

the pot. To the melt 25 g. of the sodium salt of dianilido-succinic acid was added. The temperature was held at 230–240° for 1½ hours. The melt was dissolved in water and blown with air. Indigo precipitated and was filtered off. The yield was 11.5 g. or 60.4% of that calculated on the basis of 100% indigo from pure (100%) dianilido-succinic acid, or 25% on the fumaric acid added.

This indigo was 96.5% pure by the method of Bloxam⁵ and showed satisfactory dyeing qualities.

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The Occurrence of Terpin Hydrate in Nature.—Terpin hydrate, (C₁₀H₂₀O₂.H₂O), a well crystallized substance, has long been known as a product of the synthetic laboratory. It is easily prepared by allowing turpentine oil to stand in the air in contact with water for a long time or more rapidly by adding nitric acid and alcohol to the mixture. It seems strange, then, that it should not have been formed by natural agencies, yet until recently it was unknown in nature. In October, 1920, the writer described a crystalline substance, flagstaffite, found in buried pine logs, giving the result of chemical analyses, molecular weight determinations and crystallographic measurements.¹ At that time he was unable to find any natural or synthetic product that corresponded to it, but later, on the suggestion of Dr. Francis D. Dodge of Brooklyn, N. Y., careful comparisons were made with terpin hydrate with the result that both crystallographically and chemically they were found identical.² The discovery of this substance in logs buried at least 500 years as shown by tree rings in stumps still rooted in the debris, adds a new mineral species, while its identity with a well-known synthetic product is of general interest.

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The Action of Halogens on Aceto-acetic Ester.—The action of chlorine and of bromine on aceto-acetic ester has been the subject of many investigations and of considerable controversy. In a series of researches extending from 1890–4 Hantzsch finally proved, by a method that is both elegant and conclusive, that the product obtained by passing chlorine into the ester is an α -chloro derivative, while that obtained by adding bromine to solutions of the ester is a γ -bromo compound. Hantzsch also discovered that in the presence of hydrogen bromide, the α -bromo ester obtained by

⁵ Bloxam, *J. Soc. Chem. Ind.*, **25**, 735 (1906).

¹ Guild, *American Mineralogist*, **5**, 155 (1920).

² Guild, *ibid.*, **6**, 133 (1921).

brominating the copper derivative passes more or less rapidly into the γ -bromo isomer.

I have found that when the bromination is conducted as nearly as possible in the manner in which the ester is commonly chlorinated the product is the α -bromo ester. Thus when 22 g. of bromine was carried into 27 g. of aceto-acetic ester by a rapid current of air which both introduced the bromine as vapor and swept out the hydrogen bromide, the sole product was the α -bromo ester: with thio-urea it gave only amino-thiazol-carboxylic ester.

The action of bromine on aceto-acetic ester is therefore exactly the same as that of chlorine, and the differences heretofore observed are due to differences in procedure.

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Correction.—In the paper on "Preparation and Hydrolysis of Benzyl Esters" in the July, 1921, number of THIS JOURNAL, p. 1674, in lines 2 and 3, the words "salicylate product" should read "a product," and in line 11, the words "about 20°" should read "about -20°."

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NEW BOOKS.

Die Elektrometrische Massanalyse. (Electrometric Volumetric Analysis.) By DR. ERICH MÜLLER, Ord. Professor and Director of the Laboratory of Electrochemistry and Physical Chemistry at the Technische Hochschule, Dresden. Theodor Steinkopff, Dresden and Leipzig, 1921. vi + 110 pp. 19 fig. 15.5 × 23 cm. Price £0-8-3.

The scope of electrometric titration has been greatly extended during the past few years by the researches of Treadwell, Dutoit, and particularly of Pinkhof and of Liebisch. Moreover, these last mentioned authors have published their results in dissertations which are comparatively inaccessible. The present volume, therefore, containing a collection and critical discussion of this material, is decidedly opportune.

In it, the author first gives a clear and simple presentation of the theoretical principles underlying this method of analysis. He includes a discussion of those requirements which must be met if a given chemical reaction is to be utilized for electrometric titration, and of those measures which can be taken if an indicator-electrode fails to respond to either of the partial reactions involved in the chemical equilibrium.

Next, the author describes 4 general methods for the execution of electrometric titrations, and considers the relative advantages and disad-