April, 1932

PREPARATION OF 7,7'-DIMETHYL-8,8'-DIQUINOLYL AND OF 5,5',7,7'-TETRA-METHYL-8,8'-DIQUINOLYL

Sir:

The possibility of optical isomerism in substituted diquinolyls has been suggested by Mascarelli [Gazz. chim. ital., **58**, 627 (1928)]. The preparation of such compounds has been under way at this Laboratory for nearly two years.

7,7'-Dimethyl-8,8'-diquinolyl was made by coupling two molecules of 3-nitro-2-iodotoluene by means of copper powder. The resulting dinitrodimethyldiphenyl was reduced and converted by a Skraup synthesis to 7,7'-dimethyl-8,8'-diquinolyl. It is a white solid, melting at 213-215°. It is insoluble in water, but soluble in dilute acids and in alcohol, benzene and ether.

5,5',7,7'-Tetramethyl-8,8'-diquinolyl was made by coupling two molecules of 5-nitro-4-iodo-1,3-dimethylbenzene with copper powder. The resulting dinitrotetramethyldiphenyl was reduced and converted by a Skraup synthesis to 5,5',7,7'-tetramethyl-8,8'-diquinolyl. The substance is a white solid similar in properties to the dimethyldiquinolyl. The preparation of larger quantities of these and other substituted diquinolyls is now under way and attempts are being made to resolve the compounds.

DEPARTMENT OF CHEMISTRY THE CATHOLIC UNIVERSITY OF AMERICA WASHINGTON, D. C. RECEIVED MARCH 11, 1932 PUBLISHED APRIL 6, 1932 Henry P. Ward Mary Grace Waring

THE STRUCTURE OF ALPHA-PENTAACETYLFRUCTOSE AND ALPHA-CHLOROACETYLFRUCTOSE

Sir:

In 1915 Hudson and Brauns [THIS JOURNAL, **37**, 1283, 2736 (1915)] described two crystalline pentaacetates of fructose which they believed to constitute an α,β -stereoisomeric pair.

In 1920 Brauns [*ibid.*, **42**, 1846 (1920)] prepared from tetraacetylfructose two chloro compounds which he assumed to be α - and β -stereoisomers. Subsequently his designation of the two forms was reversed at the suggestion of Dr. Hudson and now the substance showing $[\alpha]_D - 161^\circ$ in chloroform solution is known as β -chloroacetylfructose whereas the one with $[\alpha]_D + 45^\circ$ is assigned the α -configuration.

Using the rotations of these chloro compounds to determine the applicability of the principle of optical superposition to derivatives of the ketone sugars, Dr. Hudson [*ibid.*, **46**, 477 (1924)] calculated the rotations of the fructose pentaacetates. From his results he concluded that the compound with the positive rotation is probably not the true α -form. This conclusion is supported by the differences in properties of the two known pentaacetates. However, the extreme dissimilarity of the two chloroacetylfructoses suggests that they, too, may not constitute an α,β -pair. Dr. Brauns has remarked on their great difference in stability.

We now have experimental evidence that the so-called " α -chloroacetylfructose" and the " α -pentaacetylfructose" differ *structurally* from their isomer in that they are derivatives of the open-chain fructose and contain a free ketone group. The strongest evidence for the presence of a ketone group in " α -pentaacetylfructose" is its catalytic reduction to the alcohol. On account of the new asymmetric carbon atom formed during the reduction, sorbitol and mannitol derivatives should be obtained. After acetylation two compounds were isolated and identified as hexaacetylmannitol and hexaacetylsorbitol with melting points 121 and 97°, respectively.

Under the same conditions of reduction the " α -chloroacetylfructose" took up hydrogen and there resulted a substance which, like the starting material, contained a very stable chlorine atom.

The chlorine atom in " α -chloroacetylfructose" could not be replaced by heating the substance in acetic anhydride solution with silver acetate. This behavior suggests the presence of a firmly bound, primary chlorine atom.

For these reasons we conclude that the " α -chloroacetylfructose" represents a derivative of the open-chain fructose with a chlorine atom at carbon atom 6.

The details of this investigation will be published within a short time.

FRICK CHEMICAL LABORATORY PRINCETON UNIVERSITY PRINCETON, NEW JERSEY RECEIVED MARCH 12, 1932 PUBLISHED APRIL 6, 1932 EUGENE PACSU FRANK V. RICH

THE CONSTANT *a* IN THE DEBYE-HÜCKEL LIMITING EQUATION Sir:

In THIS JOURNAL for February, 1932 (p. 831), Professor Hall discusses the numerical value of the constant a in the Debye-Hückel limiting equation: $-\log f = aC^{1/2}$, and refers to a publication ("Conductivity of Solutions," 1930) in which I pointed out that attempts to determine aexperimentally have always led to values nearer to 0.4 than to the theoretical value 0.5.

In the same place I remarked that further data on the point are needed, and that conductivity measurements probably provide the most accurate way of obtaining them. Since then, Mr. Banks in this Laboratory has made conductivity measurements on mandelic acid at 25° which agree, after applying Onsager's correction for the mobility changes, with the theoretical value of a. We had intended to study further weak acids, but abandoned this plan when MacInnes and Shedlovsky [THIS JOURNAL, 53,