

NOTES.

The Reducing Action of a Grignard Reagent. By HAROLD BURTON.

IN an attempt to obtain *p*-toluoyldiphenylcarbinol by a method analogous to that used by McKenzie and Wren (J., 1908, **93**, 310; 1909, **95**, 1583) for the preparation of benzoin, powdered benzilamide (4.5 g.) was added during 20 minutes to the Grignard reagent from magnesium (2.9 g.), *p*-iodotoluene (26.2 g.), dry amyl ether (50 c.c.), and a trace of iodine. The mixture was refluxed for 8 hours and then decomposed with ice and dilute sulphuric acid. Filtration of the undissolved solid (1.5 g.) and crystallisation from benzene gave pure diphenylacetamide, m. p. 167—168°. A further small amount was isolated from the amyl ether, but none of the carbinol was found.

Benzilamide, m. p. 155°, is conveniently prepared in good yield when a concentrated solution of methyl benzilate in alcohol is saturated with ammonia gas first at the ordinary temperature and then below 0°. Crystals of the amide separate during 3 days; these are filtered off and crystallised from benzene.

When benzilamide was refluxed during 8 hours with ethereal magnesium *p*-tolyl iodide, and the mixture decomposed with ice and dilute sulphuric acid, the amide was recovered unchanged.—THE UNIVERSITY, LEEDS. [*Received, September 10th, 1930.*]

The Action of Hydrobromic Acid on Certain Arsinic Acids. By MONTAGUE ALEXANDRA PHILLIPS.

THE action of hydriodic acid on 3-nitro-4-aminophenylarsinic acid gives a good yield of 4-iodo-2-nitroaniline (Mameli, *Boll. Chim. Farm.*, 1909, **48**, 682); and bromine and 3:5-dinitro-4-aminophenylarsinic acid give 4-bromo-2:6-dinitroaniline (Benda, *Ber.*, 1912, **45**, 53).

The following table shows the results of the action of concentrated hydrobromic acid on various arsinic acids. The arsinic acid was boiled for a few minutes with three or four times its weight of hydrobromic acid (*d* 1.445), and the resulting oily suspension poured on ice. In the cases marked with an asterisk, the method is a useful way of preparing the bromo-compounds. In these cases, also, the bromo-compounds were recrystallised from alcohol or aqueous alcohol.

Phenylarsinic acid.	Product.	M. p.	Yield %.
*3-Nitro-4-amino-	4-Bromo-2-nitroaniline	111°	97
*4-Nitro-3-amino-	5-Bromo-2-nitroaniline	153	96
*3-Nitro-4-methylamino-	4-Bromo-2-nitromethylaniline	102	92
*4-Nitro-3-methylamino-	5-Bromo-2-nitromethylaniline	112	80
3-Nitro-4-hydroxy-	Mixture of polybrominated nitrophenols from which 2 : 4-dibromo-6-nitrophenol, m. p. 118°, was isolated in 20% yield.		
3-Amino-4-hydroxy-	4-Bromo-2-aminophenol (isolated as acetyl derivative)	177	ca. 20
3-Acetamido-4-hydroxy-	4-Bromo-2-aminophenol (isolated as acetyl derivative)		
*3 : 5-Dinitro-4-amino-	4-Bromo-2 : 6-dinitroaniline	160	96

Of the above arsenic acids, 4-nitro-3-methylaminophenylarsinic acid has not hitherto been described; it is obtained as yellow plates of indefinite melting point by the action of methylamine hydrochloride on 3-chloro-4-nitrophenylarsinic acid for 3 hours at 150–160° (Found : As, 26.95. $C_7H_9O_5N_2As$ requires As, 27.1%).

The action of hydrobromic acid on 4-nitro-3-hydroxy- and 2-nitro-3-hydroxy-phenylarsinic acids gave mixtures of polybrominated nitrophenols which could not be separated. No decomposition of 6-nitro-3-aminophenylarsinic acid occurred after 3 hours' treatment with boiling concentrated hydrobromic acid.—RESEARCH LABORATORIES, MESSRS. MAY & BAKER LTD., LONDON, S.W.18. [Received, August 13th, 1930.]

The Action of Ferric Chloride on o-, m-, and p-Toluidine. By
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WHEN treated with hydrochloric acid (slightly more than 1 mol.), followed by ferric chloride, *o*-toluidine yields after some minutes a dark bluish-green precipitate with purple reflex, *m*-toluidine gives a brown colour and then a precipitate similar in appearance to the above, but *p*-toluidine only develops an intense plum-red colour, slowly in the cold, more quickly when warmed (compare Biehringer and Busch, *Chem.-Ztg.*, 1902, **26**, 1128). The reactions are given by mixtures of the three toluidines, but filtration may then be necessary to reveal the red coloration.

The reaction with *m*-toluidine, with excess of ferric chloride, is complete at the ordinary temperature after 28 days; the weight of the precipitate obtained (and also in the case of *o*-toluidine) is about half that of the toluidine. The precipitate obtained after 7 days from a mixture of 30.5% of *p*- and 69.5% of *o*-toluidine to which hydrochloric acid (1.06 mols.) and ferric chloride (0.98 mol.) have been added is 32% by weight of the *o*-toluidine : the content of *p*-toluidine in the residual mixture is 37.6%.

The precipitates are complex insoluble substances containing only organic matter and burn without melting when heated in air.—EAST LONDON COLLEGE. [Received, August 19th, 1930.]