COMMUNICATIONS TO THE EDITOR

FORMATION OF AN ACID ANHYDRIDE BY THE ACTION OF WATER ON ORGANOMETALLIC COMPLEXES

Sir:

The formation of an acid anhydride by the addition of water to an organometallic complex has been observed in two different instances. A Grignard reagent, prepared from 4-bromo-7-isopropylhydrindene, when added to pure α-naphthoyl chloride in ether, yielded 50% of the expected ketone, 4-α-naphthoyl-7-isopropylhydrindene, together with 28% of the hydrocarbon, 4-isopropylhydrindene, and 22% of α-naphthoic anhydride. Another instance was found in the reaction between α-naphthoyl chloride and the lithium derivative from 2,7-dimethyl-4-bromohydrindene.[1] In this reaction the yield of ketone was small, but that of hydrocarbon and anhydride large. Particularly in this case, the formation of colored solutions showed the formation of complexes. A fleeting bright red color[2] gave place to a pale orange which disappeared on addition of water to give rise to the granular yellow anhydride.

The experimental procedure in both cases involved addition of the organometallic solution to α-naphthoyl chloride dissolved in absolute ether, ensuring an excess of acid chloride. To a solution of 15 g. of α-naphthoyl chloride (m. p. 21°) in absolute ether at −5° was added dropwise with stirring a Grignard reagent made from 10 g. of 4-bromo-7-isopropylhydrindene, 2 g. of magnesium and 60 cc. of ether. The solution was then refluxed for four hours. An equal volume of saturated sodium bicarbonate solution was added in order to remove the unchanged acid chloride. Upon distilling most of the ether and cooling, a yellow granular solid appeared. This proved to be α-naphthoic anhydride melting at 145°, and giving the same value upon admixture with an authentic sample. Upon distillation of the remaining material, 2 g. of 4-isopropylhydrindene, b. p. 88–90° at 1 mm., and 7.3 g. of 4-α-naphthoyl-7-isopropylhydrindene, b. p. 225–235° at 1.2 mm., were secured.

In the second instance, 0.70 g. of lithium wire was dissolved in a solution of 7 g. of 2,7-dimethyl-4-bromohydrindene[1] in 100 cc. of ether. This orange-colored solution was added over a period of three hours to 15 g. of α-naphthoyl chloride in 200 cc. of ether. The residue of lithium salt was washed with 50 cc. of ether and 100 cc. of benzene. Addition of 300 cc. of saturated sodium bicarbonate solution with stirring until the evolution of carbon dioxide had practically stopped (four hours) left a clear light red solution which was concentrated to about 50 cc. Upon standing, 7 g. of α-naphthoic anhydride, m. p. 145–146°, separated. The substance was identified by its analysis and melting point, and by hydrolysis with alcoholic sodium hydroxide to give α-naphthoic acid melting at 160–161°. From the bicarbonate solution was recovered 9 g. of α-naphthoic acid (air-dried overnight). Distillation of the filtrate from the anhydride gave 3.5 g. of 2,4-dimethylhydrindene, b. p. 100–105° at 23 mm., and 1 g. of an oil, contaminated with α-naphthoic acid, b. p. 200–235° at 2 mm., presumably 4-α-naphthoyl-2,7-dimethylhydrindene.

Further study is in progress to determine the mechanism and limits of this curious reaction.

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Received August 8, 1938

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[1] Bruce with Fieser, This Journal, **59**, 480 (1937).

[2] Professor E. P. Kohler suggested at the time that this color may have been caused by iron in the lithium; however, no ferric hydroxide is found upon solution of the lithium in water.

CRYSTALLINE DIMETHYL ACETAL OF *d*-FRUCTOSE

Sir:

Application of the method developed in this Laboratory for the preparation of glycofuranosides [Pacsu and Green, This Journal, **58**, 1823 (1936); Green and Pacsu, *ibid.*, **59**, 1205, 2569 (1937); **60**, 2056 (1938)] to fructosediethylmercaptal resulted in the unexpected formation of crystalline dimethyl acetal of *d*-fructose. The substance was obtained in practically quantitative yield on the treatment of fructosediethylmercaptal with mercuric chloride in absolute methyl alcohol at −80°, in the presence of an excess of yellow mercuric oxide; m. p. 107–108° and $[\alpha]^{20}\mathrm{D}$ −45.6° in water solution. On acetylation, it readily gave a crystalline pentaacetate, with m. p. 109° and $[\alpha]^{20}\mathrm{D}$ 0° in chloroform solution. The free acetal crystallized from *n*-propyl alcohol in beautifully developed large prisms, which were not hygroscopic and were devoid of action toward Fehling's solution. The compound was found to be stable in neutral and alkaline solutions, but it suffered rapid decomposition at room temperature in acidic media. Experiments carried out in fermentation saccharimeters showed that while yeast was capable of fermenting fructosedimethylacetal in distilled water to give carbon dioxide, methyl and ethyl alcohols in almost quantitative yield, it was without any effect on the acetal in a citric acid–disodium phosphate buffer solution of *p*H 7. The action of different invertase samples on the acetal at *p*H 4.5 and *p*H 7 was found to be completely negative, although the same samples were very active on sucrose under identical conditions.

In view of the extreme sensitiveness of the acetal toward acid, the action of yeast in an unbuffered solution might be due to the fermentation of fructose liberated from the acetal by a trace of the acid of the yeast, rather than to a genuine enzymatic effect. This problem is now being investigated. A detailed account of the work will be published shortly.

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RECEIVED AUGUST 11, 1938

NEW BOOKS

Modern Theories of Organic Chemistry. By H. B. WATSON, D.Sc. (Wales), F.I.C., Head of the Department of Chemistry at the City of Cardiff Technical College. Oxford University Press, 114 Fifth Avenue, New York, N. Y., 1937. vii + 218 pp. 21 figs. 16.5 × 25 cm. Price, $4.50.

"Professor G. N. Lewis's conception of the sharing of one or more electron pairs by two atoms gave a new and illuminating picture of the bonds which link carbon atoms into chains and rings, and set organic chemists the task of interpreting the reactions of carbon compounds of various types in terms of the electronic structures of the molecules. .

"In this volume an attempt is made to present the modern viewpoint in a concise and simple form, and to show how the new conceptions have followed logically from the earlier views." As is evident from its size, the book does not undertake to be complete in detail, nor to provide an exhaustive bibliography. The chapters deal with: Theories of Chemical Combination; The New Physical Methods of Investigation; Applications of the Electronic Theory in Organic Chemistry, Strengths of Acids and Bases, The Inductive Effect; Substitution Reactions; General Discussion of the Application of the Electronic Theory in Organic Chemistry; Free Radicals; Compounds of Divalent Carbon and Allied Problems; Addition to Unsaturated Compounds; Tautomeric Change; Migrations from Side-Chain to Nucleus and Other Rearrangements; The Factors Determining Reaction Velocity; A Review of Some Stereochemical Problems.

The author has an exceptionally clear and logical style. This is at its best in the introductory chapters, which can be recommended not only to students, but to every organic chemist who wishes to consider what modern physics has done for the understanding of his science. Briefly Professor Watson has put the last fifteen years into their place in chemical history, and in this placing has built a vigorous viewpoint for the present.

In the electronic interpretation of organic reactions, certain English chemists have been pioneers. Their views might originally have been more cordially received in this country if presented inductively and in terms whose meanings are well known. Professor Watson has accomplished this. He has placed the horse consistently before the cart and has shown the necessity of each concept introduced. Proceeding on this basis, he uses fewer ultimate variables than have appeared in some discussions in this field.

Chapters 6 to 10 and 12 make a less unique contribution, for in their brevity they contain little material not usually included in courses in advanced organic chemistry. Even the consideration of evidence on specific problems is far from complete. Nevertheless, the clear and discriminating presentations of some of the problems are likely to be a better introduction for students than a more exhaustive descriptive treatment.

The printing of the book is up to the usual good standard of the Oxford University Press. The publishers have done well to put the price within the reach of most students and teachers.

PAUL D. BARTLETT

The Chemistry of the Sterids. By HARRY SOBOTKA, Chemist to the Mount Sinai Hospital, New York. The Williams and Wilkins Company, Mt. Royal and Guilford Avenues, Baltimore, Maryland, 1938. xiii + 634 pp. 15 × 23.5 cm. Price, $8.50.

The word "Sterids" is a newcomer to the terminology of the organic chemist. According to the author it "is meant to comprise sterols and steroids, *i. e.*, sterol-like