



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.

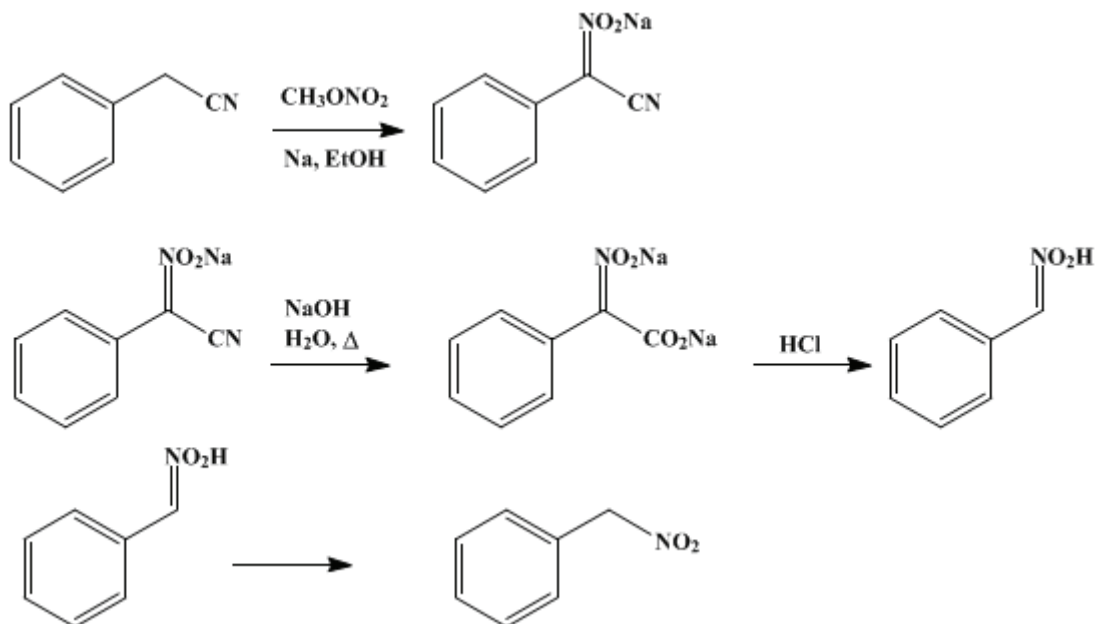
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.512 (1943); Vol. 19, p.73 (1939).

PHENYLNITROMETHANE

[Toluene, α -nitro-]



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1. Procedure

(A) *Sodium Phenyl-aci-nitroacetone*.—In a 2-l. round-bottomed flask fitted with an efficient reflux condenser is placed 400 cc. of absolute ethyl alcohol. Through the condenser tube 46 g. (2 gram atoms) of freshly cut metallic sodium is added as rapidly as possible, and the flask is heated in an oil bath after all the sodium has been added. After about one-half hour only a small globule of molten sodium (0.5–1.0 g.) remains and sodium ethoxide begins to precipitate. At this point 100 cc. of absolute alcohol is added and the mixture is cooled to 0° . A second 100-cc. portion of cold absolute alcohol is then poured on top of the solid cake of sodium ethoxide in the flask (Note 1). The reflux condenser is replaced by a stopper carrying a separatory funnel and a calcium chloride tube. An ice-cold mixture of 234 g. (2 moles) of freshly distilled benzyl cyanide (Org. Syn. Coll. Vol. I, 1941, 107) and 216 g. (180 cc., 2.8 moles) of methyl nitrate (Note 2) is added with constant shaking, at such a rate that the temperature is kept between 4° and 8° . After this addition is completed (about one hour is required), the reaction mixture is allowed to remain at 4 – 8° and shaken intermittently for one hour. The flask is then provided with a stopper fitted with a Bunsen valve and placed in a freezing mixture for twenty-four hours. The sodium salt of the *aci*-nitro compound which precipitates is filtered with suction on a Büchner funnel, washed thoroughly with dry ether (Note 3), and air dried. The first crop of material weighs 215–275 g. (58–75 per cent of the theoretical amount). The mother liquor and ether washings are combined and concentrated stepwise to about 150 cc. under reduced pressure. Successive crops of the sodium salt which separate are filtered with suction and washed with dry ether. The total weight of the crude sodium salt is 275–300 g. (75–82 per cent yield). This material is used directly without purification.

(B) *Phenylnitromethane*.—In a 4-l. beaker 300 g. of sodium hydroxide is dissolved in 1.2 l. of water. The beaker is placed in an enameled pan (as a precaution against breakage), and the solution is heated to boiling. Over a period of one hour the air-dried, crude sodium salt of phenylnitroacetone (275–300 g.) is added in small portions to the boiling alkali. Boiling is continued until the evolution of

ammonia ceases (about three hours); hot water is added from time to time to keep the volume of the solution fairly constant (Note 4). The hot alkaline solution is poured into a shallow porcelain dish and on cooling solidifies to a waxy mass.

The cake of crude **sodium salt of phenylnitroacetic acid** is broken up with a spoon, transferred to a 4-l. beaker, and stirred with 500 g. of ice. The beaker is placed in a large crock packed with ice-salt mixture, and is provided with a mechanical stirrer. When the solution in the beaker has cooled to -5° , concentrated **hydrochloric acid** is added slowly from a separatory funnel, with vigorous stirring, until the solution is faintly acid to Congo red. During the addition of acid the temperature is not allowed to rise above -5° (Note 5). Usually about 900 cc. of acid is needed and the addition requires about two hours. The cold solution is extracted with one 500-cc. portion of **ether**, followed by two 250-cc. portions. The combined **ether** extracts are washed with ice-cold portions of saturated **sodium bicarbonate** solution until the wash liquid is colorless or only faintly yellow (usually two 100-cc. portions suffice). The **ether** solution is then washed with 250 cc. of ice water containing two drops of **hydrochloric acid**, and finally with three 50-cc. portions of ice water. The **ether** solution is dried over anhydrous **sodium sulfate** and allowed to stand for three or four days to complete the isomerization of the labile *aci*-form. The solution is filtered and the **ether** removed at $15-20^{\circ}$ under reduced pressure. The residual oil is distilled at 3 mm. pressure in an ordinary Claisen flask, and the **phenylnitromethane** is obtained as a light yellow oil, b.p. $90-92^{\circ}/3$ mm. (Note 6). The yield is 135–150 g. (50–55 per cent of the theoretical amount, based upon the **benzyl cyanide**) (Note 7).

2. Notes

1. The supernatant layer of alcohol prevents the reactants dropping directly onto the **sodium ethoxide** and causing local overheating.
2. The large excess of **methyl nitrate** increases the yield appreciably. Freshly prepared **methyl nitrate** (p. 412) was dried and used directly without distillation. It is convenient to use the entire product (usually 210–230 g.) obtained from 120 g. of **methyl alcohol**.
3. Ordinary **ether** that has been allowed to stand for several days over anhydrous **calcium chloride** may be used.
4. The reaction must be watched carefully. Vigorous foaming sometimes occurs, necessitating the addition of small quantities of cold water from a wash bottle.
5. At -5° the *aci*-nitro compound separates as a gray, pasty solid. When the solution becomes acid the colloidal precipitate tends to undergo coagulation.
6. In the distillation of the crude product it is essential to maintain a low pressure and to avoid overheating. If the distillation is pushed too far, decomposition occurs and the distillate discolors rapidly on standing. If the distillation is not carried out carefully violent decomposition may occur which will blow out all connections.

The distilled product decomposes on standing and should be used promptly. **Phenylnitromethane** should not be stored in a glass-stoppered bottle, as the stopper is likely to become frozen and explosions may occur in attempting to remove it.

7. The procedure outlined can be shortened and simplified considerably by operating at somewhat higher temperatures than those specified. Thus it was found advantageous to add the **benzyl cyanide-methyl nitrate** solution to the **sodium ethoxide** with shaking at $5-15^{\circ}$, at which temperature the reaction proceeds smoothly and at a steady rate. The total yield of satisfactory sodium salt is 300–320 g. The hydrolysis of the nitrile and the acidification operation are best carried out in the same 4-l. beaker, thus avoiding the necessity for making a transfer. In dissolving the **sodium hydroxide** required for hydrolysis, 1.5 l. of water is used. As soon as no more **ammonia** is liberated (litmus) the beaker is placed in an ice-salt bath and the mixture stirred vigorously with a mechanically driven glass stirrer. When the temperature has dropped to 30° , 500 g. of ice is added. The acidification with **hydrochloric acid** (800–850 cc.) is conducted at $0-10^{\circ}$ with continued stirring. The reaction mixture is allowed to stand overnight and is extracted the next day. The ethereal solution of the product need be allowed to stand over **sodium sulfate** for only twenty to twenty-four hours before distillation. The yield is then 153–163 g. of very light-colored product boiling at $92-94^{\circ}/4$ mm. (bath at 135°). Some 10–15 g. of darker material can be distilled from the residue at a slightly higher temperature. (Louis F. Fieser and E. Berliner, private communication.)

3. Discussion

Phenylnitromethane has been prepared by the nitration of toluene with dilute nitric acid in a sealed tube,¹ by the interaction of benzenediazonium chloride and nitromethane in alkaline solution,² by the action of silver nitrite on benzyl chloride³ or iodide,⁴ and by the condensation of ethyl nitrate with benzyl cyanide and subsequent hydrolysis.⁵ The use of methyl nitrate, which can be prepared with less danger and difficulty than ethyl nitrate, is advantageous.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 412](#)

References and Notes

1. Konowalow, Ber. **28**, 1860 (1895).
2. Bamberger, Schmidt, and Levinstein, *ibid.* **33**, 2053 (1900).
3. Hollemann, Rec. trav. chim. **13**, 405 (1894).
4. Hantzsch and Schultze, Ber. **29**, 700 (1896).
5. Wislicenus and Endres, *ibid.* **35**, 1755 (1902); cf. Gattermann-Wieland, "Laboratory Methods of Organic Chemistry," p. 256. Translated from the twenty-fourth German edition by W. McCartney, The Macmillan Company, New York, 1937.

Appendix

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

Congo red

Sodium Phenyl-aci-nitroacetonitrile

sodium salt of phenylnitroacetonitrile

benzyl cyanide-methyl nitrate

ethyl alcohol,
alcohol (64-17-5)

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methyl alcohol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

nitric acid (7697-37-2)

sodium sulfate (7757-82-6)

benzenediazonium chloride

toluene (108-88-3)

sodium,
metallic sodium (13966-32-0)

sodium ethoxide (141-52-6)

benzyl chloride (100-44-7)

Benzyl cyanide (140-29-4)

Nitromethane (75-52-5)

silver nitrite (7783-99-5)

Methyl nitrate (598-58-3)

Phenylnitromethane,
Toluene, α -nitro- (622-42-4)

ethyl nitrate (625-58-1)

sodium salt of phenylnitroacetic acid