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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[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