Organic Syntheses

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.

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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.

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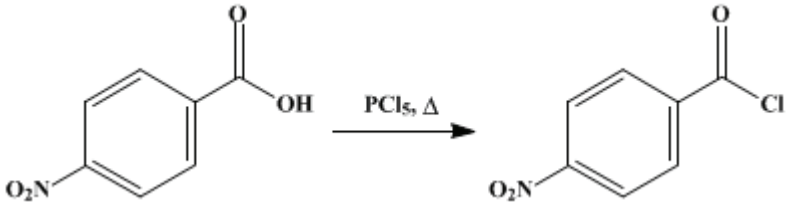
p-NITROBENZOYL CHLORIDE

[Benzoyl chloride, *p*-nitro-]



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1. Procedure

In a 3-l. round-bottomed flask are mixed 501 g. (3 moles) of pure *p*-nitrobenzoic acid (p. 392) and 626 g. (3 moles) of pure phosphorus pentachloride (Note 1). The flask is provided with a calcium chloride tube from which emerges a tube leading to the surface of a flask of water, in order to absorb the hydrogen chloride formed during the reaction (Note 2). The flask is placed on a water bath and heated with occasional shaking until the reaction starts (fifteen to forty-five minutes). Vigorous evolution of hydrogen chloride takes place, and the heating is continued until the reaction is complete (fifteen to thirty minutes after the reaction starts). There is thus formed a light yellow, homogeneous liquid.

The reaction mixture is now transferred to a Claisen flask connected with a water-cooled condenser, and the phosphorus oxychloride is removed at ordinary pressure by raising the temperature of the oil bath (Note 3) gradually to 200–220°. The water condenser is then replaced by a *short* air-cooled condenser, and the residual liquid is distilled under reduced pressure (Note 4). A small quantity of phosphorus oxychloride first distils over, after which the receiver is changed and the temperature rises rapidly to the boiling point of *p*-nitrobenzoyl chloride, 197°/73 mm. (155°/20 mm.). During this distillation the oil bath should be kept at a temperature of about 230–250° (or at 210–215° if 20 mm. pressure is used). The yield is 500–534 g. (90–96 per cent of the theoretical amount). The distillate solidifies to a yellow crystalline mass melting at 71° (Note 5). The product may be recrystallized from ligroin or carbon tetrachloride, from which it separates in fine yellow needles melting at 73° (Note 6).

2. Notes

1. The yield of *p*-nitrobenzoyl chloride depends to a great extent upon the quality of the reagents used. With impure phosphorus pentachloride and pure *p*-nitrobenzoic acid, yields of 70–80 per cent of the product are obtained. With pure phosphorus pentachloride and a less pure grade of *p*-nitrobenzoic acid, yields of 85–90 per cent are obtained. When neither reagent is of high grade, yields may fall as low as 40–50 per cent of the theoretical amount. In all such cases the color of the original reaction mixture varies from a deep yellow to a black.
Phosphorus pentachloride purchased as pure is occasionally of inferior quality and gives poor results. It is not a difficult matter to prepare in the laboratory a product suitable for this reaction. To 1 kg. (620 cc., 7.3 moles) of phosphorus trichloride, chlorine is added until the increase in weight is 500 g. The gas should be added above the surface of the liquid, which is stirred occasionally during the addition. The stirring should not be continuous, however, as this tends to allow the formation of the pentachloride in the tube, which thus becomes clogged. At the end of the reaction the mixture becomes practically solid.
2. A gas-absorption trap (Fig. 7 on p. 97) may be used for this purpose.
3. If the reaction mixture is heated with a free flame during the distillation under reduced pressure, there is considerable danger of superheating and consequent decomposition (sometimes violent) of the *p*-nitrobenzoyl chloride.
Experience with many preparations of this acid chloride has shown that it is desirable to have a safety

water bottle between the receiving flask and the manometer to use during the distillation under reduced pressure. This avoids the passage of vapors of phosphorus oxychloride or acid chloride into the pump.
4. At the beginning of the distillation under reduced pressure the air condenser is warmed gently with a free flame to prevent solidification of the first portion of the distillate.
5. The product is best placed while hot in small wide-mouthed bottles and allowed to solidify. This prevents any moisture from the air from decomposing more than the surface layer of the acid chloride.
6. It is suggested that *p*-nitrobenzoyl chloride can be prepared in excellent yields by heating *p*-nitrobenzoic acid under reflux with an excess of thionyl chloride, the *p*-nitrobenzoyl chloride being distilled under reduced pressure after the excess of thionyl chloride has been removed by distillation at atmospheric pressure (J. Kenyon, private communication).

3. Discussion

p-Nitrobenzoyl chloride can be prepared from *p*-nitrobenzoic acid with phosphorus pentachloride;[1] with phosphorus trichloride, oxychloride, and chlorine;[2] with thionyl chloride;[3] and with thionyl chloride and pyridine.[4]

References and Notes

1. Gevekoht, Ann. **221**, 335 (1883).
2. E. I. du Pont de Nemours and Co., U. S. pat. 2,048,768 [C. A. **30**, 6010 (1936)].
3. J. Kenyon, private communication.
4. Carré and Libermann, Compt. rend. **199**, 1422 (1934).

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

ligroin

hydrogen chloride (7647-01-0)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

carbon tetrachloride (56-23-5)

Phosphorus Oxychloride (21295-50-1)

pyridine (110-86-1)

chlorine (7782-50-5)

phosphorus trichloride (7719-12-2)

phosphorus trichloride, oxychloride

p-NITROBENZOIC ACID (62-23-7)

p-Nitrobenzoyl chloride,
Benzoyl chloride, p-nitro- (122-04-3)

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