Organic
Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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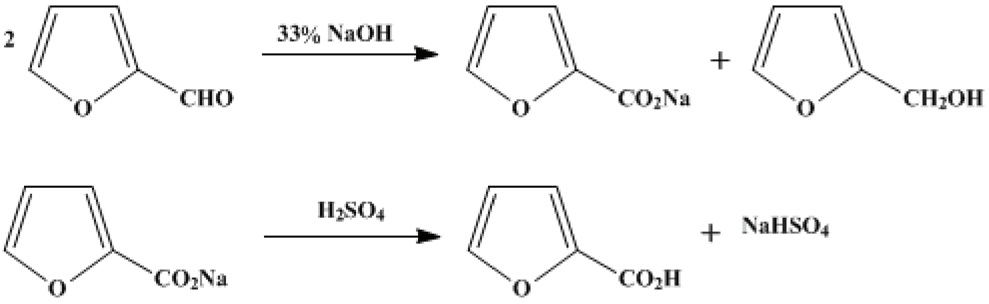
Organic Syntheses, Coll. Vol. 1, p.276 (1941); Vol. 6, p.44 (1926).

2-FURANCARBOXYLIC ACID and 2-FURYLCARBINOL

[(2-Furoic acid) (Furfuryl alcohol)]



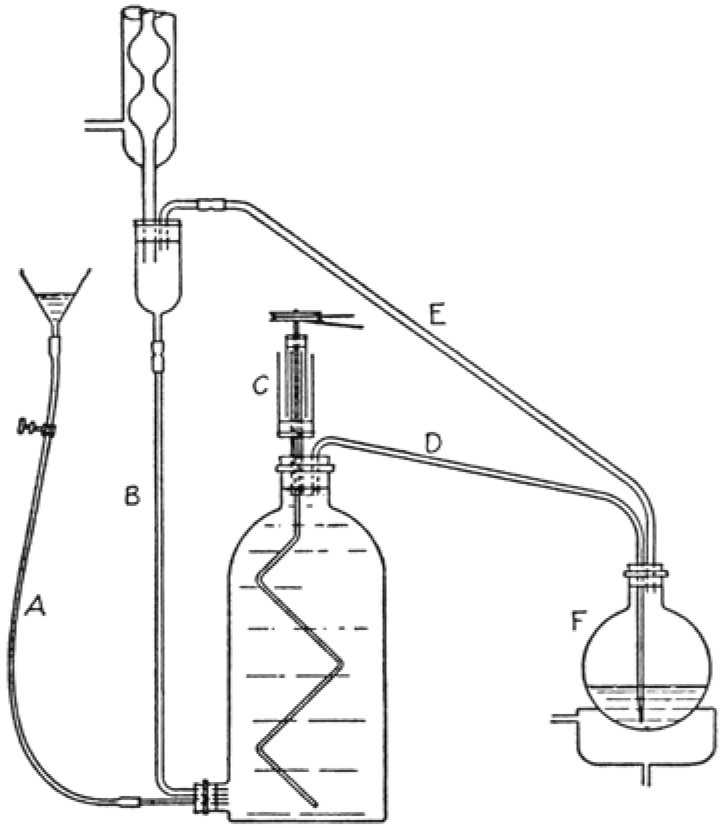
Submitted by W. C. Wilson
Checked by C. S. Marvel and C. G. Gauerke.

1. Procedure

One kilogram (862 cc., 10.2 moles) of furfural (Note 1) is placed in a 4-l. copper can (Note 2) provided with a mechanical stirrer and surrounded by an ice bath. The stirrer is started and the furfural is cooled to 5–8°. When the temperature has fallen to this range, 825 g. of 33.3 per cent technical sodium hydroxide solution (Note 3) is added from a separatory funnel at such a rate that the temperature of the reaction mixture does not exceed 20°. This requires twenty to twenty-five minutes. The rate of addition will depend on the efficiency of the cooling. The stirring is continued for one hour after the addition of the sodium hydroxide solution.

During the reaction considerable sodium 2-furancarboxylate separates in fine scale-like crystals. The reaction mixture is allowed to come to room temperature and just enough water is added to dissolve this precipitate. This requires about 325 cc. The solution is then placed in a continuous extraction apparatus (Fig. 16) and the 2-furylcarbinol is extracted with 1500–2000 cc. of ether (Note 4). The extraction is complete after six to seven hours (Note 5).

Fig. 16.



When extraction is complete the ether solution of 2-furylcarbinol is distilled until the temperature of the liquid (not the vapor) reaches 95°. Then the residue is distilled under diminished pressure. Some ether and water come over first, and the temperature then rises rapidly to the boiling point of 2-furylcarbinol. The yield of 2-furylcarbinol boiling at 75–77°/15 mm. is 310–325 g. (61–63 per cent of the theoretical amount) (Note 6).

The water solution containing the sodium 2-furancarboxylate is made acid to Congo red paper with 40 per cent sulfuric acid. This requires about 400 cc. On cooling, the 2-furancarboxylic acid crystallizes and is filtered with suction. The crude acid contains considerable sodium hydrogen sulfate and is deeply colored. For purification it is dissolved in 2300 cc. of boiling water containing about 60 g. of decolorizing carbon (Norite) and the solution is boiled for about forty-five minutes. It is then filtered and cooled with stirring to 16–20° (Note 7) and the 2-furancarboxylic acid which crystallizes is filtered by suction. The product thus obtained is light yellow in color but darkens somewhat on standing. The yield is 360–380 g. (60–63 per cent of the theoretical amount) (Note 8). This acid melts at 121–124° and by titration is 93–95 per cent pure. It is pure enough for many purposes.

For further purification the material may be recrystallized from hot water, or dissolved in alkali and reprecipitated, or distilled under reduced pressure or sublimed. Each of these operations involves considerable loss of product, either through solubility or through decomposition by heat. The best-appearing product is obtained by distillation under reduced pressure. The crude acid is distilled from a Claisen flask with a delivery tube set low in order that the acid need not be heated much above the boiling point. The product boiling at 141–144°/20 mm. is pure white and melts at 125–132° (Note 9). The yield of distilled acid is about 75–85 per cent of the weight of the crude acid.

2. Notes

1. Technical furfural (sp. gr. 1.15) (p. 280) was used in this preparation. It boiled over a range of 140–160° and contained about 2 per cent water.
2. A 1-gallon (4-l.) ice-cream freezer is a very convenient apparatus to use for the reaction, and a copper container is not necessary.

3. This amounts to about 28 per cent pure sodium hydroxide or 5.77 moles.

4. The apparatus shown (Fig. 16) is a very convenient form of continuous extractor for the laboratory. In the flask F is placed two-thirds of the solvent to be used for the extraction. The remainder is placed in the bottle, which should be just large enough to accommodate the solution to be extracted and the rest of the solvent. The flask is heated on a bath, causing the vapors to pass through E into the condenser, and the liquid therefrom flows through B into the bottom of the bottle, the contents of which must be mechanically stirred during the extraction in order to obtain efficient contact of the liquids. The stirrer and mercury seal are represented by C. For emptying and filling the bottle without disconnecting the apparatus, the tube A with pinchcock is provided. The only precaution to be mentioned is that occasionally the solution in the flask F becomes too concentrated, and consequently so hot that the ether cannot flow back through D owing to its rapid vaporization. If this happens, the contents of the flask must be removed and replaced by fresh solvent.

Carbon tetrachloride may be used for the extraction of the 2-furylcarbinol. This requires altering the extraction apparatus to remove the solvent from the bottom of the extraction bottle. Some difficulties are met in working with carbon tetrachloride, due to the liberation of acid which causes the 2-furylcarbinol to change into the water-insoluble form. The yields of both 2-furancarboxylic acid and 2-furylcarbinol are much lower when carbon tetrachloride is used as a solvent.

5. It is reported that the necessity of extracting the carbinol with ether after completion of the Cannizzaro reaction can be avoided and the yields improved if the excess alkali is neutralized with furoic acid or ammonium sulfate or if a slight deficiency of alkali is used in the first place.[1]

6. The 2-furylcarbinol thus obtained is entirely soluble in water and has only a slight yellow tinge. If it is to be stored, about 0.5 to 1 per cent of its weight of urea should be added as a stabilizer.

7. If the solution is cooled lower than 16°, sodium hydrogen sulfate ($NaHSO_4 \cdot 10H_2O$) begins to separate with the 2-furancarboxylic acid.

8. The low yields of 2-furancarboxylic acid are due partly to the formation of tarry by-products and partly to loss through water solubility. The mother liquors contain about 2.5 g. of 2-furancarboxylic acid per 100 cc. This may be recovered by extraction with ether.

9. The melting point of the 2-furancarboxylic acid is not very sharp. The distilled acid which titrates 100 per cent softens noticeably at 125° and melts completely at 132°.[2]

It is suggested that the 2-furancarboxylic acid is satisfactorily purified by recrystallizing from carbon tetrachloride. A few cubic centimeters of water should be added to coagulate and float the dark impurities. The clear lower layer is separated and deposits colorless crystals of correct melting point. It has also been suggested that the addition of water be omitted and the carbon tetrachloride solution be heated with Norite and then filtered.

3. Discussion

2-Furancarboxylic acid can be prepared from furfural by oxidation with dichromate,[3] or permanganate,[4] or oxygen in an alkaline solution in the presence of a suitable catalyst;[5] and by condensation using sodamide[6] or concentrated alkali.[7]

2-Furylcarbinol can be prepared from furfural by reduction with sodium amalgam[8] and catalytically,[9] and by condensation using sodamide[6] or concentrated alkali.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 274
- Org. Syn. Coll. Vol. 1, 285
- Org. Syn. Coll. Vol. 2, 531
- Org. Syn. Coll. Vol. 3, 621
- Org. Syn. Coll. Vol. 4, 493
- Org. Syn. Coll. Vol. 4, 834

References and Notes

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

oxygen in an alkaline solution

sulfuric acid (7664-93-9)

ether (60-29-7)

sodium hydroxide (1310-73-2)

carbon tetrachloride (56-23-5)

Norite,
decolorizing carbon (Norite) (7782-42-5)

sodium (13966-32-0)

urea (57-13-6)

2-furancarboxylic acid,
2-Furoic acid,
furoic acid (88-14-2)

Furfural (98-01-1)

2-FURYLCARBINOL,
Furfuryl alcohol (98-00-0)

sodium 2-furancarboxylate

sodium hydrogen sulfate (7681-38-1)

ammonium sulfate (7783-20-2)

sodamide (7782-92-5)