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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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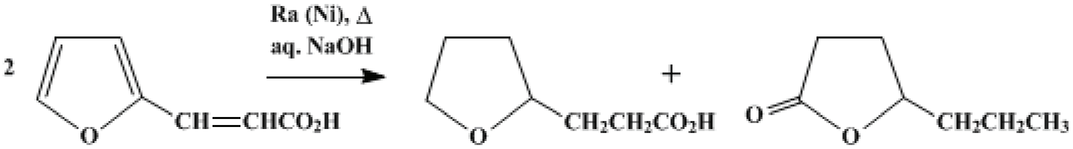
γ-*n*-PROPYLBUTYROLACTONE AND β-(TETRAHYDROFURYL) PROPIONIC ACID

[Enanthic acid, γ-hydroxy-, lactone, and 2-furanpropionic acid, tetrahydro-]



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1. Procedure

In a 2-l. beaker resting on a hot plate and equipped with a mechanical stirrer are placed 150 g. of sodium hydroxide (Note 1) dissolved in 800 ml. of water and 41.4 g. (0.3 mole) of furylacrylic acid (p. 425). The stirrer is started, and to the warm solution (Note 2) 100 g. of Raney nickel-aluminum alloy is added, in small portions, over a period of 4–4.5 hours (Note 3) and (Note 4). During the addition of the alloy, the temperature of the mixture is kept at 60–70° and then is raised to approximately 95° where it is held for an additional 2–3 hours, with stirring. From time to time sufficient water is added to the reaction mixture to maintain approximately the original volume. The hot solution is filtered by decantation, and the nickel residue (Note 5) is washed with two 50-ml. portions of hot 2% sodium hydroxide solution. The combined filtrates and washings are cooled and then immediately added slowly (Note 6), with good stirring, to 800 ml. of concentrated hydrochloric acid (Note 7). The solution at this point is strongly acid to Congo red paper (Note 8). The acidified solution is cooled and thoroughly extracted with three 200-ml. portions of ether (Note 9). The ether extracts are combined and washed once with 100 ml. of 10% sodium chloride solution, the ether is evaporated, and the residue is fractionally distilled in a modified Claisen flask. The yield of γ-*n*-propylbutyrolactone boiling at 84–85°/5 mm., n_D^{25} 1.4385, is 13.0–14.9 g. (33–37%), while the yield of β-(tetrahydrofuryl) propionic acid boiling at 123–124°/5 mm., n_D^{25} 1.4578, is 15.0–17.0 g. (34–39%) (Note 10), (Note 11).

2. Notes

1. Solid sodium hydroxide is used in order to take advantage of the heat of solution. If the mixture at this stage is allowed to cool, it will be necessary to heat the solution to 50–60° before the addition of the alloy is begun.
2. Some of the furylacrylic acid remains undissolved but goes into solution readily after the addition of the nickel-aluminum alloy is begun.
3. If any excessive frothing occurs during the addition of the alloy, a few drops of octyl alcohol can be added from time to time.
4. During the addition of the alloy, it is advantageous to stir the solution efficiently, the alloy being added in the vortex of the solution. If the addition of the alloy is made on the surface of the liquid, most of the hydrogen developed is lost without entering into the reaction.
5. The Raney nickel residue is quite active and will ignite if allowed to become dry. It may readily be disposed of by pouring into dilute mineral acid. This nickel residue is sufficiently active for various types of catalytic hydrogenations requiring the use of Raney nickel catalyst.
6. If the acidified mixture is allowed to become too hot, some of the material may be lost by steam distillation.
7. The alkaline solution is added to the hydrochloric acid in the manner described, since the reverse order of addition usually results in the precipitation of aluminum salts which dissolve only after considerable heating and stirring. The alkaline solution is added at such a rate that at no time is there any appreciable amount of solid present.
8. If insufficient hydrochloric acid is used at this stage, aluminum salts will precipitate and will make

the ether extractions difficult because of the formation of emulsions.

9. The acidified solution has also been extracted with ether in a continuous liquid-liquid extractor, this extraction requiring approximately 20 hours. Only slightly higher yields of the two products are obtained by this modification.

10. According to the submitters an alternative procedure for the separation of γ-*n*-propylbutyrolactone and β-(tetrahydrofuryl) propionic acid is the following:

The ether extracts, after washing with salt solution, are extracted with one 100-ml. and two 50-ml. portions of 5% sodium carbonate solution. It is important that the ether solution be free of any mineral acid before the carbonate extractions are made. The residual ether solution, after being washed with 10% sodium chloride solution, is dried over sodium sulfate. The ether is removed by distillation, and the residue is distilled under reduced pressure. The yield of γ-*n*-propylbutyrolactone is 14.5 g. (36%), b.p. 78–80°/2 mm. The combined sodium carbonate extracts are acidified to Congo red paper with concentrated hydrochloric acid and then thoroughly extracted with one 100-ml. and two 50-ml. portions of ether. The combined ether extracts are washed with 10% sodium chloride solution and dried; and, after the ether is removed by distillation, the residue is distilled under reduced pressure. The yield of β-(tetrahydrofuryl)propionic acid is 15.9 g. (36%), b.p. 118–120°/2 mm.

11. The submitters have used this procedure for the reduction of β-(α-thenoyl) propionic acid[1] from which ω-hydroxycaprylic acid[2] has been obtained in a yield of 38%, melting at 54–55°, and δ-*n*-propylvalerolactone in a yield of 31%, boiling at 116–117°/10 mm.

3. Discussion

γ-*n*-Propylbutyrolactone has been obtained from γ-bromoenanthic acid on boiling with water,[3] from β,γ-hepteneoic acid and sulfuric acid,[4] and by distilling γ-propylparaconic acid.[5]

β-(Tetrahydrofuryl) propionic acid has been obtained from furylacrylic acid by catalytic reduction with platinum oxide,[6] with nickel on kieselguhr,[7] with platinum black,[8] or with Raney nickel.[9] It has also been obtained from β-furyl-β-propiolactone by reduction,[10] and from 2-tetrahydrofurylpropanol by oxidation.[11]

The reduction procedure described has been published.[12]

References and Notes

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

platinum black

β-(α-thenoyl) propionic acid

β,γ-hepteneoic acid

γ-propylparaconic acid

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

platinum oxide

nickel (7440-02-0)

Furylacrylic acid (539-47-9)

octyl alcohol (111-87-5)

nickel-aluminum

γ-n-PROPYLBUTYROLACTONE,
Enanthic acid, γ-hydroxy-, lactone (105-21-5)

β-(Tetrahydrofuryl)propionic acid,
2-furanpropionic acid, tetrahydro-,
β-(tetrahydrofuryl) propionic acid (935-12-6)

ω-hydroxycaprylic acid (764-89-6)

γ-bromoenanthic acid

β-furyl-β-propiolactone

2-tetrahydrofurylpropanol

δ-n-propylvalerolactone (698-76-0)