



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.

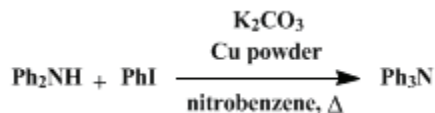
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.544 (1941); Vol. 8, p.116 (1928).

TRIPHENYLAMINE



Submitted by F. D. Hager

Checked by Henry Gilman and R. McCracken.

1. Procedure

In a 2-l. three-necked, round-bottomed flask, fitted with a very efficient mechanical stirrer, a 100-cc. separatory funnel, and a large air-cooled reflux condenser (Note 1), the upper part of which is bent downwards and attached to a vertical water condenser, are placed 176 g. (1.04 moles) of ground diphenylamine (Note 2), 204 g. (1 mole) of iodobenzene, 1 l. of nitrobenzene (Note 3), 138 g. (1 mole) of finely powdered anhydrous potassium carbonate, and 5 g. of copper powder (Note 4).

The reaction mixture is then stirred very vigorously and boiled at such a rate that the nitrobenzene condenses in the upper third of the air-cooled reflux condenser and flows back in an almost steady stream. The water formed in the reaction passes over, together with a small amount of nitrobenzene and iodobenzene, and is condensed by the water-cooled condenser. This distillate is freed of water by shaking with a small quantity of sodium sulfate and returned at intervals through the separatory funnel to the reaction flask. Heating is continued for about twenty-four hours or until the reaction is complete, as is evidenced by the non-evolution of water (Note 5).

The reaction mixture is allowed to cool somewhat and is then transferred to a 5-l. flask, and the nitrobenzene together with a little of the excess diphenylamine is removed by steam distillation. During distillation the flask should be heated to prevent excessive condensation of steam (Note 6). Steam distillation should be continued until a liter of distillate contains less than 5 cc. of water-insoluble material (Note 7).

The reaction mixture is cooled, and the crude amines which separate are collected on a suction funnel and washed twice with 400-cc. portions of water. The filtrate and washings should be saved for the recovery of iodine (Note 8). The precipitate on the funnel is transferred to a 2-l. beaker, dissolved in about 1 l. of benzene, filtered, and the benzene-insoluble part washed three times with 75-cc. portions of benzene. The benzene solution and washings are combined and separated mechanically from as much water as possible. The water is then completely removed by distilling until the distillate comes over clear. If necessary, dry benzene is added to the solution in order to have a final volume of about 1200 cc.

When the water is entirely removed, the benzene solution is cooled and an excess of dry hydrogen chloride is passed into it to precipitate the diphenylamine as the hydrochloride (Note 9).

After standing about three hours, the diphenylamine hydrochloride is filtered and washed with benzene (Note 10). The benzene is distilled from the filtrate (Note 11), and the residual triphenylamine is transferred to a 500-cc. modified Claisen flask (p. 130) and distilled under reduced pressure. The first fraction consists of some benzene, then the temperature rises rapidly and a few cubic centimeters of deeply colored distillate come over just before the amine fraction, which is collected at 195–205°/10–12 mm. The distillate is a yellow liquid which soon solidifies to a light yellow solid. The side arm of the distilling flask should be of rather large bore (about 10 mm.) to prevent clogging by the amine which solidifies. The crude product weighs 220–235 g. and melts at 120–124°.

In order to obtain a pure product the amine is dissolved in about 700 cc. of boiling ethyl acetate under a reflux condenser. When the amine has dissolved the solution is rapidly cooled and stirred, whereupon the amine separates in almost white crystals. Further crops of crystals may be obtained on concentrating the solution and cooling. The last portions may be colored, but one recrystallization from

ethyl acetate gives a nearly colorless product (Note 12). The total yield of pale yellow product which melts at 126° is 200–210 g. (82–85 per cent of the theoretical amount) (Note 13).

2. Notes

1. The air condenser used here was 65 cm. long and of 13-mm. bore, and the vertical water condenser, 40 cm. in length. Cork stoppers were used, and it was found desirable to protect their exposed surfaces by coating them with water-glass, allowing these to dry, and then coating with lead foil. It is best to boil the mixture on a sand bath and to cover with asbestos that part of the flask not immersed in the sand.
2. Technical diphenylamine which has been distilled under reduced pressure and collected over a 5° range (159–164°/4 mm.) is satisfactory.
3. The nitrobenzene should not contain any free acid. Should there be free acid present, it can be removed by shaking with solid potassium carbonate.
4. "Natur Kupfer C" is a good catalyst, but ordinary copper bronze may be used.
5. The time required for the completion of reaction varies with the rate of stirring. When the stirring is very vigorous most of the water comes over within twelve hours.
6. This heating should be done carefully, preferably on a sand bath, because of the danger of breaking the flask due to the caking of some undissolved potassium carbonate.
7. In general, about 8–10 l. of aqueous distillate is required, and practically all but about 25 cc. of the nitrobenzene is recovered. It is recommended that the removal of nitrobenzene by steam distillation be fairly complete in order to avoid a gummy residue.
8. Most of the iodine can be recovered as potassium iodide mixed with some potassium carbonate. A little cuprous iodide is also present.
9. The hydrogen chloride is introduced through a delivery tube at least 25 mm. in diameter and about 10 cm. under the surface of the liquid. If the gas is introduced rapidly enough and the mixture stirred occasionally there is little trouble with clogging of the delivery tube.
10. The crude diphenylamine may be recovered by decomposing the hydrochloride with water and filtering the mixture.
11. A large amount of hydrogen chloride is evolved during the distillation, and some provision must be made to keep it out of the room. A gas-absorption trap (Fig. 7 on p. 97) may be used.
12. Because of the lower solubility of triphenylamine in ethyl alcohol this solvent may be used advantageously in washing the crystals and in recrystallizing small amounts of the compound.
13. *N*-Phenylcarbazole may be made in an analogous manner by substituting carbazole for diphenylamine. If stirring and heating are both very vigorous, twelve hours suffices for the reaction. The yield of purified product is about 88 per cent of the theoretical amount, and the compound melts at 88–89°. The crystals, when crushed, emit a strong violet light.

3. Discussion

The procedure described is a modification of that by Goldberg and Nimerovsky.¹ Triphenylamine can also be prepared by the treatment of aniline or diphenylamine with potassium and then bromobenzene,² by the action of sodium on diphenylamine and bromobenzene,³ and from aniline and anhydrous hydrogen chloride under pressure at about 250°.⁴

References and Notes

1. Goldberg and Nimerovsky, Ber. **40**, 2452 (1907).
 2. Merz and Weith, Ber. **6**, 1514 (1873).
 3. Heydrich, Ber. **18**, 2156 (1885).
 4. General Aniline Works, U. S. pat. 2,051,123 [C. A. **30**, 6760 (1936)].
-

Appendix

Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

copper bronze

ethyl alcohol (64-17-5)

potassium carbonate (584-08-7)

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

ethyl acetate (141-78-6)

aniline (62-53-3)

sodium sulfate (7757-82-6)

potassium iodide (7681-11-0)

copper powder (7440-50-8)

iodine (7553-56-2)

sodium (13966-32-0)

Nitrobenzene (98-95-3)

bromobenzene (108-86-1)

potassium (7440-09-7)

Iodobenzene (591-50-4)

Triphenylamine (603-34-9)

diphenylamine (122-39-4)

diphenylamine hydrochloride (537-67-7)

cuprous iodide (7681-65-4)

carbazole (86-74-8)

N-Phenylcarbazole (1150-62-5)