NOTES.

Preparation of Bisacetamide Hydrochloride and its Use as an Acetylating Agent. By HENRY STEPHEN.

WHEN a suspension of acetamide in dry ether is treated with thionyl chloride, a vigorous reaction ensues with simultaneous deposition of bisacetamide hydrochloride as a white crystalline solid (Found :

Cl, 23·4; N, 18·0. Calc. for $C_4H_{11}O_2N_2Cl$: Cl, 23·6; N, 18·4%). The reactions appear to be as follows:

$$CH_3{\cdot}CO{\cdot}NH_2 + SOCl_2 = CH_3{\cdot}CN + SO_2 + 2HCl$$
$$2CH_3{\cdot}CO{\cdot}NH_2 + HCl = (CH_3{\cdot}CO{\cdot}NH_2)_2,HCl$$

Hence only one-third of a given weight of acetamide is converted into nitrile, and this has been confirmed by weighing the bisacetamide hydrochloride produced. The hydrochloride, which has previously been obtained by treatment of acetamide with hydrogen chloride (Strecker, *Annalen*, 1857, **103**, 325), is stable and may be preserved indefinitely without decomposition.

When bisacetamide hydrochloride is fused with an equimolecular proportion of the hydrochloride of a primary aromatic amine, the acetyl derivative of the latter is formed together with a trace of an amidine. Brunner, Matzler, and Mössmer (*Monatsh.*, 1927, **48**, 125) and Brunner and Haslwanter (*ibid.*, p. 133), using diacylamines and the hydrochlorides of primary bases, have obtained mainly amidine together with some of the acylated base. Their observations, coupled with the fact that bisacetamide hydrochloride decomposes on heating, to give, together with other products, diacetamide (Strecker, *loc. cit.*) and acetyl chloride, afford a definite clue to the mechanism of the present method of acetylation.

The reagent has been applied with success to the preparation of acetanilide, aceto-*o*-, -*m*-, and -*p*-toluidides, and aceto-α- and -β-naphthalides.

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The Preparation of Ethyl Methylenedimalonate. By KENNETH NORMAN WELCH.

THE variable yields of ethyl methylenedimalonate obtained by Knoevenagel's method (compare Welch, J., 1930, 257) are due to (1) the occurrence of side reactions, as pointed out by Gault (*Bull. Soc. chim.*, 1912, **11**, 381), and (2) the presence of an alkaline catalyst during the distillation: decomposition occurs according to the balanced Michael reaction

$$CH_2[CH(CO_2Et)_2]_2 \rightleftharpoons (EtO_2C)_2C{:}CH_2 + CH_2(CO_2Et)_2,$$

the products being removed by distillation as formed.

Otterbacher ("Organic Syntheses," Vol. X) reported a yield of only 61%, obtained by a modification of Knoevenagel's method.

The following process gives more than 90% of the theoretical yield, allowing for recovered malonic ester. The use of paraformaldehyde avoids the separation from water, which is troublesome in large-scale preparations.

Ethyl malonate (36 g.) and paraformaldehyde (3 g.) were heated together on the water-bath and 10% alcoholic potassium hydroxide was added drop by drop until reaction commenced : the paraformaldehyde then quickly went into solution. Heating was continued for 6 hours, with the occasional addition of a drop of alcoholic potassium hydroxide, a few c.c. of alcoholic hydrogen chloride were added to destroy the catalyst, and the product was distilled. After removal of the water, ethyl malonate (8 g.), b. p. 80—100°/20 mm., and ethyl methylenedimalonate (28 g.), b. p. 194—198°/20 mm., were obtained, there being hardly any residue.—UNIVERSITY OF MELBOURNE. [*Received, February 2nd,* 1931.]