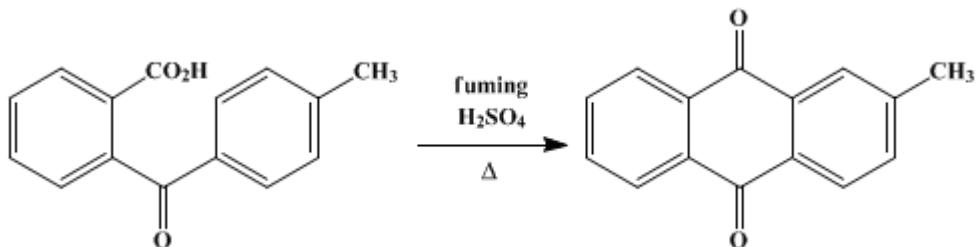


β-METHYLANTHRAQUINONE

[Anthraquinone, 2-methyl-]



Submitted by L. F. Fieser

Checked by Roger Adams and R. L. Shriner.

1. Procedure

The *p*-toluyl-*o*-benzoic acid which is obtained from 100 g. of [phthalic anhydride](#) (p. 517), and which should weigh 157 g. (0.65 mole), is mixed with 1400 g. (725 cc.) of fuming [sulfuric acid](#) (20 per cent anhydride) ([Note 1](#)) in a 2-l. flask protected by a calcium chloride tube, and the mixture is heated on the steam bath for two hours with occasional shaking ([Note 2](#)). The clear, deep red solution is poured when cold upon cracked ice in a 4-l. beaker. The [methyl anthraquinone](#) separates and is digested for twenty minutes by passing in steam, after which it is filtered by suction. A flannel cloth is used in the filter, or a filtros plate may be cemented into a Büchner funnel with water-glass. The precipitate is washed well with hot water, after which it is returned to the beaker and digested as before with hot water to which is added a slight excess of [ammonia](#), beyond that required to neutralize any acid present.

The product is filtered and dried to constant weight. The filtrate will be clear and will give no precipitate with [hydrochloric acid](#) if the conditions of condensation have been correct.

The [β-methylanthraquinone](#) is pale tan in color and weighs from 118 to 130 g. (81–90 per cent of the theoretical amount, based upon the weight of acid taken). It is practically pure, melting at 173°. Upon crystallization from alcohol in the presence of animal charcoal, it forms long, silken, almost colorless needles, melting constantly at 173.5° (176° corr.).

2. Notes

1. Some investigators have used concentrated instead of fuming [sulfuric acid](#) for the condensation, but the yield is usually low and the product is always colored bright yellow by some impurity which cannot be removed by crystallization.
2. The time allowed for condensation may be shortened to one-half, without affecting the yield, by maintaining the temperature at 125–130°.

3. Discussion

[β-Methylanthraquinone](#) can be prepared by the oxidation of [β-methylanthracene](#)¹ and material of the same origin, obtained by the benzene-extraction of crude commercial [anthraquinone](#);² from the intramolecular condensation of *p*-toluyl-*o*-benzoic acid;³ and from *o*-carbomethoxybenzoyl chloride and toluene.⁴

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 517

References and Notes

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 2. Perkin and Cope, J. Chem. Soc. **65**, 843 (1894); Wachendorff and Zincke, Ber. **10**, 1485 (1877); Börnstein, Ber. **15**, 1820 (1882); Römer and Link, Ber. **16**, 696 (1883).
 3. Elbs, J. prakt. Chem. (2) **33**, 319 (1886); (2) **41**, 4 (1890); Gresby, Ann. **234**, 239 (1886); Limpicht, Ann. **299**, 300 (1898); Ber. **28**, 1134 (1895); Limpicht and Weigand, Ann. **311**, 180 (1900); Heller and Schülke, Ber. **41**, 3632 (1908); Krassovski, J. Russ. Phys. Chem. Soc. **46**, 1067 (1914) [Chem. Zentr. **I** 999 (1915)].
 4. Smith, J. Am. Chem. Soc. **43**, 1922 (1921).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

p-Tolyl-o-benzoic acid

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

phthalic anhydride (85-44-9)

Anthraquinone (84-65-1)

toluene (108-88-3)

β -Methylanthraquinone,
Anthraquinone, 2-methyl- (84-54-8)

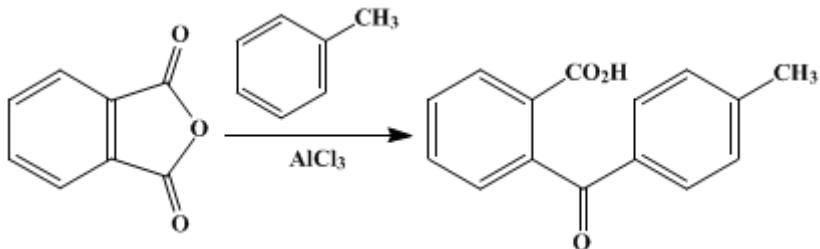
methyl anthraquinone

β -methylanthracene (613-12-7)

o-carbomethoxybenzoyl chloride

p-TOLUYL-*o*-BENZOIC ACID

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



Submitted by L. F. Fieser

Checked by Roger Adams and R. L. Shriner.

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*-tolyl-*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 $1C_6H_4(CO)_2O:2AlCl_3$ 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 Limprecht,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. Limprecht, Ann. **299**, 300 (1898).
2. Friedel and Crafts, Bull. soc. chim. (2) **35**, 505 (1881), Ann. chim. phys. (6) **14**, 447 (1888); Limprecht, 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)

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