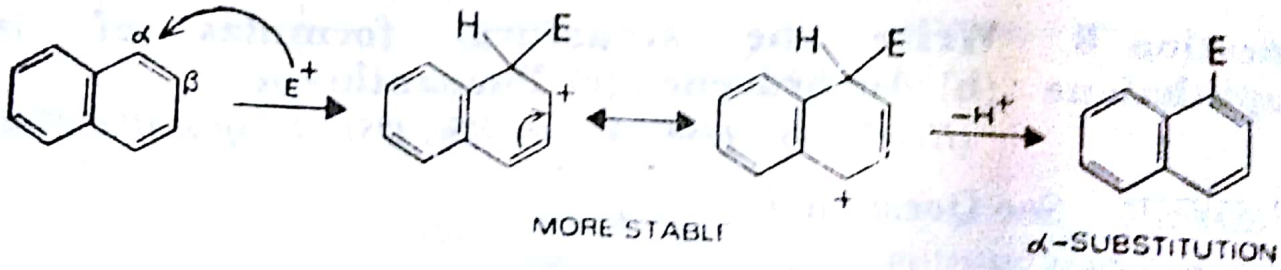
Question 11. Explain why electrophilic substitution in naphthalene takes place at the α-position.

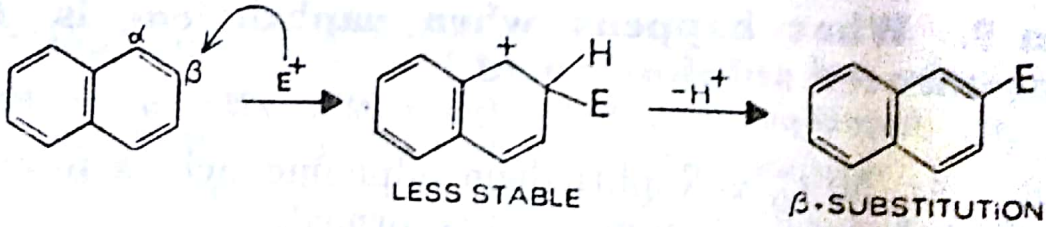
(Guru Nanak Dev BSc, 1980; Maharshi Dayanand BSc, 1981; Panjab BSc, 1981; Udaipur BSc, 1981; Allahabad BSc, 1982; Madras BSc, 1982; Nagpur BSc, 1982; Punjabi BSc, 1982; Sri Venkateswara BSc, 1982)

ANSWER. Naphthalene, like benzene, undergoes electrophilic substitution reactions. Substitution takes place mainly at the α-position (C-1 position). This can be understood if we examine the intermediate carbonium ion. Two resonance structures can be written for the intermediate carbonium ion obtained from attack at α-position (without involving the other ring), whereas only one such structure is possible for substitution at β-position (C-2 position). E^+ in the following equations represents an electrophile.

Attack at α-position



Attack at β-position



Consequently, the former intermediate is more stable and the product with a substituent at α-position predominates. Substitution at β-position occurs only when the reactions are carried at high temperatures or when bulkier solvents are used.

Question 12. What is the ...

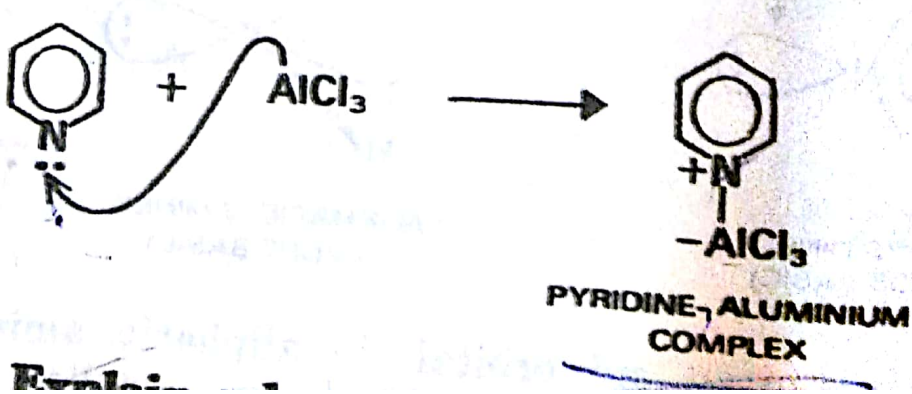
Question 29. Explain why pyridine has low reactivity toward electrophilic substitution.

ANSWER. Pyridine contains an electronegative nitrogen and therefore is polar. Because the nitrogen is more electronegative than carbon, the rest of the pyridine ring is electron-deficient. *An electron deficient ring means that the carbon atoms in the ring carry a partial positive charge.* A pyridine ring therefore has low reactivity toward electrophilic substitution.

E+ attack on pyridine ring is not favoured because the ring carbons carry a positive charge.

Question 30. Explain why pyridine does not undergo Friedel-Crafts alkylation or acylation ?

ANSWER. This is because the Lewis acids ($FeCl_3$ or $AlCl_3$) which are used as catalysts in these reactions coordinate with the lone pair of electrons on nitrogen to form a complex.



PYRIDINE–ALUMINIUM COMPLEX

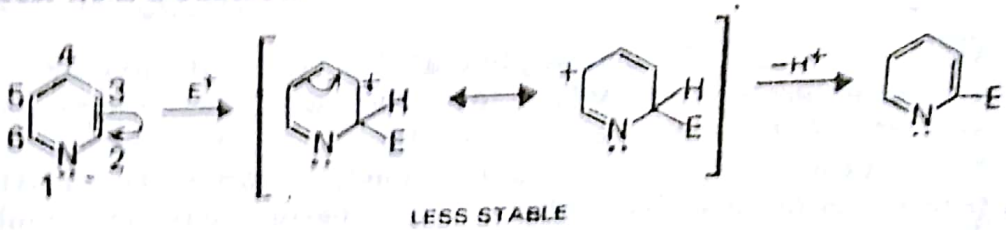
Question 31. Explain

Question 31. Explain why pyridine undergoes electrophilic substitution at 3-position ?

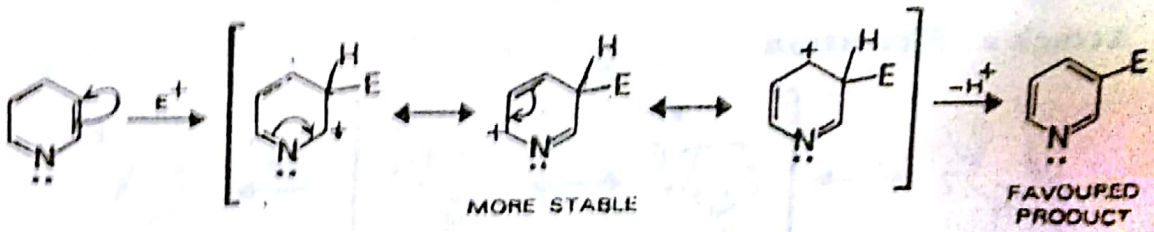
(Himachal BSc, 1980 ; Kurukshetra BSc, 1980 ; Visva Bharti BSc, 1980 ; Nagpur BSc, 1980 ; North Bengal BSc, 1981 ; Panjab BSc, 1981 ; Udaipur BSc, 1981 ; Allahabad BSc, 1982 ; Delhi BSc, 1982 ; Mysore BSc, 1982 ; Osmania BSc, 1982)

ANSWER. Attack of the electrophile at 2-position (*or* 4-position) in pyridine leads to an intermediate with only two important resonance contributing structures. Three resonance structures are possible for the intermediate produced by attack at 3-position. *That is, the intermediate produced by the attack at 3-position is more stable.* This is the reason that electrophilic attack occurs at 3-position. E^+ in the following equations represents an electrophile.

Attack at 2-Position



Attack at 3-Position

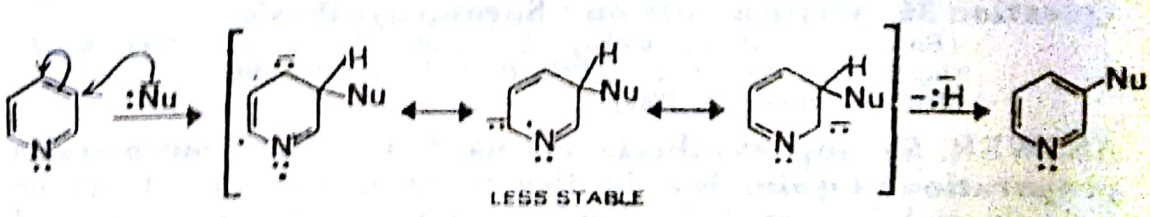


Question 32. Explain why pyridine undergoes nucleophilic substitution at 2-position ?

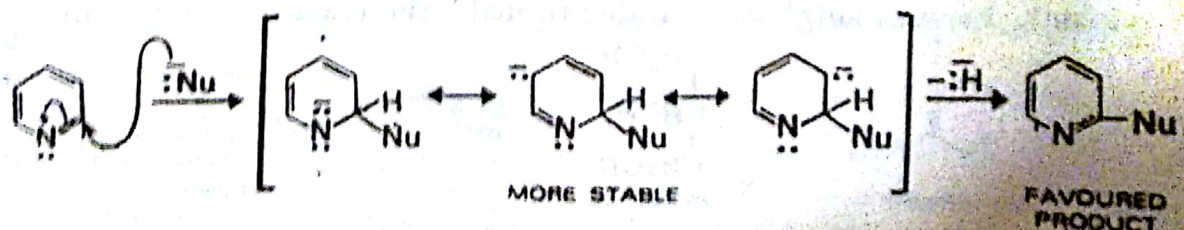
(Banaras BSc, 1980 ; Visva Bharti BSc, 1980 ; Punjabi BSc, 1980 ; Panjab BSc, 1981 ; Udaipur BSc, 1981 ; Berhampur BSc, 1982 ; Visva Bharti BSc, 1982)

ANSWER. Attack of the nucleophile at 3-position in pyridine leads to an intermediate with three resonance contributing structures. Attack of the nucleophile at 2-position (or 4-position) also gives an intermediate with three resonance structures. (Attack at 4-position resembles attack at 2-position). This position is attacked only when 2-position is blocked). Nu : in the following equations represents a nucleophile.

Attack at 3-Position



Attack at 2-Position



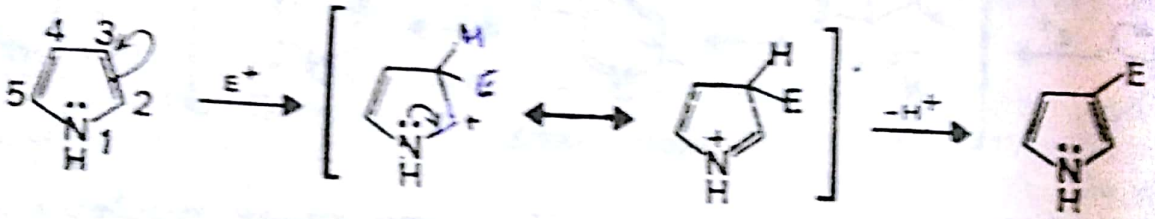
2-position rather than at 3-position.

Question 33. Explain why pyrrole undergoes electrophilic substitution at 2-position ?

(Madras BSc, 1996)

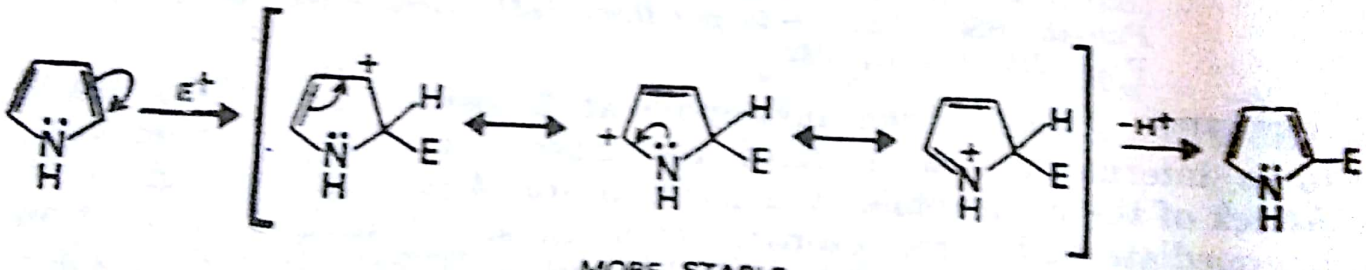
ANSWER. Attack of the electrophile at 3-position in pyrrole leads to an intermediate with only two resonance structures. Three resonance structures are possible for the intermediate produced by attack at 2-position. That is, the intermediate produced by attack at 2-position is more stable. This is the reason that electrophilic attack occurs at 2-position rather than at 3-position. E^+ in the following equations represents an electrophile.

Attack at 3-Position



LESS STABLE

Attack at 2-Position



MORE STABLE

FAVOURED PRODUCT