



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](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.

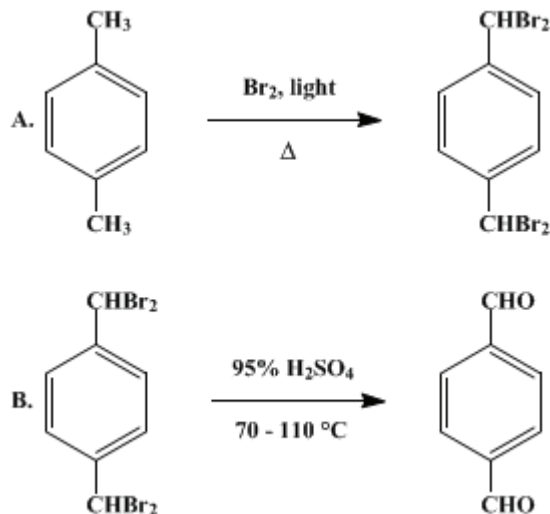
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures 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.*

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## TEREPHTHALALDEHYDE



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### 1. Procedure

A.  *$\alpha,\alpha,\alpha',\alpha'$ -Tetrabromo-*p*-xylene*. A 1-l. three-necked flask is fitted with an oil-sealed mechanical stirrer, a 500-ml. dropping funnel, and a reflux condenser, the top of which is connected to a gas-absorption trap. A 300-watt tungsten lamp is clamped in such a position that its bulb is within 1 in. of the flask (Note 1). Into the flask is introduced 100 g. (0.94 mole) of dry *p*-xylene (m.p. 11–12°), and the flask is heated in an oil bath maintained between 140° and 160°. The stirrer is started, and, when the xylene starts boiling, 700 g. (224 ml., 4.38 moles) of dry bromine (Note 2) is gradually added through the dropping funnel at such a rate that there is never any large amount of unreacted bromine in the flask. Stirring and heating are continued throughout the reaction, which requires 6–10 hours. After all the bromine has reacted, the mixture is cooled and dissolved in 1 l. of warm chloroform. The chloroform solution is cooled in an ice bath and the product removed by filtration. It is light gray, melts at 165–169°, and weighs 250–258 g. After a second recrystallization from 1 l. of chloroform, 190–200 g. of light-gray crystals melting at 168–170° is obtained. An additional 15–20 g. may be obtained by concentrating the chloroform filtrate to 250 ml. and recrystallizing the precipitate from fresh chloroform. The total yield is 205–220 g. (51–55%).

B. *Terephthalaldehyde*. A 2-l. round-bottomed flask is fitted with a still head, capillary ebullition tube, and receiver in an assembly for a vacuum distillation. Into the flask are introduced 84.3 g. (0.2 mole) of finely powdered tetrabromo-*p*-xylene and 200 ml. of concentrated sulfuric acid (95%). The reactants are thoroughly mixed by shaking. A vacuum is applied by means of a water pump, and a stream of air is allowed to pass through the capillary tube in order to facilitate the rapid removal of hydrogen bromide. The flask is heated in an oil bath to 70°, and, as the evolution of gas becomes less vigorous, the temperature of the bath is gradually raised to 110° (Note 3). The reaction is complete when a perfectly clear solution is obtained and no more gas is evolved (about 2.5 hours). The flask is then cooled and the contents are poured on 600 g. of crushed ice. The crystalline solid is collected on a filter, washed with a little water, and recrystallized from 600 ml. of 10% methanol with the aid of 1 g. of decolorizing carbon to remove the yellow color. The small amount of tetrabromoxylene which remains undissolved is separated with the carbon and washed on the filter with two 100-ml. portions of hot 10% methanol. The yield of pure product, m.p. 115–116°, is 21.7–22.5 g. (81–84%).

### 2. Notes

1. It is important to have light shining on the reaction mixture throughout the bromination. The bromination may also be accomplished by placing the flask in direct sunlight.
2. The bromine is dried by shaking it with two 200-ml. portions of concentrated sulfuric acid.
3. The mixture foams considerably and must be watched. The foaming can be controlled by raising the temperature slowly and regulating the vacuum. For this reason it is difficult to hydrolyze larger amounts of the tetrabromide.

### 3. Discussion

Terephthalaldehyde has been made by the action of lead nitrate on  $\alpha,\alpha'$ -dichloro-*p*-xylene<sup>1</sup> or  $\alpha,\alpha'$ -dibromo-*p*-xylene;<sup>2</sup> by the action of fuming nitric acid on dibromo-*p*-xylene;<sup>3</sup> by the hydrolysis of terephthalaldehyde tetraacetate;<sup>4</sup> by the action of phosphorus pentachloride on *p*-xylyleneglycol monoethyl ether;<sup>5</sup> by the hydrolysis of  $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*p*-xylene;<sup>6</sup> by the hydrolysis of  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene;<sup>7</sup> and by the Sommelet procedure.<sup>8</sup> The method described here is essentially the modification described by Weissberger and Bach.<sup>9</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 578](#)

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### References and Notes

1. Grimaux, *Bull. soc. chim. France*, (2) **25**, 337 (1876); *Compt. rend.*, **83**, 825 (1877).
2. Löw, *Ann.*, **231**, 361 (1885).
3. Löw, *Ber.*, **18**, 2072 (1885).
4. Thiele and Winter, *Ann.*, **311**, 341 (1900).
5. Colson, *Bull. soc. chim. France*, (2) **42**, 152 (1884).
6. Colson and Gautier, *Bull. soc. chim. France*, (2) **45**, 506 (1886); *Ann. chim.*, (6) **11**, 25 (1887).
7. Hömig, *Monatsh.*, **9**, 1150 (1888); Thiele and Gunther, *Ann.*, **347**, 106 (1906).
8. Angyal, Morris, Tetaz, and Wilson, *J. Chem. Soc.*, **1950**, 2141.
9. Weissberger and Bach, *Ber.*, **65**, 24 (1932).

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### Appendix

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

sulfuric acid (7664-93-9)

methanol (67-56-1)

phosphorus pentachloride (10026-13-8)

chloroform (67-66-3)

nitric acid (7697-37-2)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

decolorizing carbon,  
carbon (7782-42-5)

lead nitrate (10099-74-8)

xylene,  
p-xylene (106-42-3)

Terephthalaldehyde (623-27-8)

$\alpha,\alpha,\alpha',\alpha'$ -Tetrabromo-p-xylene,  
a,a,a',a'-Tetrabromo-p-xylene (1592-31-0)

terephthaldehyde tetraacetate

p-xylyleneglycol monoethyl ether

$\alpha,\alpha'$ -dichloro-p-xylene (623-25-6)

dibromo-p-xylene,  
 $\alpha,\alpha'$ -dibromo-p-xylene

$\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-p-xylene