Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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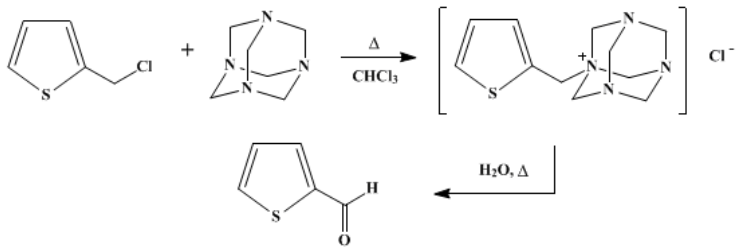
2-THIOPHENEALDEHYDE



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1. Procedure

A. 2-*Thienylmethylhexamethylenetetrammonium chloride.* In a 1-l. round-bottomed flask are placed 67 g. (0.5 mole) of 2-chloromethylthiophene (p. 197), 400 ml. of chloroform, and 70 g. (0.5 mole) of hexamethylenetetramine. The flask is fitted with a reflux condenser, and the mixture is boiled gently for 30 minutes. The mixture is cooled, and filtered on a Büchner funnel. The precipitate is washed with 100 ml. of cold chloroform, drained thoroughly, and air-dried. The yield is 128–136 g. (94–99%) of a white powder.

B. 2-*Thiophenealdehyde.* The hexamethylenetetrammonium salt is placed in a 2-l. round-bottomed flask containing 400 ml. of warm water. The flask is fitted for steam distillation, and steam is passed in until all the aldehyde has distilled (Note 1). The distillate is cooled, 10 ml. of 6 *N* acetic acid is added (Note 2), and the aldehyde is extracted with two 100-ml. portions of ether. The ether solution is dried over anhydrous calcium chloride, and the ether is evaporated on a steam bath until the volume of the solution has decreased to about 50 ml. The solution is placed in a 100-ml. Claisen flask, the ether is removed by distillation, and the aldehyde distilling at 89–91°/21 mm., n_D^{25} 1.5880, is collected. The yield is 27–30 g. (48–53%) of a colorless oily liquid which darkens slowly on standing (Note 3) and (Note 4).

2. Notes

1. About 1.5 l. of distillate is collected before all the thiophenealdehyde is distilled over.
2. The acetic acid is added to remove traces of amines that come over in the steam distillation. This method of purification must be used because of the high solubility of the bisulfite addition compound of the aldehyde.
3. If the aldehyde is to be stored for any period of time, the addition of a small amount of hydroquinone is advisable.
4. It has been reported (S. J. Angyal and D. F. Penman) that the procedure for 1-naphthaldehyde [*Org. Syntheses*, **30**, 67 (1950)] may also be followed with slight modification for the preparation of 2-thio-phenealdehyde. A mixture of 41.5 g. (0.31 mole) of 2-chloromethylthiophene, 88 g. (0.60 mole) of hexamethylenetetramine, 130 ml. of glacial acetic acid, and 130 ml. of water is swirled until, with considerable evolution of heat, the mixture has become homogeneous. The mixture is heated under reflux for 4 hours; at the end of this period, 125 ml. of concentrated hydrochloric acid is added, and heating under reflux is continued for 5 minutes. After cooling, the mixture is extracted with three 100-ml. portions of ether. The combined ether extracts are dried (with anhydrous sodium or magnesium sulfate), and the ether is removed. The crude product is distilled through a short column under reduced pressure; after a fore-run of acetic acid the product is collected at 63–66°/6 mm. or 115–118°/65 mm. The yield is 25–26 g. (71–74%).

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3. Discussion

2-Thiophenealdehyde has been prepared by the decarboxylation of 2-thienylglyoxalic acid,[1] by the action of 2-thienylmagnesium iodide on ethyl orthoformate followed by hydrolysis of the acetal,[2] in small yields by the Rosenmund reduction of 2-thiophenecarboxylic acid chloride,[3] in small yields by the action of hydrogen cyanide, hydrogen chloride, and aluminum chloride on thiophene, using benzene as a solvent,[4] by a series of reactions from 1-chloro-2,3-diketocyclopentane,[5] by the hydrolysis of 2-thenylmethylhexamethylenetetrammonium chloride in neutral solution,[6] by the action of N-methylformanilide on thiophene in the presence of phosphorus oxychloride,[7] by the acid hydrolysis of N-(2-thenyl)-2'-thenaldimine,[8] and by the oxidation of N,N-di-(2-thenyl)hydroxylamine with alkaline potassium permanganate.[9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 915
- Org. Syn. Coll. Vol. 5, 121

References and Notes

1. Biedermann, *Ber.*, **19**, 636 (1886).
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7. King and Nord, *J. Org. Chem.*, **13**, 635 (1948); *Org. Syntheses*, **31**, 108 (1951).
8. Hartough, *J. Am. Chem. Soc.*, **69**, 1355 (1947).
9. U. S. pat. 2,463,500 [*C. A.*, **43**, 4302 (1949)].

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

2-thio-phenealdehyde

N-(2-thenyl)-2'-thenaldimine

ACETAL (105-57-7)

calcium chloride (10043-52-4)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

chloroform (67-66-3)

hydroquinone (123-31-9)

potassium permanganate (7722-64-7)

hydrogen cyanide (74-90-8)

Phosphorus Oxychloride (21295-50-1)

aluminum chloride (3495-54-3)

sodium (13966-32-0)

Ethyl orthoformate

hexamethylenetetramine (100-97-0)

Thiophene (110-02-1)

magnesium sulfate (7487-88-9)

2-thienylmagnesium iodide

N-methylformanilide (93-61-8)

2-Chloromethylthiophene (765-50-4)

hexamethylenetetrammonium

2-Thiophenealdehyde,
thiophenealdehyde (98-03-3)

2-thienylglyoxalic acid (4075-59-6)

2-thiophenecarboxylic acid chloride (5271-67-0)

1-chloro-2,3-diketocyclopentane

2-thenylmethylhexamethylenetetrammonium chloride

N,N-di-(2-thenyl)hydroxylamine

1-Naphthaldehyde (66-77-3)

2-Thienylmethylhexamethylenetetrammonium chloride