Organic Syntheses

A Publication
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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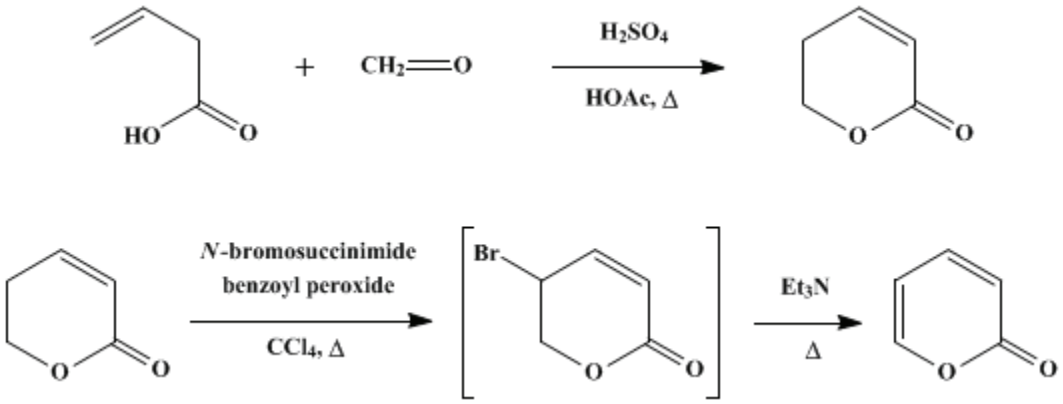
5,6-DIHYDRO-2*H*-PYRAN-2-ONE AND 2*H*-PYRAN-2-ONE



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Checked by A. Wick, D. Ehrlich, and A. Brossi.

1. Procedure

A. 5,6-*Dihydro*-2H-*pyran*-2-*one.* In a 500-ml., one-necked, round-bottomed flask equipped with a reflux condenser are combined 43 g. (0.50 mole) of vinylacetic acid (Note 1), 30 g. (1 mole as CH_2O) of paraformaldehyde (Note 2), 3 ml. of concentrated sulfuric acid, and 125 ml. of glacial acetic acid. This mixture is refluxed gently for 3 hours, then cooled to room temperature and swirled while 16 g. of anhydrous sodium acetate is added. Acetic acid is removed at 50–55° on a rotary evaporator, 100 ml. of water is added, and the flask is fitted with a two-necked adapter, a thermometer, and a magnetic stirring bar. The flask is then immersed in an ice bath, and the solution is brought to pH 8 with aqueous 20% sodium hydroxide (Note 3), which is added dropwise and with stirring at a rate such that the temperature remains below 5°. The resulting solution is transferred to a 1-l. separatory funnel and extracted with four 300-ml. portions of dichloromethane (Note 4). After being washed with one 150-ml. portion of saturated aqueous sodium chloride (Note 5), the combined organic extracts are dried over anhydrous sodium sulfate and filtered. Removal of dichloromethane with a rotary evaporator leaves a mobile yellow oil, which is distilled under reduced pressure, yielding 12.3 g. (25.1%) of 5,6-dihydro-2*H*-pyran-2-one, b.p. 114–117° (18–19 mm.) (Note 6).

B. 2H-*Pyran*-2-*one.* A mixture of 9.81 g. (0.100 mole) of 5,6-dihydro-2*H*-pyran-2-one, 200 mg. of benzoyl peroxide, 18.6 g. (0.105 mole) of *N*-bromosuccinimide (Note 7), and 800 ml. of carbon tetrachloride is prepared in a 2-l., three-necked, round-bottomed flask equipped with a reflux condenser and a mechanical stirrer. The resulting suspension is stirred and heated to reflux. After 1.5 hours at reflux, most of the solid is dissolved, and the solution gives a negative test with starch–iodide paper. The reaction mixture is then allowed to cool, during which time succinimide crystallizes out. The precipitate is removed by filtration, and the filtrate is concentrated under reduced pressure, leaving crude 5-bromo-5,6-dihydro-2*H*-pyran-2-one as an oil.

This residue is stirred at room temperature while 150 ml. of triethylamine (Note 8) is added. Triethylamine hydrobromide begins to precipitate soon after the addition is started, and the resulting slurry is refluxed gently for 15 minutes. It is then cooled to room temperature, and the insoluble material is removed by filtration and washed with benzene. Concentration of the combined filtrates under reduced pressure leaves an oily residue, which is dissolved in 600 ml. of diethyl ether. The ethereal solution is transferred to a 1-l. separatory funnel, washed with two 20-ml. portions of saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, and filtered. Ether is removed with a rotary evaporator, and the resulting oil is distilled at reduced pressure. A forerun of 265 mg. is collected below 103° (22 mm.) before 6.7 g. (70%) of 2*H*-pyran-2-one distils as a colorless oil, b.p. 103–111° (19–22 mm.) (Note 9).

2. Notes

1. Vinylacetic acid is available from Tokyokasei Company, Ltd., Japan or from Fluka AG, Buchs, Switzerland. Commercial material, which shows about 3% of crotonic acid in its ^{1}H NMR spectrum, was distilled at 90–92° (40–43 mm.) prior to use.
2. The submitters obtained paraformaldehyde from Koso Chemical Company, Inc., Japan.
3. About 180 ml. is required.
4. In these extractions, the organic layer is the lower one. If the two phases do not separate readily, fine-grained precipitates are probably at fault. These may be removed by filtration through a Büchner funnel.
5. Excess washing should be avoided, since 5,6-dihydro-2*H*-pyran-2-one is fairly soluble in water.
6. A forerun of approximately 180 mg. is collected below 110° (18 mm.). The IR spectrum of this material is practically identical with that of the main distillate. Reported physical constants for 5,6-dihydro-2*H*-pyran-2-one are: b.p. 110° (15 mm.) and n_D^{25} 1.4730.[3]
7. The submitters obtained *N*-bromosuccinimide from Nakarai Chemicals Ltd., Japan, and crystallized it from water prior to use (m.p. 168–175°).
8. Triethylamine was purified by treatment with *p*-toluenesulfonyl chloride and distillation.
9. The IR spectrum of this material was essentially identical to that of the redistillate, b.p. 115–118° (37 mm.). Reported physical constants for 2*H*-pyran-2-one are: b.p. 206–209° (atmospheric pressure), n_D^{25} 1.5272,[4] and b.p. 110° (26 mm.), n_D^{25} 1.5270.[5]

3. Discussion

5,6-Dihydro-2*H*-pyran-2-one has been prepared by reductive cyclization of 5-hydroxy-2-pentynoic acid, which is obtained in two steps from acetylene and ethylene oxide;[3] and by the reaction of dihydropyran with singlet oxygen.[6,7] 2*H*-Pyran-2-one has been prepared by pyrolysis of heavy metal salts of coumalic acid,[8] by pyrolysis of α-pyrone-6-carboxylic acid over copper,[4] and by pyrolysis of coumalic acid over copper (66–70% yield).[5]

The present one-step procedure for preparation of 5,6-dihydro-2*H*-pyran-2-one is slightly modified from that described in the original paper.[9] It is simpler and easier than the three-step method[3] used in the past and represents the most convenient synthesis currently available. The present preparation of 2*H*-pyran-2-one has several advantages compared to the alternatives mentioned above: simplicity of apparatus and technique, mild reaction conditions, availability of reactants, and ease of product isolation.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 112

References and Notes

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Appendix

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

sulfuric acid (7664-93-9)

acetylene (74-86-2)

acetic acid (64-19-7)

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

carbon tetrachloride (56-23-5)

copper (7440-50-8)

Ethylene oxide (75-21-8)

dichloromethane (75-09-2)

benzoyl peroxide (94-36-0)

Succinimide (123-56-8)

crotonic acid (3724-65-0)

N-bromosuccinimide (128-08-5)

dihydropyran

Vinylacetic acid (625-38-7)

Coumalic acid (500-05-0)

triethylamine (121-44-8)

α-pyrone-6-carboxylic acid

triethylamine hydrobromide (636-70-4)

2H-Pyran-2-one (504-31-4)

p-Toluenesulfonyl chloride (98-59-9)

5-hydroxy-2-pentynoic acid

5,6-Dihydro-2H-pyran-2-one (3393-45-1)

5-bromo-5,6-dihydro-2H-pyran-2-one

paraformaldehyde (30525-89-4)