



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.

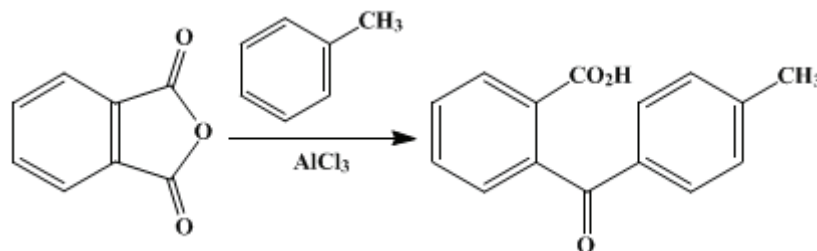
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.517 (1941); Vol. 4, p.73 (1925).

***p*-TOLUYL-*o*-BENZOIC ACID**

[Benzoic acid, *o*-(*p*-toluyl)-]



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1. Procedure

A 2-l. round-bottomed flask is clamped to a ring stand and equipped with a rubber stopper carrying a glass stirrer with mercury seal, and a reflux condenser connected with a trap (Fig. 7 on p. 97) for removing the evolved hydrogen chloride.

One hundred grams (0.68 mole) of phthalic anhydride and 400 g. (462 cc., 4.35 moles) of toluene are placed in the flask, which is cooled in an ice bath while 200 g. (1.5 moles) of anhydrous aluminum chloride (Note 1) is being ground to a fine powder. The chloride is now added all at once (Note 2). Stirring is commenced at once, and the ice bath is removed. The mixture warms up considerably and becomes olive-green in color. When the evolution of hydrogen chloride begins to slacken (ten minutes) a water bath is put into place and heated to 90° in the course of forty-five minutes. The temperature of the bath is kept at 90° and vigorous stirring continued for two and one-half hours. At this point, the evolution of hydrogen chloride will have practically ceased and the reaction will have been completed. The hot water in the bath is replaced first by cold water and then by ice, while stirring is continued.

As soon as the flask is well cooled, it is disconnected and carried to the hood, and ice is slowly added, with shaking, until the dark mass is completely decomposed and the flask is about one-half filled with the mixture. After 150 cc. of crude concentrated hydrochloric acid has been added, the mass coagulates and the solution clears; the flask is then heated on the steam bath while preparations are being made for steam distillation.

This operation, which removes the excess of toluene, may be carried out in the same flask and loss by transfer thus avoided (Note 3). The aqueous solution of aluminum chloride and hydrochloric acid, after thorough cooling, is decanted through a suction filter, the residue washed with a little cold water, and that collected on the filter returned to the flask. This residue consists almost solely of *p*-toluyl-*o*-benzoic acid, partly crystalline, partly in oily lumps.

A previously prepared and heated solution of 50 g. of sodium carbonate in 1 l. of water is added, and steam is passed in to provide heat and agitation. With a rapid stream, the acid will go into solution in about ten minutes, leaving a small amount of brown, tarry material and a little alumina undissolved (Note 4). The solution is filtered while hot and transferred to a 2-l. beaker, and the acid precipitated by the addition of 65 cc. of concentrated hydrochloric acid. The acid separates as an oil, which soon crystallizes. The solution is cooled in ice and the acid filtered and washed.

The air-dried product is pure white and weighs 170 g. (Note 5). After drying at 100°, the anhydrous acid melts at 138–139° and weighs 157 g. (96 per cent of the theoretical amount). Air-dried material is suitable for the condensation to β -methylantraquinone, p. 353. It may be recrystallized from toluene.

2. Notes

1. Although statements are found in the literature that quantitative yields may be obtained with smaller quantities of [aluminum chloride](#), the ratio $1\text{C}_6\text{H}_4(\text{CO})_2\text{O}:2\text{AlCl}_3$ is essential.
2. Leakage of [hydrogen chloride](#) at any of the connections may be stopped with paraffin.
3. The steam distillation requires about fifteen minutes, and about 340–380 cc. of [toluene](#) is recovered.
4. If, in extracting the acid with [sodium carbonate](#), more than 2–3 g. of material remains undissolved, the residue is treated with dilute [hydrochloric acid](#) to remove alumina, washed, and again extracted with a little carbonate solution. This extract is neutralized separately since some tar may separate with the *p*-toluyl-*o*-benzoic acid. In this event, it is filtered and extracted with *cold* carbonate solution, in which the tar is completely insoluble.
5. According to Limpricht,¹ the acid may crystallize either in hydrated or in the anhydrous condition, but the transition temperature is not stated. The loss of water upon drying at 100° shows the compound obtained in this experiment to be the monohydrate.

3. Discussion

p-Toluyl-*o*-benzoic acid can be prepared by the action of [aluminum chloride](#) on [phthalic anhydride](#) and [toluene](#).²

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 353](#)

References and Notes

1. Limpricht, Ann. **299**, 300 (1898).
2. Friedel and Crafts, Bull. soc. chim. (2) **35**, 505 (1881), Ann. chim. phys. (6) **14**, 447 (1888); Limpricht, Ann. **299**, 300 (1898); Heller and Schülke, Ber. **41**, 3632 (1908); McMullen, J. Am. Chem. Soc. **43**, 1965 (1921).

Appendix

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

[p-Toluyl-*o*-benzoic acid](#)

[hydrogen chloride](#),
[hydrochloric acid \(7647-01-0\)](#)

[sodium carbonate \(497-19-8\)](#)

[phthalic anhydride \(85-44-9\)](#)

[aluminum chloride \(3495-54-3\)](#)

[toluene \(108-88-3\)](#)

[β-Methylanthraquinone \(84-54-8\)](#)

[Benzoic acid, *o*-\(*p*-toluyl\)- \(7148-03-0\)](#)

