



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.

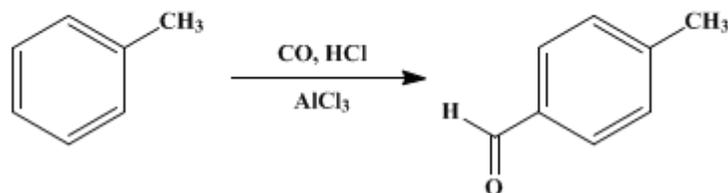
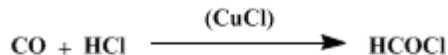
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.

Organic Syntheses, Coll. Vol. 2, p.583 (1943); Vol. 12, p.80 (1932).

p-TOLUALDEHYDE

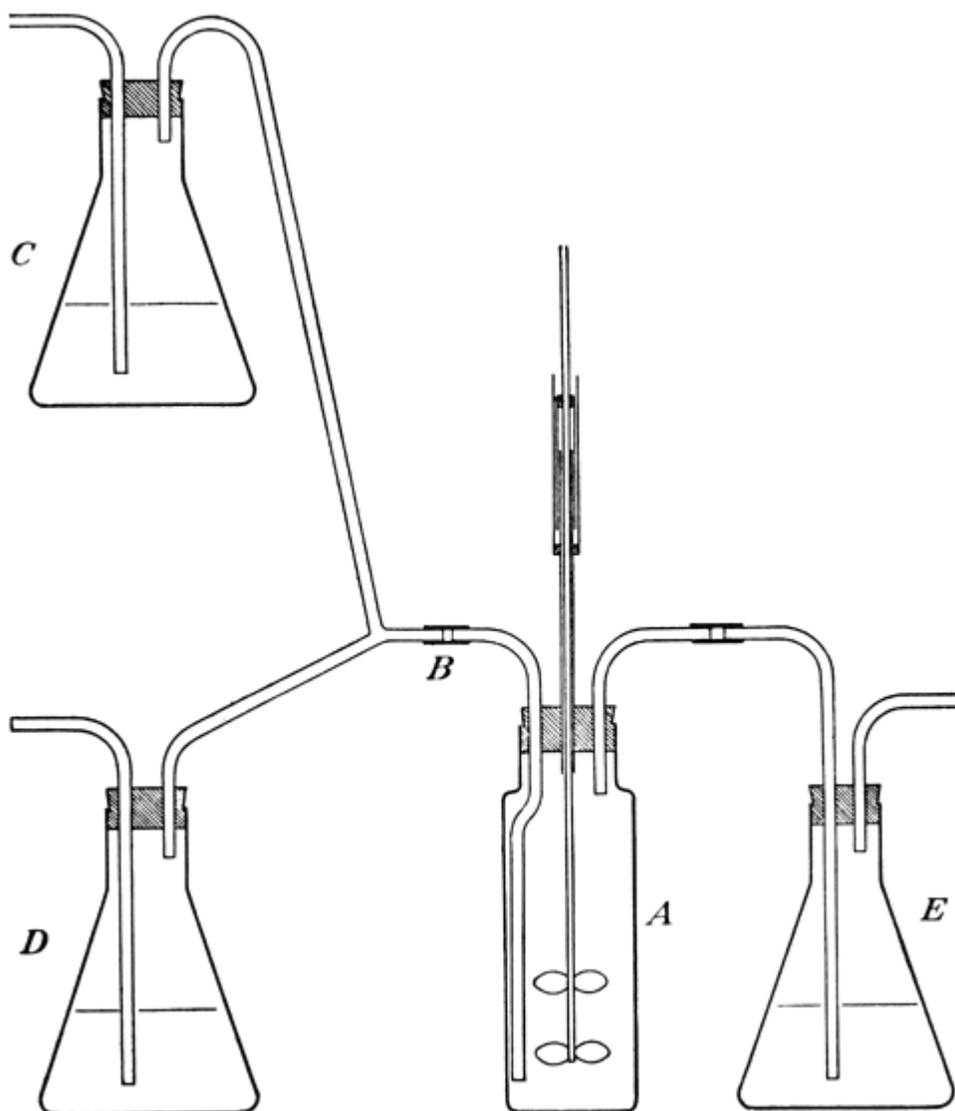


Submitted by G. H. Coleman and David Craig.
Checked by Henry Gilman and J. B. Dickey.

1. Procedure

The apparatus shown in Fig. 18 is set up in a hood. The narrow reaction bottle A, of about 500-cc. capacity and having a wide mouth, is provided with an efficient mercury-sealed mechanical stirrer, an inlet tube B for admitting the mixture of gases, and an outlet tube connected with the wash bottle E. Into A, contained in a water bath at 20°, is placed 200 g. (2.17 moles) of dry *toluene*; then 30 g. (0.3 mole CuCl) of *cuprous chloride* (Note 1) and 267 g. (2 moles) of finely powdered anhydrous *aluminum chloride* are added rapidly with active stirring.

Fig. 18



A mixture of hydrogen chloride and carbon monoxide (Note 2) is led to the bottom of the reaction bottle through tube B at such rates that the carbon monoxide is admitted uniformly during seven hours and the hydrogen chloride at about one-half this rate. The rates of flow of the two gases may be compared by the bubbling in wash bottles C and D. The extent of absorption can be estimated from the bubbling of the effluent gases in wash bottle E. The carbon monoxide is absorbed almost quantitatively at the beginning, and as the mixture thickens the absorption becomes less complete.

The mixture is hydrolyzed by adding it (Note 3) slowly and with shaking to 1.5 kg. of cracked ice in a 3-l. flask. The resulting mixture is then steam-distilled until all the aldehyde and unchanged toluene are driven over. Fifty cubic centimeters of ether is added to the distillate, the two layers are separated, and the aqueous layer is washed with 150 cc. of ether which is then added to the first non-aqueous layer (Note 4). After drying with calcium chloride, the aldehyde is obtained by distilling from a 500-cc. flask provided with a short fractionating column (Note 5). The yield of *p*-tolualdehyde distilling at 201–205° is 121–132 g. (46–51 per cent of the theoretical amount based on the toluene). Redistillation involves but a slight loss and gives an almost colorless product which distils at 203–205° (Note 6).

2. Notes

1. The cuprous chloride may be prepared according to *Org. Syn. Coll. Vol. I, 1941, 170*. The precipitate is washed several times by decantation with sulfurous acid, collected on a large Büchner funnel, washed

with glacial [acetic acid](#), and dried in an evaporating dish until the odor of [acetic acid](#) has disappeared. The [cuprous chloride](#) obtained is pure white and should not be exposed unnecessarily to the air.

An alternative procedure for preparing [cuprous chloride](#) is given on [p. 131](#).

2. The [carbon monoxide](#) may be forced by water from a 75-l. container, after which it is dried by bubbling through two wash bottles containing concentrated sulfuric acid.

In place of this large container for [carbon monoxide](#) it is possible to generate the gas more conveniently by adding 170 g. (141 cc., 3.69 moles) of pure [formic acid](#) (sp. gr. 1.2) to 250 g. (135.8 cc.) of concentrated [sulfuric acid](#) contained in a 1-l. distilling flask heated on an oil bath to 70–80°. The side arm of the flask is connected to the sulfuric acid wash bottles. In order to ensure a smooth and constant flow of [carbon monoxide](#), the [formic acid](#) is placed in a dropping funnel which extends through a two-holed rubber stopper in the neck of the distilling flask. The other hole of this stopper is connected by rubber tubing to a one-holed stopper in the dropping funnel. No frothing was evident under these conditions, but should frothing occur it is recommended that a small quantity of paraffin be added to the [sulfuric acid](#) in the generating flask.

3. The mixture frequently is too thick to be poured, and a spatula must be used to remove it.

4. The extraction of the aldehyde from the unchanged [toluene](#) with [sodium bisulfite](#) at this point in the preparation does not appreciably increase the purity of the product.

5. It is necessary to use a water-condenser until the temperature reaches 150°, after which an air-condenser is used.

6. The use of a few crystals of [hydroquinone](#) has been recommended for the storage of [p-tolualdehyde](#).

3. Discussion

The method described is that of Gattermann and Koch.¹ [p-Tolualdehyde](#) has also been prepared from [toluene](#), [hydrogen cyanide](#), [hydrogen chloride](#), and [aluminum chloride](#);² from [toluene](#), [nickel carbonyl](#), and [aluminum chloride](#);³ from [p-tolunitrile](#) by reduction with [stannous chloride](#) followed by hydrolysis of the aldimine;⁴ from [p-xylene](#) by oxidation, particularly with [chromyl chloride](#);⁵ and from [p-tolylmagnesium bromide](#) with [formaldehyde phenylhydrazone](#),⁶ [ethyl orthoformate](#), [methylformanilide](#), [ethoxymethyleneaniline](#), or [carbon disulfide](#). The syntheses involving the Grignard reagent, except the first mentioned, have been examined and evaluated by Smith and Bayliss⁷ and Smith and Nichols;⁷ the use of [ethoxymethyleneaniline](#) or of [ethyl orthoformate](#) is recommended.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 590](#)

References and Notes

1. Gattermann and Koch, *Ber.* **30**, 1622 (1897).
 2. Bayer and Company, Ger. pat. 99,568 [Frdl. **5**, 98 (1897–1900)]; Hinkel, Ayling, and Morgan, *J. Chem. Soc.* **1932**, 2796; Hinkel, Ayling, and Beynon, *ibid.* **1935**, 677.
 3. Dewar and Jones, *J. Chem. Soc.* **85**, 216 (1904).
 4. Stephen, *ibid.* **127**, 1874 (1925); Williams, *J. Am. Chem. Soc.* **61**, 2248 (1939).
 5. Law and Perkin, *J. Chem. Soc.* **91**, 258 (1907).
 6. Grammaticakis, *Compt. rend.* **210**, 303 (1940).
 7. Smith and Bayliss, *J. Org. Chem.* **6**, 437 (1941); Smith and Nichols, *ibid.* **6**, 489 (1941).
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Appendix

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

[calcium chloride](#) (10043-52-4)

sulfuric acid (7664-93-9)
hydrogen chloride (7647-01-0)
acetic acid (64-19-7)
ether (60-29-7)
methylformanilide (103-84-4)
carbon monoxide (630-08-0)
hydroquinone (123-31-9)
hydrogen cyanide (74-90-8)
formic acid (64-18-6)
stannous chloride
sodium bisulfite (7631-90-5)
aluminum chloride (3495-54-3)
toluene (108-88-3)
carbon disulfide (75-15-0)
cuprous chloride (7758-89-6)
p-xylene (106-42-3)
Ethyl orthoformate
p-Tolunitrile (104-85-8)
sulfurous acid (7782-99-2)
chromyl chloride
nickel carbonyl
formaldehyde phenylhydrazone
ethoxymethyleneaniline (6780-49-0)
p-tolylmagnesium bromide (4294-57-9)
p-Tolualdehyde (104-87-0)