

LECTURE 4

(b) The Benzyne mechanism

This mechanism only occurs with nucleophiles which are also very strong bases. The resultant nucleophile becomes attached either to the carbon bearing the departing group or the adjacent one:

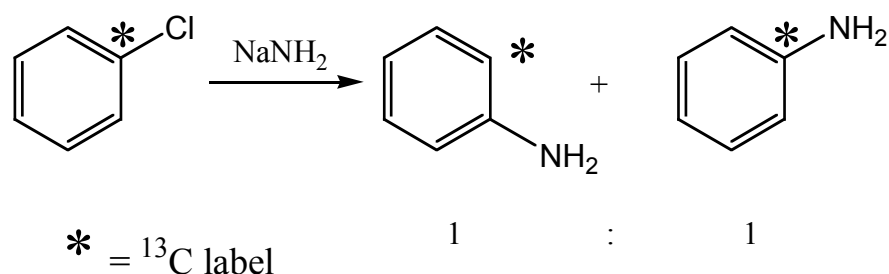


Fig. 1

In the latter case **cine**-substitution is said to have occurred and this may predominate in cases where steric hindrance prevents ipso attack e.g.:

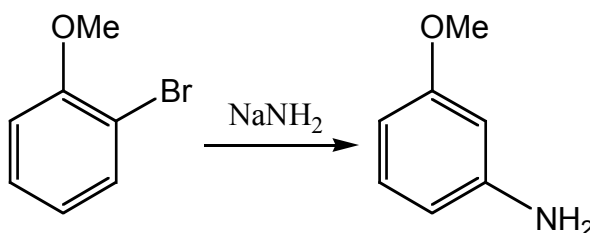
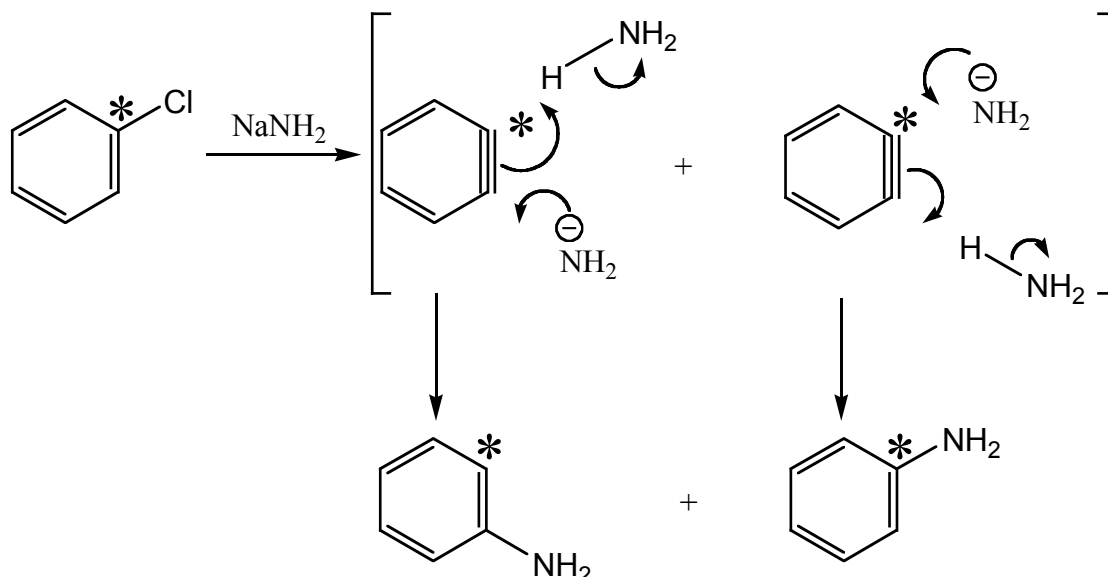


Fig. 2

The explanation for this double site of attack invokes the elimination of HX from the starting halide. Since this is difficult to do in aromatic compounds (because the resultant intermediate is very unstable), the reaction only works when the nucleophile is a very strong base:



The intermediate with a formal triple bond in the ring, called benzyne by analogy with alkynes, is very unstable and has only been detected in an argon matrix at 8 °K. Its symmetry explains why we see equal amounts of the *ipso* and *cine* substitution products. In substituted derivatives, however, the incoming nucleophile prefers to attack the carbon atom furthest from the substituent for steric reasons.

5. Reactions: Sandmeyer and Related Reactions of Diazonium Salts

Diazonium salts are readily prepared from aromatic amines (anilines) by treatment with nitrous acid in hydrochloric acid:

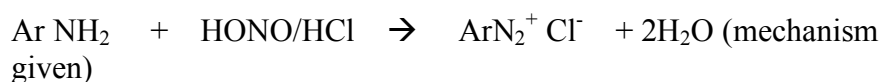


Fig. 3

Diazonium salts are weak electrophiles and will react with aromatic rings bearing electronic rich substituents (usually OH or NR₂) to give coloured diazo compounds which form the basis of a huge dyestuff industry e.g.:

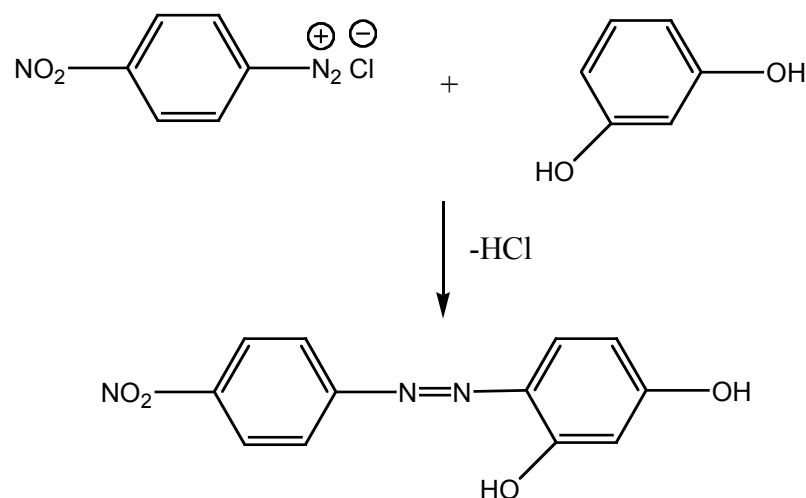


Fig. 4

However, the formation of dyestuffs is again electrophilic substitution and, therefore, is not the focus in this section where radical reactions are to be discussed.

Treatment of diazonium salts with cuprous chloride [Cu(I)Cl] or cuprous bromide [Cu(I)Br] or cuprous cyanide [Cu(I)CN] leads to aryl chlorides, bromides and cyanides respectively. Collectively, these reactions are named after the chemist who discovered them, Sandmeyer. The mechanism of Sandmeyer reactions is believed to involve radical intermediates:

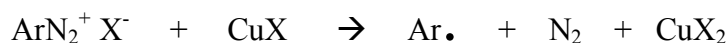


Fig. 5

A similar reaction occurs with KI (CuI is too insoluble for these reactions):



Fig. 6

Analogous reactions (although mechanistically somewhat more complicated, they also appear to be radical reactions) also occur with NaNO_2 and SO_2 :



Fig. 7

Finally, the diazonium salts may also be reduced by a radical mechanism to give the parent hydrocarbon.

In the case when hypophosphorous acid (H_3PO_2) is used as the reductant the reaction proceeds through a phosphorus-centred radical:

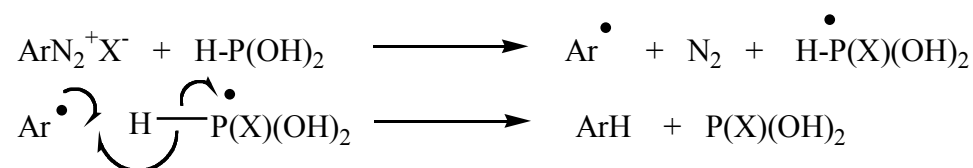


Fig. 8

All these reactions (except replacement of N_2 by H) represent ways of making these aromatic compounds other than by electrophilic substitution:

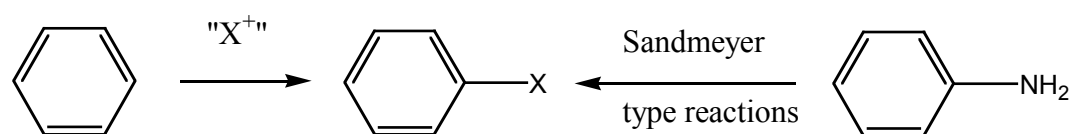


Fig. 9