benzene-like odor. In most of its reactions, it resembles benzene.

ISOLATION AND OCCURANCE

- Thiophene occurs in coal-tar and shale oils. Its B.P. (84°C) is close to that of benzene and hence it is difficult to separate from the benzene fraction obtained from coal-tar.
- Thiophene can be sulphonated more readily than benzene (from coal-tar) with cold concentrated sulphuric acid, whereby the water soluble thiophensulphonic acid is formed.
- A better means of separation is to reflux the benzene with aqueous mercuric acetate whereupon thiophene is mercurated and benzene is not. Thiophene may be recoverd from its mercurated derivative by distilling the latter with hydrochloric acid.
- The presence of thiophene in benzene may be detected by the *Indophenin reaction*

INDOPHENIN TEST

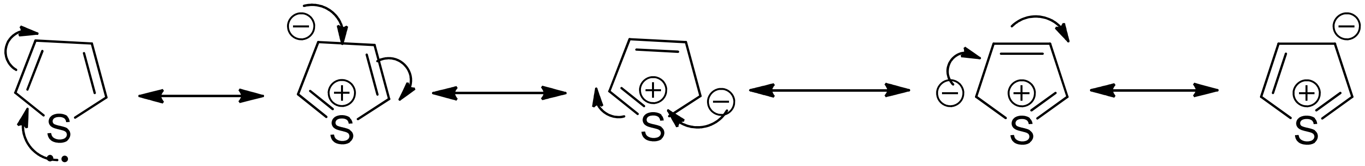
The indophenin reaction is one of the oldest color reactions in organic chemistry. It is used for the detection of thiophene and some substituted thiophenes .This is the development of a blue colour crystalline compound **$C_{24}H_{14}N_2O_2S_2$** when thiophene is treated with isatin and sulphuric acid. This is used as a colour test for the presence of thiophene and benzene.



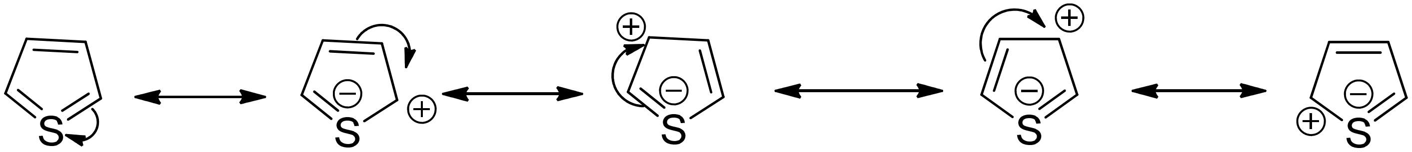
RESONATING STRUCTURES

Resonance energy of thiophene is 117 KJ/mol. Thiophene is a resonance hybrid, the S atom contributing two electrons to form a (4n+2)π electron. Sulphur is less electronegative than oxygen or nitrogen and can also use 3d orbitals (oxygen and nitrogen cannot). Hence more canonical forms are possible for thiophene than for furan and pyrrole.

The S atom use p orbitals



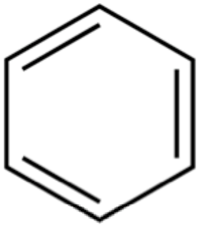
The S atom use d orbitals

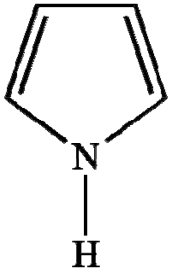


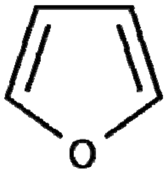
AROMATICITY

Thiophene is the most aromatic among the three heterocyclic compounds furan, pyrrole and thiophene. As sulphur atom is less electronegative than nitrogen and oxygen, it has a greater electron donating tendency. And these donated electrons take part in delocalization in the ring. Thus, greater the donating ability of the hetero atom, greater will be the aromaticity.

Thiophene is more aromatic than pyrrole and furan and less aromatic than benzene .The correct order is

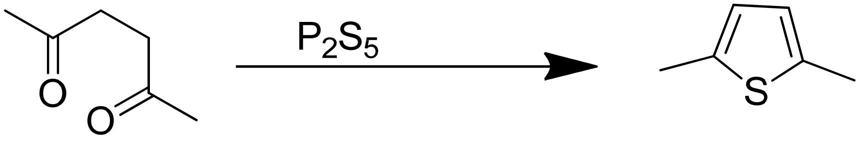




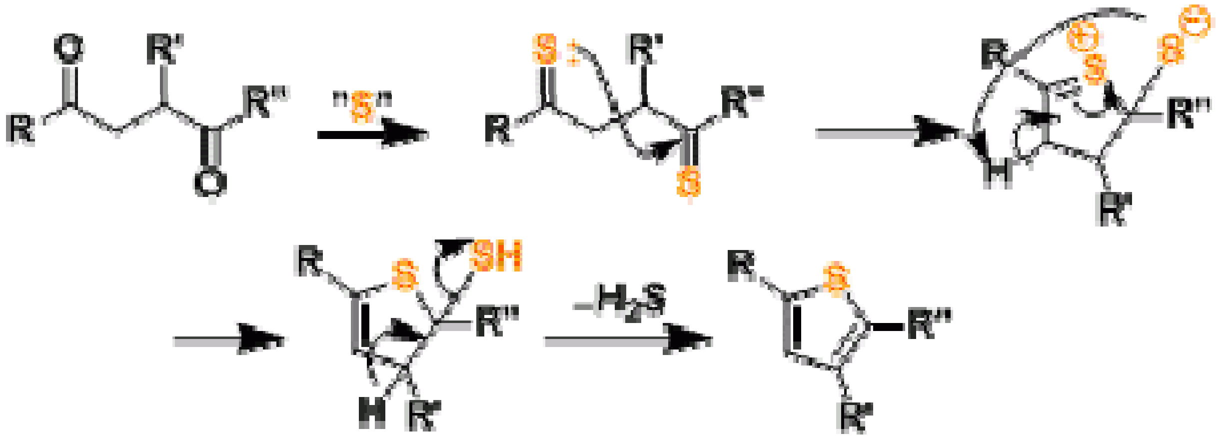


SYNTHESIS

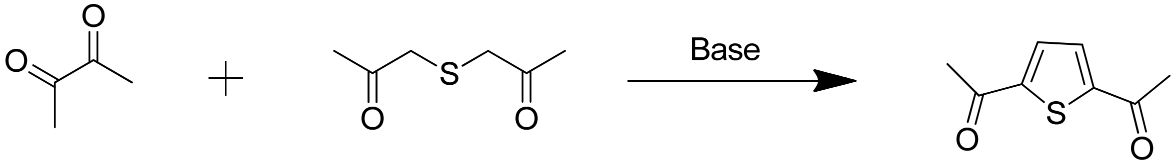
Paal – Knorr synthesis of thiophene (from 1,4-dicrbonyl compounds)



MECHANISM



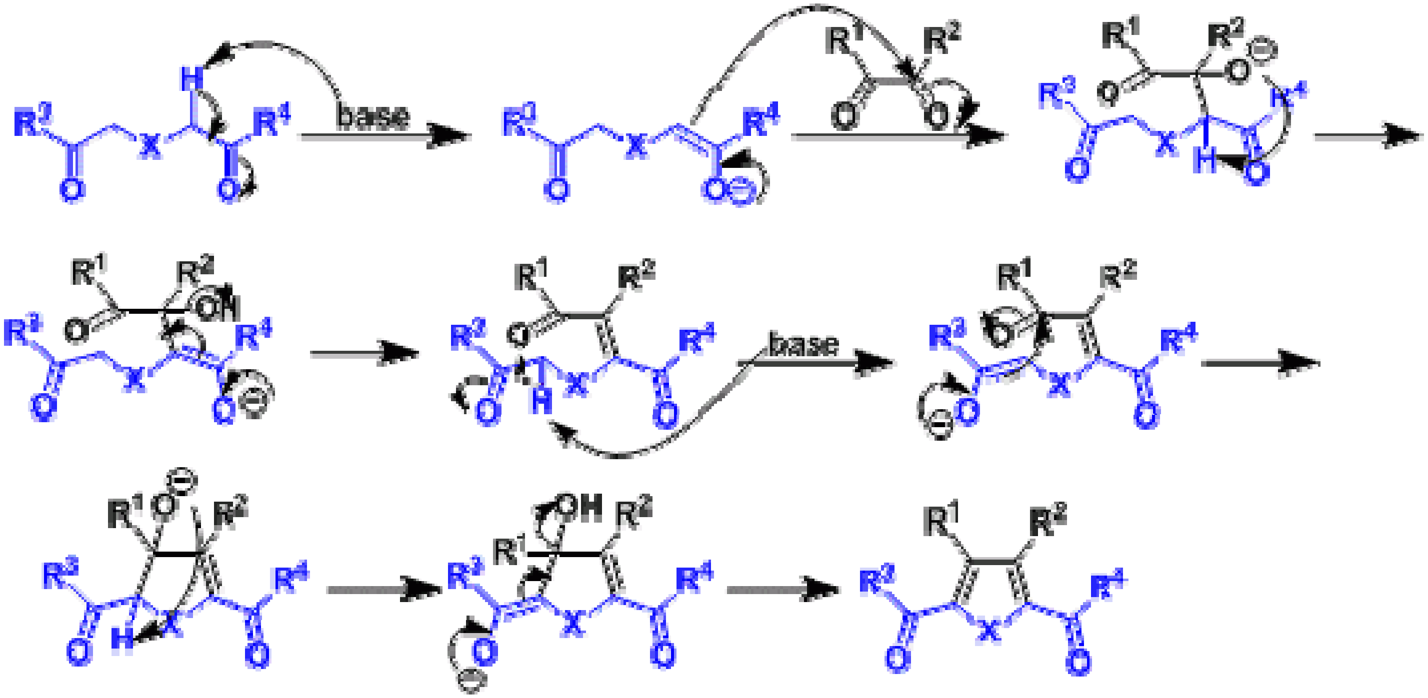
HINSBERG SYNTHESIS



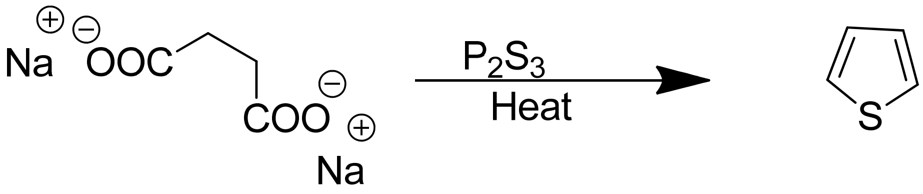
1, 2 diketone

Dithioacetate

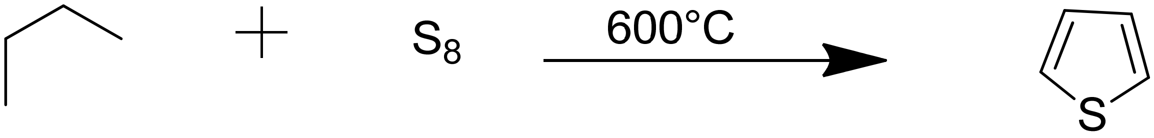
MECHANISM



FROM SODIUM SUCCINATE



COMMERCIAL PROCESS

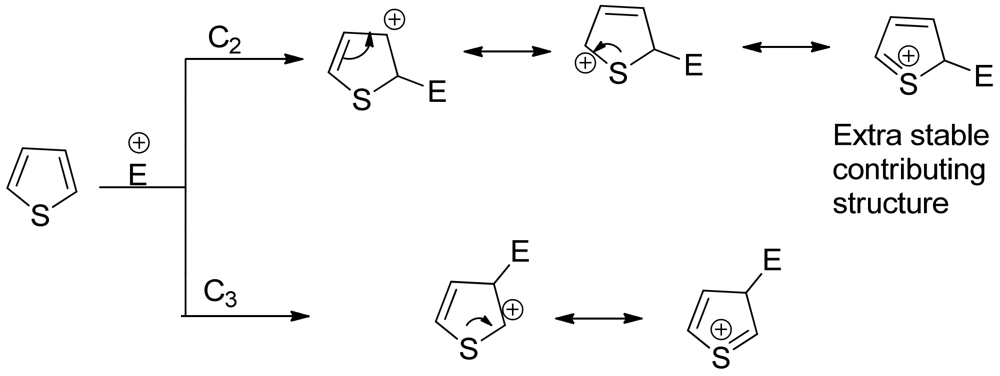


REACTIVITY

- Thiophene is somewhat less reactive (approx. 10^2) than furan towards electrophiles (and much less reactive than pyrrole), but it is still much more reactive than benzene (approx. 10^4).
- By virtue of its high resonance energy (130 KJmol-1) it is the most aromatic of the five-membered heteroaromatics and undergoes electrophilic substitution rather than addition/ring opening reaction. It does not behave as an enol thioether or diene (contrast with furan).
- Thiophene is stable to aqueous mineral acids but not to 100% sulphuric acids or strong Lewis acids, exemplified by aluminium(III) chloride.
- Electrophilic substitution occurs at position 2 (as for furan) with high positional selectivity

ELECTROPHILIC AROMATIC SUBSTITUTION

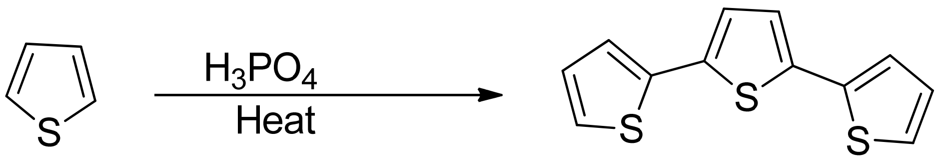
Thiophene undergoes electrophilic aromatic substitution reaction at position 2



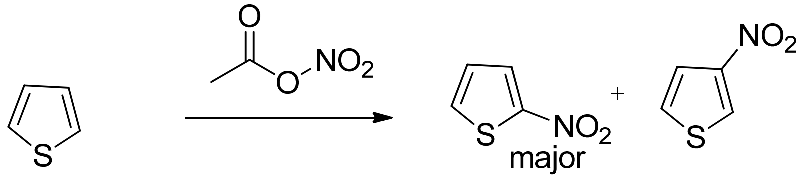
C2 attack gives more resonance contributing structure than C3, therefore the extra stable contributing structure generates upon C2 attack

ELECTROPHILIC SUBSTITUTION REACTION

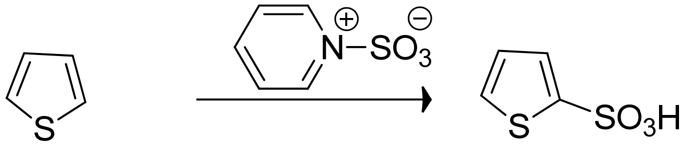
Very strongly acidic condition lead to acid catalyzed polymerization. The action of hot phosphoric acid on thiophene lead to trimer



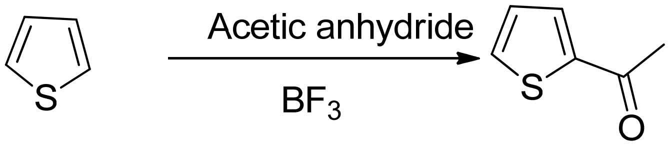
Nitration



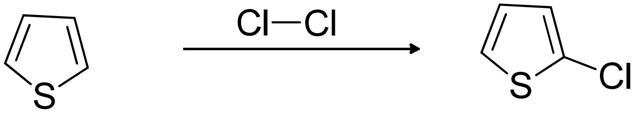
Sulphonation



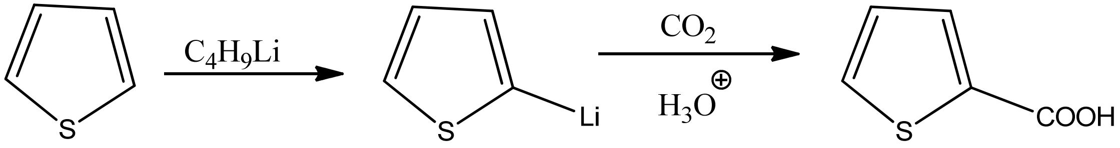
Acylation



Halogination



Reaction with organolithium



Reduction