NOTES.

Cuprous Cyanide: A Note on its Preparation and Use. By H. J. BARBER.

IN these laboratories, where a considerable number of aromatic nitriles have been prepared by the Sandmeyer reaction, using cuprocyanide solutions (J., 1942, 103), we have simplified the technique of " Organic Syntheses " (Coll. Vol. I—X, p. 500). According to that, one prepares a suspension of cuprous chloride, washes it by decantation, and dissolves it in alkali cyanide. This has the disadvantages that the cuprocyanide solution may vary in concentration, contains chloride ions, and cannot conveniently be stored ready for use. Our practice is to prepare in bulk solid cuprous cyanide, which may be kept indefinitely and merely has to be weighed out and dissolved in alkali cyanide as required.

The method given for the preparation of cuprous cyanide in text-books and other literature (*e.g.*, *op. cit.*, p. 38) is according to the equation: $2CuSO_4 + 4NaCN = 2CuCN + 2Na_2SO_4 + (CN)_2$, with the objectionable evolution of cyanogen. An excellent preparative method is afforded by the reaction $2CuSO_4 + 2NaCN + NaHSO_3 + H_2O = 2CuCN + 3NaHSO_4$. The product so obtained is much lighter in colour and gives almost colourless cuprocyanide solutions, in contrast to the dark solutions from the older method.

Experimental.—Copper sulphate (commercial crystalline; 1 kg.) is dissolved in water (3·2 l.) at 40—50°. Sodium bisulphite (commercial powder; 280 g.) is dissolved in water (800 c.c.) at 50—60° and potassium cyanide (95% w/w, " grey single salt "; 280 g.) in water (800 c.c.) at 50—80°. Each solution is filtered and, all being at 60°, the bisulphite solution is run with stirring during 1—2 mins. into the copper solution (acidified faintly to Congo-red), followed immediately by the cyanide solution. There is slight frothing and a little sulphur dioxide is evolved, but no appreciable amount of cyanogen or hydrogen cyanide. After about 10 mins. the hot solution is filtered, and the product washed thoroughly with boiling water, then with alcohol. It is dried at 100° to a fine soft powder; yield, almost quantitative (Found: Cu, 70·0. Calc.: Cu, 70·97%).—MAY & BAKER, LIMITED, DAGENHAM. [*Received, October 16th*, 1942.]

The Action of Phosphoric Oxide on Phenyl Esters. The Mechanism of the Fries Reaction. By ALEXANDER SCHÖNBERG and (MISS) AKILA MUSTAFA.

EXPLANATIONS of the Fries reaction have been advanced by Skraup and Poller (*Ber.*, 1924, **57**, 2033), Auwers and Mauss (*Ber.*, 1928, **61**, 1495; *Annalen*, 1928, **464**, 293), and Rosenmund and Schnurr (*Annalen*, 1928, **460**, 56, 88). That of the last-mentioned authors is illustrated below in the case of phenyl acetate:

$$2PhO{\cdot}CO{\cdot}CH_3 \xrightarrow{AlCl_3} PhOH + p\text{-}CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_3 \quad (I.) \xrightarrow{AlCl_3} 2CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}OH$$

It is a weak point in their theory that the intermediate product (I) has never been isolated, at least as far as we can ascertain.

We replaced the aluminium chloride (or analogous halogen compound; see Auwers, Pötz, and Noll, *Annalen*, 1938, **535**, 228) by phosphoric oxide and isolated the intermediate products (as I) in the cases of phenyl, *m*-tolyl, and α-naphthyl benzoates; this we regard as supporting Rosenmund and Schnurr's view. The yield obtained from phenyl benzoate was about 60%. The phenol formed in the reaction was converted by the phosphoric oxide into phenyl phosphates (cf. Rembold, *Z. Chem.*, 1866, 652; Genvresse, *Compt. rend.*, 1898, **127**, 522), from which it was recovered by hydrolysis and identified as tribromophenol.

In the ordinary Fries reaction with aluminium chloride or analogous halogen compound, low temperatures favour the formation of the *p*-isomer, high temperatures that of the *o*-isomer (Blatt, *Chem. Reviews*, 1940, **27**, 417). We tried to get the *o*-hydroxy-ketones by using phosphoric oxide at high temperatures, but failed because the substances charred.

The Action of Phosphoric Oxide on Phenyl, m-Tolyl, and α-Naphthyl Benzoates.—A solution of phenyl benzoate (5 g.)

in nitrobenzene (75 c.c.) was mechanically stirred while being heated under reflux (calcium chloride guard-tube) with phosphoric oxide at 150° for 3 hours. The mixture was then allowed to cool, poured into ice-cold water, and shaken with ether (250 c.c.). The ethereal layer was separated from the aqueous layer (A), washed with 10% sodium hydroxide solution (3 × 75 c.c.), and dried. The ether was evaporated, and the nitrobenzene distilled in a vacuum. The residual brown oil solidified on cooling; it crystallised from alcohol in colourless plates of *p*-benzoylphenyl benzoate, m. p. and mixed m. p. 113—114° (Found: C, 79·0; H, 4·7. Calc.: C, 79·5; H, 4·7%). The aqueous layer (A) yielded phenol (identified as tribromophenol, 0·5 g.) only after being boiled with alkali for 2 hours and acidified.

A similar experiment with *m*-tolyl benzoate yielded 6-benzoyl-*m*-tolyl benzoate, m. p. 104°, not depressed by an authentic specimen (Bartolotti, *Gazzetta*, 1900, **30**, ii, 225) (Found: C, 80·0; H, 4·7. Calc.: C, 79·8; H, 5·0%).

The product from α-naphthyl benzoate was 4-benzoyl-α-naphthyl benzoate, because after alkaline hydrolysis we obtained 4-benzoyl-α-naphthol, m. p. 164° (cf. Scholl and Scheer, *Annalen*, 1912, **394**, 152), which gives a methyl derivative, m. p. 82°.—FOUAD I UNIVERSITY, CAIRO. [*Received, November 16th*, 1942.]