CCCXLII.—*Acetylation in Aqueous Alkaline Solutions.*

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Although it is well known that acetic anhydride does not react very rapidly with cold water, and that many amines and other substances can be acetylated in aqueous solution (Hinsberg, *Ber.*, 1890, **23**, 2962; Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3407; Lumière and Barbier, *Bull. Soc. chim.*, 1905, **33**, 783), it is somewhat surprising to find that compounds containing hydroxyl and amino-groups can generally be quantitatively acetylated by adding acetic anhydride to their somewhat dilute solutions in aqueous caustic alkalis.

The amount of alkali used should be sufficient to leave the liquid slightly alkaline at the end of the operation, so much ice should be added that a little remains unmelted, and the acetic anhydride should be added quickly.

Acetylation under these conditions is so rapid as to appear almost instantaneous and in a very short time is practically complete. The best procedure is to dissolve the compound to be acetylated in an aqueous solution of a little more than the theoretical amount of sodium or potassium hydroxide, to add a suitable quantity of crushed ice, and then to pour in rapidly an equivalent amount of acetic anhydride. After a few seconds' shaking, the acetylated product separates in a practically pure condition, either at once or, when it is acidic, after addition of a mineral acid.

Many compounds hitherto obtained only with difficulty by drastic and inconvenient methods can thus be rapidly and easily prepared.

Phenyl Acetate.—94 G. of phenol (1 mol.) were dissolved in a solution of 60 g. of sodium hydroxide (1·5 mols.) in 100 c.c. of water. The liquid was cooled and mixed with 500 g. of crushed ice, 128 g. of acetic anhydride (1·25 mols.) were then quickly added, and the mixture was vigorously shaken for a few seconds. Phenyl acetate at once separated as a colourless liquid. After being washed with a little dilute aqueous sodium hydroxide and then with water, it was dried over calcium chloride and distilled, b. p. 195·3°/763·7 mm.; yield, 134 g. (98·5% of the theoretical).

By a similar procedure using appropriate quantities of sodium hydroxide and acetic anhydride the following yields of the corresponding acetyl derivatives were obtained.

o-Nitro-phenol, 14 g.; *o*-nitrophenyl acetate, 16 g., very pale yellow prisms with domed ends, m. p. 41°.

p-Nitrophenol, 14 g.; *p*-nitrophenyl acetate, 17 g., slightly yellow, compact prisms, m. p. 83°.

2 : 4 : 6-Tribromophenol, 33 g.; 2 : 4 : 6-tribromophenyl acetate, 37 g., colourless rhombic plates, m. p. 87°.

p-Aminophenol, 11 g.; *p*-acetamidophenyl acetate, 18 g., colourless flattened prisms with domed ends, m. p. 155—156°.

α-Naphthol, 15 g.; α-naphthyl acetate, 18 g., long colourless prisms with domed ends, m. p. 48—49°.

β-Naphthol, 15 g.; β-naphthyl acetate, 19 g., colourless needles, m. p. 71—72°.

Catechol, 11 g.; *o*-phenylene diacetate, 19 g., large colourless flattened prisms, m. p. 64—65°.

Resorcinol, 11 g.; *m*-phenylene diacetate, 18 g., b. p. 279°/753·3 mm.

Quinol, 11 g.; *p*-phenylene diacetate, 19 g., large colourless flattened prisms with domed ends, m. p. 123—124°.

Pyrogallol, 13 g.; 1 : 2 : 3-triacetoxybenzene, 24 g., long colourless prisms, m. p. 172—173°.

Gallic acid, 19 g.; 3 : 4 : 5-triacetoxybenzoic acid, 25 g., large colourless transparent plates, m. p. 162—163°.

Methyl salicylate, 15 g.; methyl *o*-acetoxybenzoate, 19 g., compact colourless prisms with domed ends, m. p. 52—52·5°.

Salol, 21 g.; phenyl *o*-acetoxybenzoate, 24 g., slender colourless prisms, m. p. 99·5°.

Salicylic acid itself is not acetylated under these conditions.

p-Hydroxybenzoic acid, 14 g.; *p*-acetoxybenzoic acid, 17 g., long colourless flattened prisms, m. p. 189—190°.

Anthranilic acid, 13·7 g.; *o*-acetamidobenzoic acid, 15 g., compact colourless prisms, m. p. 185—186°.

Sulphanilic acid, 17 g.; *p*-acetamidobenzenesulphonic acid, 18 g., colourless needles which when heated blacken and decompose without previously melting.

Glycine, 11 g.; acetamidoacetic acid, 14 g., colourless, compact, much twinned, rhombic prisms, m. p. 206—207° (decomp.).

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