réf: A textbook of Practical organic chemistry Arthur I Vagel.

3 édétion 0577

Y [IV,

45] AROMATIC COMPOUNDS

577

1 misable

ed either with acetic its. Primary amines , in the first instance,

+ CH₃COOH

NES

is employed, variable

+ CH₃COOH

the presence of subdiacetyl-o-toluidine gent:

 $I_3)_2 + 2CH_3COOH$

e in the presence of bund, so that when crystallised from an erivative is obtained. absence of a solvent sent in the reaction bromoaniline, react ce of a few drops of apidly, for example:

 $COCH_3 + CH_3COOH$

tanilide

de alone are absent ding to the following one equivalent of acetic anhydride is to neutralise the ne which is liberated hydrolysis of acetic he free amine reacts ter: this forms the ation.

pensive because of acetic acid depends

 $H_{2}O$

cid) by distillation. tions, is to employ 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-tribomo 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 ACETANILIDE

Method 1. In a 1 litre beaker or flask containing 500 ml. of water, introduce 18.3 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 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 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

anhydride de l'eau es il faut se dépêcher.

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