acid esterification procedure (mostly diacetin) was treated with 110 cc. of glycerol and 5 cc. of phosphoric acid. The technique of the preceding experiment was followed with the result that a practically quantitative yield of monacetin was obtained.

Repetition of the experiment in which triacetin, made by the interaction of glycerol and an excess of acetic anhydride, was heated with twice its volume of glycerol under the conditions outlined above led to the same results.

Conclusions

Esterification of glycerol proceeds in three stages, but a mixture of acetins containing representatives of each type of ester is obtained when the reaction is uncontrolled in so far as a catalyst is concerned. Under definite weight relationships as to reactants, the presence of sulfuric acid favors the formation of diacetin while zinc chloride tends to aid in the production of a mixture of the mono and di esters. Monacetin in practically quantitative yield is formed when molar quantities of acetic acid and glycerol are made to react in the presence of phosphoric acid or its anhydride. The formation of monacetin can also be accomplished from the other direction in that both diacetin and triacetin, when heated with an excess of glycerol, may be converted into the mono ester in the presence of phosphoric acid.

Madison, Wisconsin

[Contribution from the Laboratory of Foods and Sanitation, University of Wisconsin]

NORMAL VALEROLACTONE

By H. A. Schuette and Peter P. T. Sah

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n-Valerolactone has been known for many years, yet there is a conspicuous gap in the literature on some of its simpler physical constants. Its structure was proved by Messerschmidt[1] and by Wolff.[2] The former made it by boiling the addition compound of allylacetic and hydrobromic acids with water. The latter, by means of sodium amalgam, reduced levulinic acid to γ-hydroxyvaleric acid[3] from which he then removed the elements of a molecule of water. Since levulinic acid is a substance which can be made from cheap raw materials with no undue difficulties, the latter procedure is preferred, but the use of sodium amalgam as reducing agent in this instance cannot be recommended for not only is its reaction velocity

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[1] Messerschmidt, *Ann.*, **208**, 96 (1881).

[2] Wolff, *Ann.*, **208**, 104 (1881).

[3] Sabatier has effected the same results with hydrogen at 250° in the presence of nickel as catalyst [*Ann. chim. phys.*, [8] **16**, 70 (1909)] and Tafel and Emmert have done it electrolytically from an alkaline solution [*Z. Elektrochem.*, **17**, 569 (1911)].

under the conditions under which it functions extremely slow, but the first cost of the reagent makes recovery of the mercury desirable, and this is a tedious and troublesome operation.

By using a procedure which is in a sense a modification of a method devised by Losanitsch[4] it has been possible to accomplish the same reduction with a greater degree of dispatch and effectiveness than that obtained before. As a by-product of the reduction, about 80% of the alcohol originally used is recovered in a very pure condition.

It is the purpose of this communication to describe the procedure devised in preparing *n*-valerolactone of a degree of purity requisite for a determination of some of its simpler physical constants.

Experimental Procedure

Preparation of Levulinic Acid.—Levulinic acid was prepared from cane sugar by the method of Rischbieth[5] after attempts to synthesize it by condensing diethyl malonate with monochloro-acetone were abandoned because of very poor yields. It melted at 35° and boiled at 145° (4 mm.). Inasmuch as the mechanism of the hydrolysis whereby hot dilute acids acting upon a carbohydrate convert it into levulinic acid is not well understood at the present time, control of the reaction is very difficult. The long time necessary to effect the conversion and the large amount of so-called humic substances formed during this reaction emphasize the need of a better and more rapid method of preparation.

Reduction.—Three hundred and forty g. of the liquefied acid was dissolved in a solution of 120 g. of sodium hydroxide in 1 liter of 95% ethyl alcohol in a large flask fitted with a reflux condenser. Into this solution, during four hours, there was introduced 138 g. of sodium shavings, the contents of the flask being thoroughly stirred during the reaction in order to restrain the escape of hydrogen. After all of the sodium had been added, 800 cc. of alcohol was distilled from the reaction mixture. The residue, which consisted now of the sodium salt of valeric acid and sodium ethoxide, was treated with 250 cc. of water for the purpose of decomposing the latter. The resulting alcohol was removed by distillation, the residual liquors were cooled in ice water, and 755 cc. of dil. sulfuric acid (225 cc. of acid, d. 1.84, in 500 cc. of water) was cautiously added. The brown, oil-like liquid which separated was removed, the yellow aqueous solution neutralized with potassium carbonate and repeatedly extracted with ether. After recovery of the ether, the residue was mixed with the impure lactone which had separated, and the whole fractionated under reduced pressure. The fraction distilling between 115° and 135° (60 mm.) was collected and redistilled. Repeated distillation gave a colorless product of a faint but agreeable odor; yield, about 60%.

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[4] Losanitsch, *Monatsh.*, **35**, 301 (1914).

[5] Rischbieth, *Ber.*, **20**, 1775 (1887).

The following constants of the purified valerolactone were determined: b. p., 206–207°; 125° (60 mm.) 78° (4 mm.) n_D^{25}, 1.4301; d^{25}, 1.04608. It is miscible with ethyl alcohol, water and ether, in all proportions.

Summary

By substituting metallic sodium for sodium amalgam in the reduction of levulinic acid, a quicker and more convenient method for the preparation of *n*-valerolactone was devised. The latter was highly purified and a few of its physical constants were determined.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF INDIANA UNIVERSITY]

SIDE-CHAIN OXIDATIONS BY MEANS OF NITRO COMPOUNDS

BY LEE T. SMITH WITH ROBERT E. LYONS

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Introduction

The oxidation of a side chain by means of a nitro compound presents a new type of double decomposition in which each of the reacting organic substances yields a product, or products, of value. Thus, if it were possible to oxidize the side chain of an aromatic hydrocarbon, such as toluene, with an aromatic nitro compound, such as nitrobenzene, the possible products would be benzyl alcohol, benzaldehyde or benzoic acid on the one hand and azoxybenzene, azobenzene, hydrazobenzene or aniline on the other. If nuclear substitution products of toluene and nitrobenzene were used, corresponding derivatives would be anticipated. The products formed and the amount of each would depend, in part, on the acidity or alkalinity of the reacting medium.

Few instances of the employment of nitro compounds as oxidizing agents are recorded in the literature. Such use has been made of nitrobenzene in the manufacture of fuchsin (magenta),[1] and in the Skraup synthesis. Anthranilic acid is formed by an intramolecular rearrangement of *o*-nitrotoluene when heated with alkali.[2]

The general problem, as considered in this paper, relates to the conditions most favorable for the aggressive action of nitro compounds as extramolecular oxidizing agents for side chains.

Experimental Part

Pure toluene was treated with nitrobenzene, first in an acid, then in an alkaline solution, with and without catalysts. There was no indication

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[1] Brüning, *Ber.*, **6**, 25, 1072 (1873). Coupier, *Ber.*, **6**, 423 (1873).

[2] Ullmann, "Enzyklopadie der technischen Chemie," Urban u. Schwarzenberg, **1915**, vol. 2, p. 332.