Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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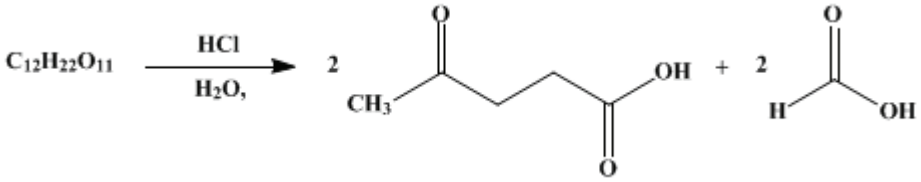
LEVULINIC ACID



Submitted by B. F. McKenzie
Checked by H. T. Clarke and R. Phillips.

1. Procedure

To a solution of 500 g. (1.46 moles) of cane sugar (Note 1) in 1 l. of water in a 2-l. flask is added 250 cc. of concentrated hydrochloric acid (sp. gr. 1.16). The flask is heated on a steam bath for twenty-four hours, during which time considerable carbonization takes place. The black solid is filtered off with suction and washed with 300 cc. of water. The filtrate is placed in a large evaporating dish on a steam bath and allowed to evaporate overnight. The black solid residue obtained on the following morning is ground to a powder and placed in a folded filter paper of 34-cm. diameter. This is placed in a 25-cm. funnel fitted with a water-cooled 12-l. flask as described on p. 375. The solid is extracted with 500 cc. of ether for six to eight hours. The ether is distilled and the residue (Note 2) fractionated under reduced pressure. The fraction distilling at 150–160°/15 mm. or 135–140°/10 mm. forms a rather dark liquid which does not completely solidify on cooling.

On redistillation under reduced pressure a fraction boiling over a range of not more than 2° (e.g., 137–139°/10 mm.) is obtained with very little loss; this fraction solidifies almost completely at 30°. The yield is 72–76 g. (21–22 per cent of the theoretical amount).

2. Notes

1. Equally good results may be obtained with starch; the mixture however, must be warmed more slowly as it is apt to foam at the outset.
2. When larger quantities of levulinic acid are to be prepared it has been found by the checkers to be more convenient to fractionally distil the first filtrate under reduced pressure, without evaporating to dryness and extracting with ether. In this case a considerable quantity of tarry residue remains in the distilling flask. The yields are equally good.

3. Discussion

The only practical methods for preparing levulinic acid depend upon the action of mineral acids upon carbohydrates, a reaction discovered by Grote and Tollens,[1] who heated cane sugar with dilute sulfuric acid. The procedure described is essentially that of Conrad,[2] descriptions of which frequently have appeared[3] in the subsequent literature. Improved yields have been reported[4] by digesting sucrose under pressure for one hour with dilute hydrochloric acid at 162° in the presence of water vapor. The use of distillation under reduced pressure was suggested by Kent and Tollens.[5] Levulinic acid can also be prepared from starch[6] and from glucose[7] by the action of hydrochloric acid, and from furfuryl alcohol or hydroxymethylfurfural by the action of dilute mineral acids.[8]

References and Notes

1. Grote and Tollens, Ann. **175**, 181 (1875); **206**, 226 (1880).
2. Conrad, Ber. **11**, 2177 (1878).
3. Fittig and Wolff, Ann. **208**, 104 (1881); Neugebauer, Ann. **227**, 97 (1885); Seissl, Ann. **249**, 272

(1888).
4. Thomas and Schuette, J. Am. Chem. Soc. **53**, 2324 (1931).
5. Kent and Tollens, Ann. **227**, 229, Note 2 (1885).
6. Rischbieth, Ber. **20**, 1773 (1887).
7. Sah and Ma, J. Am. Chem. Soc. **52**, 4881 (1930).
8. Teunissen, Rec. trav. chim. **50**, 1 (1931).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

cane sugar

starch

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sucrose

Furfuryl alcohol (98-00-0)

LEVULINIC ACID (123-76-2)

glucose (492-62-6)

hydroxymethylfurfural