

ref: A textbook of  
Practical organic chemistry  
Arthur I Vogel.

3<sup>rd</sup> edition p 577.

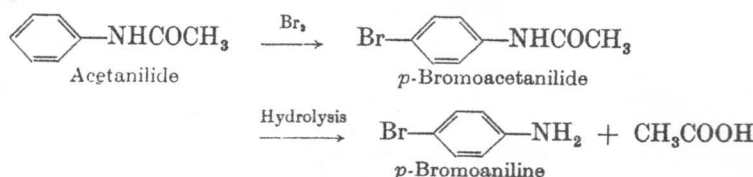
[IV,

45]

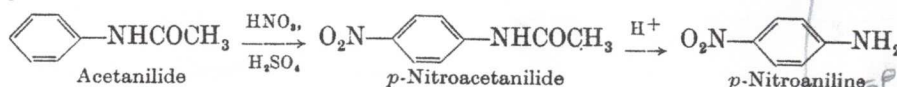
AROMATIC COMPOUNDS

577

Mono-substitution products of primary amines cannot easily be prepared by direct action of the appropriate reagent; for example, bromination of aniline yields largely the 2:4:6-tribromo derivative and nitration results in much oxidation. If, however, the amino group is **protected** as in acetanilide, smooth substitution occurs. Thus with bromine, **p-bromoacetanilide** is the main product; the small quantity of the *ortho* isomeride simultaneously formed can be easily eliminated by crystallisation. Hydrolysis of **p-bromoacetanilide** gives **p-bromoaniline**:



Nitration leads similarly to **p-nitroacetanilide**, which can be hydrolysed to **p-nitroaniline**:



IV,45.

### ACETANILIDE

**Method 1.** In a 1 litre beaker or flask containing 500 ml. of water, introduce 18.5 ml. of concentrated hydrochloric acid and 20.5 g. (20 ml.) of aniline. Stir until the aniline passes completely into solution. (If the solution is coloured, add 3-4 g. of decolourising carbon, warm to about 50° with stirring for 5 minutes, and filter at the pump or through a fluted filter paper.) To the resulting solution add 27.7 g. (25.6 ml.) of redistilled acetic anhydride, stir until it is dissolved, and immediately pour in a solution of 33 g. of crystallised sodium acetate in 100 ml. of water. Stir vigorously and cool in ice. Filter the acetanilide with suction, wash with a little water, drain well, and dry upon filter paper in the air. The yield of colourless, almost pure acetanilide, m.p. 113°, is 24 g. Upon recrystallisation from about 500 ml. of boiling water to which about 10 ml. of methylated spirit has been added (compare **Method 3**), the m.p. is raised to 114°; the first crop weighs 19 g. *method*

**Method 2.** In a 500 ml. round-bottomed flask, equipped with a reflux condenser, place 20.5 g. (20 ml.) of aniline, 21.5 g. (20 ml.) of acetic anhydride, 21 g. (20 ml.) of glacial acetic acid, and 0.1 g. of zinc dust (1). Boil the mixture gently for 30 minutes, and then pour the hot liquid in a thin stream into a 1 litre beaker containing 500 ml. of cold water whilst stirring continually. When cold (it is preferable to cool in ice), filter the crude product at the pump, wash with a little cold water, drain well and dry upon filter paper in the air. The yield of acetanilide, m.p. 113°, is 30 g. It may be recrystallised as in **Method 1** affording 21 g. of pure acetanilide, m.p. 114°.

**Method 3.** Fit up the apparatus shown in Fig. IV, 45, 1 using a 250-ml. round-bottomed flask. Do not pass water through the glass jacket since the condenser will be employed only as an air condenser: the empty filter flask is used merely as a trap to prevent the escape of vapours into

1,89 - 78,22

= 3,539

anhydride de l'eau -> il faut se dépêcher.