position products of the *trans*-diazo compound. The proportion of the unsaturated ester is different in the two decompositions.

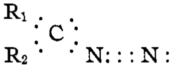
The two diazo compounds give by their decomposition approximately the following products: *cis*-diazocamphonanic methyl ester

Esters of hydroxy acids	39.5%
Esters of unsaturated acids	60.5%

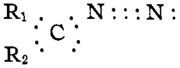
trans-diazocamphonanic methyl ester

Methyl ether of *cis*-camphonolic acid	5.0%
Esters of hydroxy acids	68.0%
Esters of unsaturated acids	27.0%

The above results furnish conclusive proof that the two diazo compounds have an asymmetric structure, in part. This is most simply explained by the electronic formulas



$$\begin{array}{l} R_1\,\cdot\;\;\cdot \\ \quad :C: \\ R_2\,\cdot\;\;\cdot\,N:::N: \end{array}$$



$$\begin{array}{l} R_1\,\cdot\;\;\cdot\,N:::N: \\ \quad :C: \\ R_2\,\cdot\;\;\cdot \end{array}$$

GRINNELL, IOWA

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

NORMAL VALEROLACTONE. III. ITS PREPARATION BY THE CATALYTIC REDUCTION OF LEVULINIC ACID WITH HYDROGEN IN THE PRESENCE OF PLATINUM OXIDE

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n-Valerolactone has been prepared in the past by reducing levulinic acid to γ-hydroxyvaleric acid and then removing the elements of a molecule of water from the latter. Reduction of the levulinic acid has been effected either through the agency of sodium amalgam[1] or of ethyl alcohol and sodium,[2] procedures which are time-consuming, expensive and ill-suited to the preparation of this lactone in quantity.

The basis for a simplification and an improvement in method of preparation was announced some years ago by Sabatier and Mailhe,[3] who by passing levulinic acid in gas phase together with hydrogen over a nickel catalyst at 250° succeeded in hydrogenating the former and dehydrating the resulting reaction product all in one operation. Certain facts[4] recently ascertained with respect to the stability of *n*-valerolactone at its boiling point having cast some doubt upon the quality of a product obtained at

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

[2] Losanitsch, *Monatsh.*, **35**, 301 (1914); Schuette and Sah, THIS JOURNAL, **48**, 3163 (1926).

[3] Sabatier and Mailhe, *Ann. chim. phys.*, [8] **16**, 78 (1909).

[4] Schuette and Thomas, THIS JOURNAL, **52**, 2028 (1930).

this temperature, it seemed desirable, for this and other reasons, to investigate again the application of this form of hydrogenation to levulinic acid in the hope of harmonizing in principle Sabatier's procedure[3] with these newer observations. That this reduction can be carried out very conveniently at room temperature (22–24°) in the presence of platinum oxide[5] as catalyst, and that the rate of hydrogenation and efficiency of reduction are in this instance influenced by the solvent employed have been demonstrated in this Laboratory. The presentation of these facts is the object of this communication.

Experimental

For the purpose of making a comparison of the relative speeds with which the catalytic hydrogenation of levulinic acid[6] proceeds when the latter is dissolved in one of three common solvents (diethyl ether, ethyl alcohol, acetic acid), a series of reductions was made during the course of which several variables were introduced. What are deemed to be the most significant results of the series were obtained under the following conditions.

To 0.5 mole of levulinic acid in 150 cc. of anhydrous solvent there was added 0.4 g. of platinum oxide catalyst.[5] The usual form of mechanical shaker, operating at room temperature, was used with hydrogen under a pressure of 2.3 to 3.0 atmospheres. At the end of forty-four hours the reaction was interrupted because it was apparent that the consumption of hydrogen had practically ceased. Data pertinent to this series are presented in the form of curves (Fig. 1).

The best yield of lactone (87%), based upon the quantity of levulinic acid reduced, was obtained when ethyl ether was employed as solvent. Corresponding yields when ethyl alcohol and acetic acid were in turn substituted for the former proved to be 52 and 48%, respectively.

Anal. Subs., 0.2037: CO_2, 0.4449; H_2O, 0.1488. Calcd. for $C_5H_8O_2$: C, 59.97; H, 8.05. Found: C, 59.58; H, 8.17.

Physical constants were found to be n_D^{25} 1.4303; d^{25} 1.0465; $M_{\text{calcd.}}$, 24.88; M_{found} 24.70.

During the course of a second series of reductions in ethyl ether solution fresh portions of catalyst were added at the end of seven and twenty hours, respectively. This modification of the procedure resulted in the theoretical yield of lactone at the end of forty-four hours.

Discussion

The reduction of levulinic acid proceeds in its initial stages approximately 3.5 times as fast in diethyl ether solution as when it is dissolved in ethyl alcohol, and 4.5 times as fast as in acetic acid. This statement is

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[5] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

[6] Grateful acknowledgment is made to Milford A. Cowley for assistance given us in the preparation of the levulinic acid. This acid was made from sucrose, in part by the method of Rischbieth [*Ber.*, **20**, 1775 (1887)], and in part by the modified procedure of Conrad [*ibid.*, **11**, 2177 (1878); "Organic Syntheses," Vol. IX, p. 50].

based on the observation (Fig. 1) that at the end of seven hours, 0.27 mole of hydrogen was consumed when the reaction was being carried out in ethyl ether. The speed of reduction in ethyl alcohol was such that this quantity of hydrogen was not consumed until the reaction had proceeded for twenty-five hours and, similarly, in acetic acid for thirty-three hours.

That a reaction takes place between the acid and the solvent when reduction is carried out in the presence of ethyl alcohol was evident by the formation of some, as yet unidentified, ester. Glacial acetic acid is apparently inert in this respect since only the lactone and unreduced levulinic acid were found in the flask when the reaction had come to equilibrium.

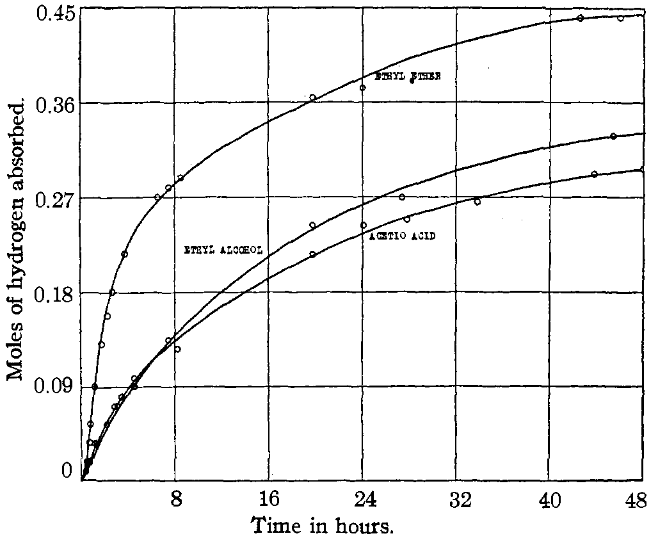

Fig. 1.—Effect of solvent upon the rate of hydrogenation of levulinic acid.

The superiority of diethyl ether over ethyl alcohol or acetic acid in this reduction lies not only in the production of larger yields of valerolactone, but also in the ease and certainty with which, because of marked differences in vapor pressure, solvent and reaction product can be separated.

Summary

The catalytic hydrogenation of levulinic acid can be most advantageously carried out at room temperature in the presence of diethyl ether as solvent. Theoretical yields of *n*-valerolactone are obtainable by this procedure.

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