NOTES.

Methylfurfuraldehyde Oxide as a By-product in the Preparation of Hydroxymethylfurfuraldehyde. By J. P. C. Chandrasena.

In the course of a preparation of hydroxymethylfurfuraldehyde by Troje's method (*Z. Ver. Deut. Zuckerind.*, 1925, 635) an interesting by-product has been isolated. The method consists in heating sucrose and oxalic acid in aqueous solution in an autoclave under a pressure of 3 atm., extracting the product with ethyl acetate, removing the solvent, and distilling the residual liquid in a very high vacuum. After the hydroxymethylfurfuraldehyde had passed over there remained a considerable quantity of a dark brown sludge, which, after standing for a few days on porous earthenware, gave a light brown solid. This was recrystallised from hot water (charcoal) and gave bright yellow needle-shaped crystals, m. p. 120° (Found : C, 61·6; H, 4·4. Calc. for $C_{12}H_{10}O_5$: C, 61·5; H, 4·3%).

Kiermayer (*Chem. Ztg.*, 1895, **19**, 1003) prepared a substance of this formula, *viz.*, methylfurfuraldehyde oxide, by dehydrating β-hydroxy-δ-methylfurfuraldehyde over concentrated sulphuric acid, and the author's product resembles this substance in reducing Fehling's solution and giving the silver mirror test. Kiermayer, however, crystallised his material from alcohol.

Cold alkaline permanganate and 2*N*-nitric acid at 80° oxidised the substance to oxalic acid, but hot alkaline permanganate gave a product which did not melt at 250° and was not obtained in sufficient quantity to be identified. The compound is obviously derived from the fructose residue of the sucrose molecule.—Ceylon University College, Colombo. [*Received, June* 30*th*, 1930.]

The Action of Freshly Precipitated Mercuric Oxide on a Suspension of 3 : 5-*Dinitrotoluene in Aqueous Sodium Hydroxide. A Novel Preparation of* 3 : 5-*Dinitro*-p-*cresol.* By Herbert Henry Hodgson and Ernest Walter Smith.

This reaction affords 3 : 5-dinitro-*p*-cresol in approximately 50% yield, the other products being amorphous substances mixed with metallic mercury. Mercuric oxide has no action upon 3 : 5-dinitrotoluene in the absence of sodium hydroxide, and the latter reagent alone gives no simple hydroxylated product; moreover, no reaction takes place even after 10 hours' boiling when sodium carbonate is substituted for the hydroxide. Neither *m*-nitrotoluene nor nitrobenzene reacts under the conditions employed, whilst *m*-dinitro- and *s*-trinitro-benzene give amorphous complex products accompanied by copious evolution of ammonia. It is suggested that the very positive 4-carbon atom first forms an unstable complex with a hypothetical mercurate ion (compare Fuseya, *J. Amer. Chem. Soc.*, 1920, **42**, 368), and subsequent hydrolysis gives the above result.

A mixture of mercuric chloride (13 g., dissolved in a little water), 20% sodium hydroxide (120 c.c.), and 3 : 5-dinitrotoluene (3 g.) was diluted to 500 c.c. with water and boiled under reflux for 10 hours, some ammonia being evolved. The filtrate, from the black residue of amorphous substances and metallic mercury, was acidified, and the precipitate purified by distillation in superheated steam; 3 : 5-dinitro-*p*-cresol crystallised (1·5 g.) from hot water in pale yellow needles, m. p. 79—80° (Found : N, 13·8. Calc., N, 14·1%), and was proved to be dissimilar from 3 : 5-dinitro-*o*-cresol, m. p. 86°.

To ensure that no 3 : 5-dinitro-*p*-cresol was present in the initial 3 : 5-dinitrotoluene, which had been prepared from 3 : 5-dinitro-*p*-toluidine by the usual diazotisation–elimination procedure, the dinitrotoluene was steam distilled several times from sodium carbonate solution (boiling caustic soda solution slowly converts it into a dark brown insoluble amorphous product). When the reaction is carried out on the water-bath instead of at the boil, it proceeds much more slowly and the 3 : 5-dinitro-*p*-cresol can be removed as formed by filtration and acidification of the filtrate as above, the residue containing the unchanged 3 : 5-dinitrotoluene being subsequently boiled with fresh aqueous sodium hydroxide to give further amounts of the cresol.

The authors desire to thank the Department of Scientific and Industrial Research for a grant to one of them (E. W. S.), and Messrs. J. W. Leitch and Co. for gifts of chemicals used in this investigation.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, May* 26*th*, 1930.]