



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.

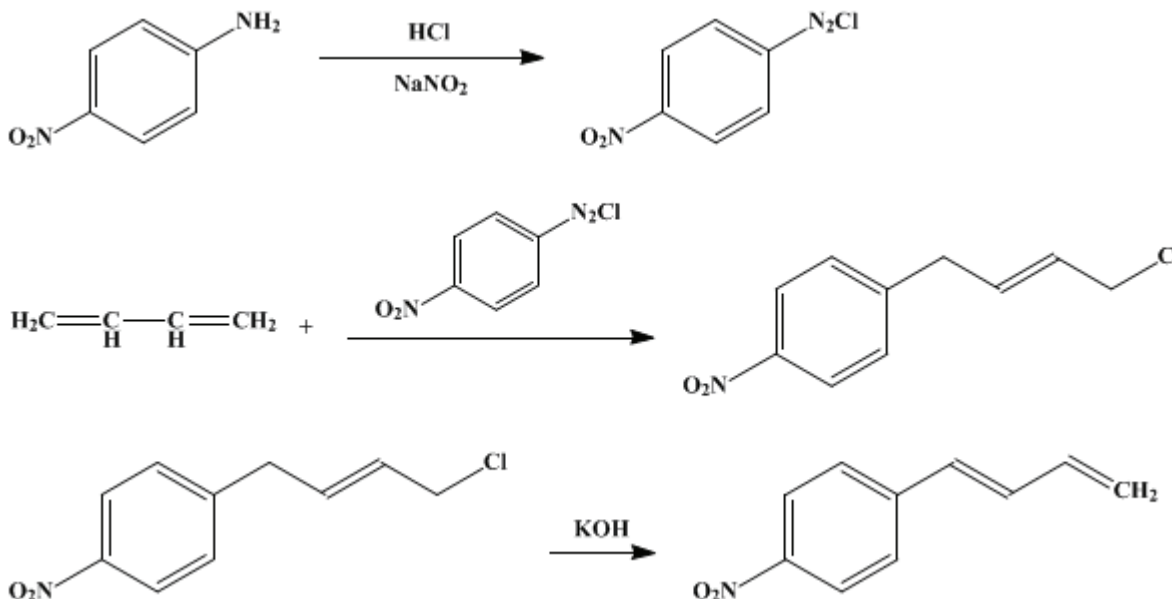
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.727 (1963); Vol. 31, p.80 (1951).

1-(*p*-NITROPHENYL)-1,3-BUTADIENE

[1,3-Butadiene, 1-(*p*-nitrophenyl)-]



Submitted by Gus A. Ropp and Eugene C. Coyner¹.
Checked by Arthur C. Cope and David J. Marshall.

1. Procedure

A. *1-(p-Nitrophenyl)-4-chloro-2-butene*. *p*-Nitroaniline hydrochloride is prepared by heating 138 g. (1.0 mole) of *p*-nitroaniline (Note 1) with 240 ml. of concentrated hydrochloric acid and 100 ml. of water on a steam bath for 15 minutes with occasional stirring. The mixture is cooled in an ice-salt bath and stirred rapidly in order to precipitate the hydrochloride as fine crystals. Cracked ice (100 g.) is added, and a solution of 70 g. of sodium nitrite is added dropwise with rapid mechanical stirring during a 1-hour period while the temperature of the reaction mixture is held between -4° and $+4.5^{\circ}$ by cooling with the ice-salt bath. The mixture is stirred for an additional period of 20 minutes and then is filtered through a chilled funnel into an ice-cooled filter flask. The filtrate is kept below 4° (Note 2) and is added through a dropping funnel during 90 minutes to a cold, vigorously stirred mixture composed of 1 l. of acetone, a solution of 80 g. of sodium acetate trihydrate in 100 ml. of water, a solution of 30 g. of cupric chloride in 50 ml. of water, and 130 ml. of liquid butadiene (Note 3). The reaction mixture is kept at -3° to $+2^{\circ}$ by means of an ice-salt bath while the diazonium salt solution is added. After the addition is completed the cooling bath is removed and the mixture is stirred for 16 hours. One liter of ether is added, and after several minutes' stirring the ethereal layer is separated, washed with four 1-l. portions of water, and dried over 20 g. of anhydrous magnesium sulfate. The solvent is removed by distillation at 15 mm. by heating on a steam bath, leaving a dark brown oily residue (187–199 g.) of crude 1-(*p*-nitrophenyl)-4-chloro-2-butene (Note 4).

B. *1-(p-Nitrophenyl)-1,3-butadiene*. The crude 1-(*p*-nitrophenyl)-4-chloro-2-butene obtained in Part A is dissolved in a mixture of 500 ml. of ligroin, b.p. $90-100^{\circ}$, and 500 ml. of benzene; 5 g. of decolorizing carbon is added, and the mixture is heated under reflux for 2 hours. After filtration to separate the decolorizing carbon the solvents are removed by distillation from a steam bath under reduced pressure, and the residual clear oil is dissolved in 400 ml. of methanol. A solution of 112 g. of potassium hydroxide in 600 ml. of methanol is added from a dropping funnel during 30 minutes while the mixture is stirred mechanically and kept at $15-30^{\circ}$ by cooling with a bath of cold water. After being stirred for an additional period of 5 minutes the mixture, which contains some precipitated product, is

poured into 1.2 l. of cold water. The crude product is collected on a filter, washed well with cold water, and air-dried. It is dissolved in 700 ml. of hot ligroin, b.p. 90–100°, and the solution is treated with 5 g. of [decolorizing carbon](#), and filtered. On cooling, [1-\(p-nitrophenyl\)-1,3-butadiene](#) separates as a yellow crystalline solid which is collected on a filter and dried in a desiccator. The yield of pure product, m.p. 77–79° ([Note 5](#)), is 100–108 g. (57–62% based on [p-nitroaniline](#)).

2. Notes

1. Either a pure grade of [p-nitroaniline](#) obtained from the Eastman Kodak Company or a technical grade purified by one recrystallization from [ethanol](#) was used, m.p. 147.5–148°.
2. The filtrate is kept in an ice-salt bath and transferred to the dropping funnel in small amounts in order to keep the temperature below 4°.
3. [Butadiene](#) from a commercial cylinder is passed through an 8-mm. glass tube leading to the bottom of a graduated cylinder cooled with Dry Ice and [acetone](#), where it condenses and is measured as a liquid.
4. The submitters report that small samples of the crude product can be distilled in order to obtain pure [1-\(p-nitrophenyl\)-4-chloro-2-butene](#), b.p. 160–165°/1 mm.
5. Two recrystallizations from ligroin raise the melting point of the [1-\(p-nitrophenyl\)-1,3-butadiene](#) to a constant value of 78.6–79.4°. The product can be kept for several weeks in a dark bottle at room temperature without evidence of decomposition.

3. Discussion

[1-\(p-Nitrophenyl\)-1,3-butadiene](#) has been prepared only by the method described,² which is an example of the Meerwein reaction (addition of diazonium salts to a carbon-carbon double bond with the elimination of [nitrogen](#)).³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 21](#)

References and Notes

1. University of Tennessee, Knoxville, Tennessee.
2. Coyner and Ropp, *J. Am. Chem. Soc.*, **70**, 2283 (1948); Dombrovskii, *Doklady Akad. Nauk S.S.S.R.*, **111**, 827 (1956) [*C. A.*, **51**, 9507 (1957)].
3. Müller, *Angew. Chem.*, **61**, 179 (1949).

Appendix

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

ligroin

[ethanol](#) (64-17-5)

[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

[methanol](#) (67-56-1)

ether (60-29-7)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

acetone (67-64-1)

decolorizing carbon (7782-42-5)

potassium hydroxide (1310-58-3)

cupric chloride (7758-89-6)

magnesium sulfate (7487-88-9)

butadiene (106-99-0)

sodium acetate trihydrate (6131-90-4)

1-(p-Nitrophenyl)-1,3-butadiene,
1,3-Butadiene, 1-(p-nitrophenyl)- (20264-89-5)

p-nitroaniline (100-01-6)

p-nitroaniline hydrochloride (15873-51-5)

1-(p-Nitrophenyl)-4-chloro-2-butene (98011-65-5)