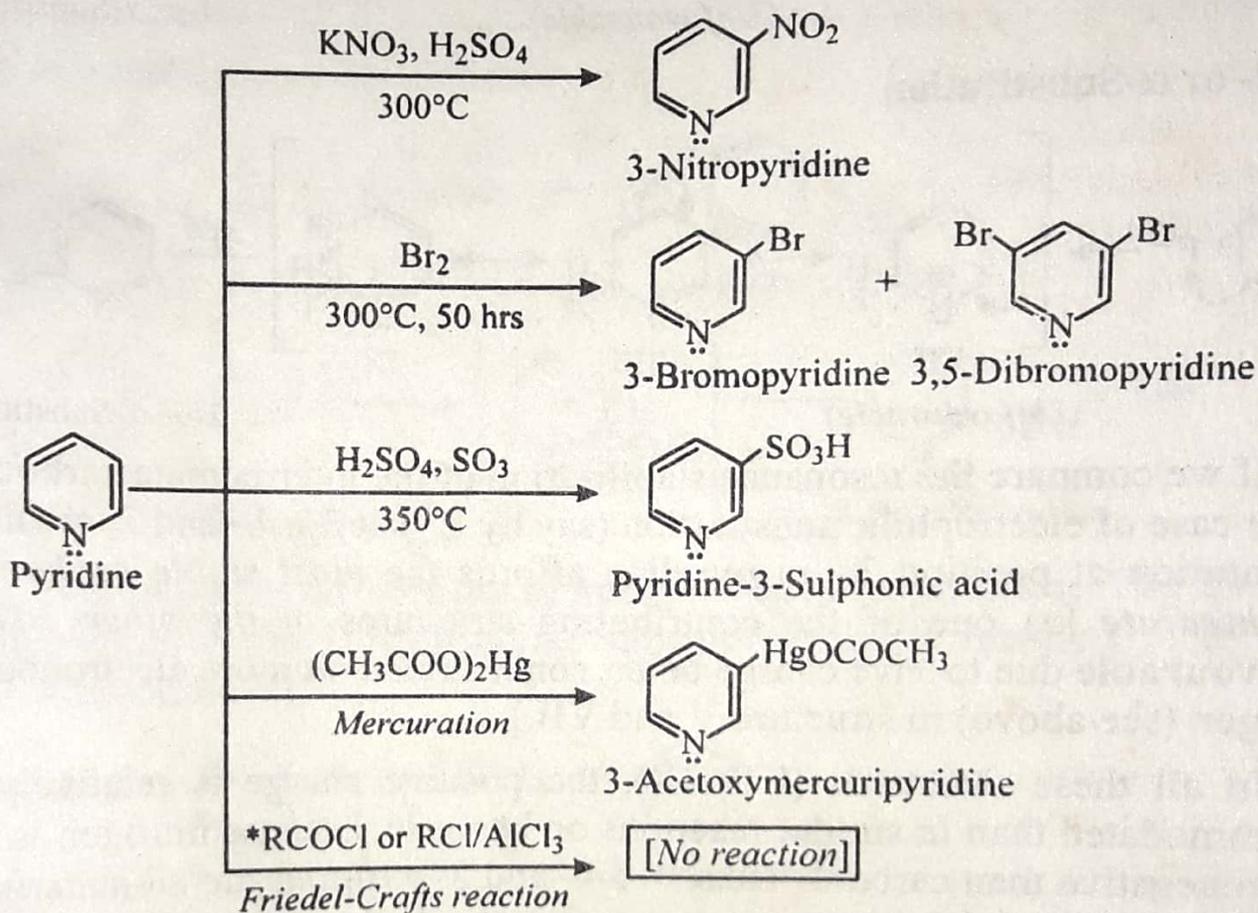
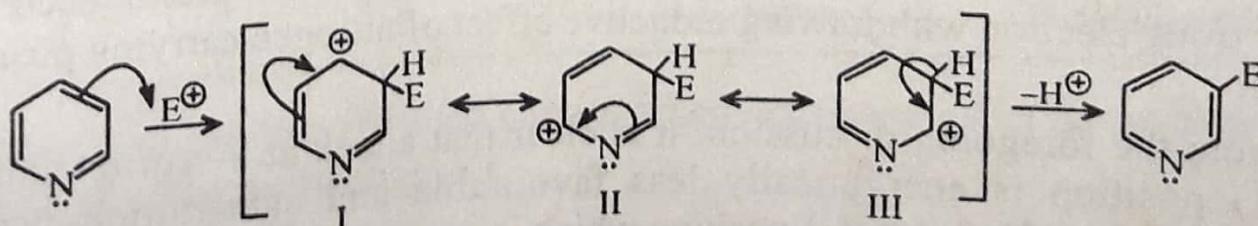


(iii) **Electrophilic substitution reactions.** It undergoes electrophilic aromatic substitution reactions like *nitration*, *sulphonation* and *halogenation*, but under vigorous conditions. It does not undergo *Friedel-Crafts* reaction at all. *Electrophilic substitution* occurs mainly at 3 or (β -) position. For example,

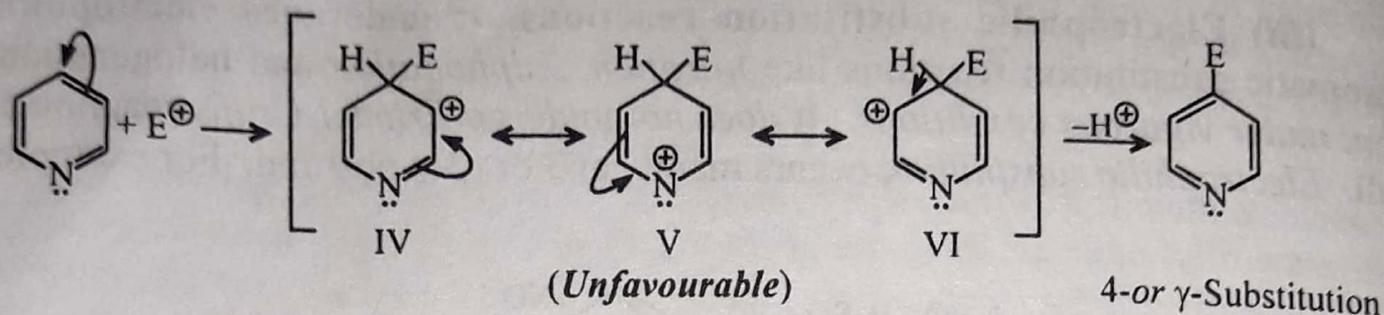


Explanation for Orientation/reactivity in electrophilic substitutions of pyridine. The general pattern of *electrophilic substitution* (say at 3- or β -position) in pyridine can be outlined as follows :

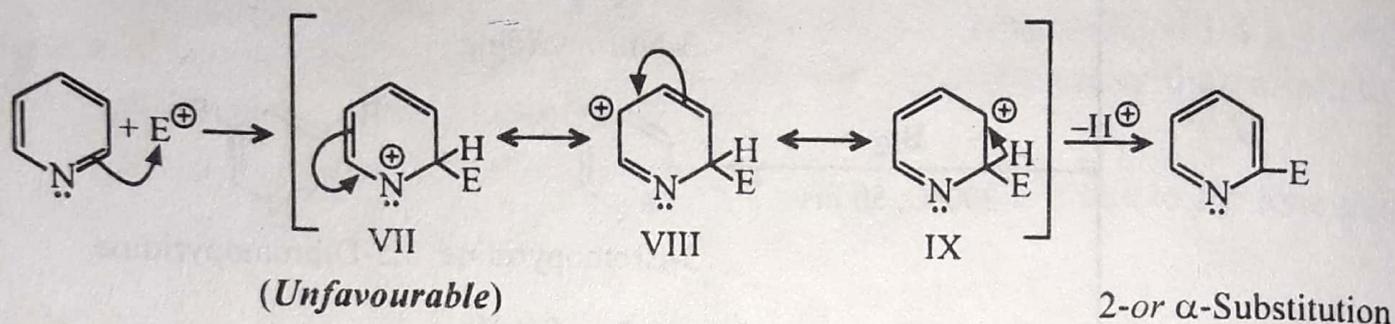
3- or β -Substitution :



4- or γ -Substitution



2- or α -Substitution



If we compare the resonance stabilisation of the intermediate carbocation in the case of electrophilic substitution (say by E^{\oplus}) at 3-, 4- and 2- positions, substitution at position 3- in pyridine affords the *most stable carbocation intermediate* [as one of the contributing structures in the other cases is unfavourable due to +ive charge being concentrated on more electronegative nitrogen (see above) in structure V and VII.]

In all these structures (I to IX), the positive charge is relatively less accommodated than in similar reactions on benzene, because nitrogen is more electronegative than carbon. Thus, 3-, 4- and 2-positions are all *deactivated*, although the 2- and 4-positions are more *strongly deactivated* because of the high energy of the *contributing structures* with *divalent positive nitrogen* (in structures V and VII, having sextet of electrons only). *Pyridine is, therefore, highly deactivated towards electrophilic substitution reactions and vigorous reaction conditions are required to perform these reactions (cf. nitrobenzene).* In acidic media, as in nitration and sulphonation, pyridine is present almost entirely in its protonated form, and deactivation is still more pronounced due to the strong electron withdrawing inductive effect of nitrogen carrying positive charge.

From the foregoing discussion, it is clear that attack at 2- (or α) and 4- (or γ -) position is energetically less favourable and substitution occurs *predominantly* at the 3- (or β -) position which is *energetically more favourable*.