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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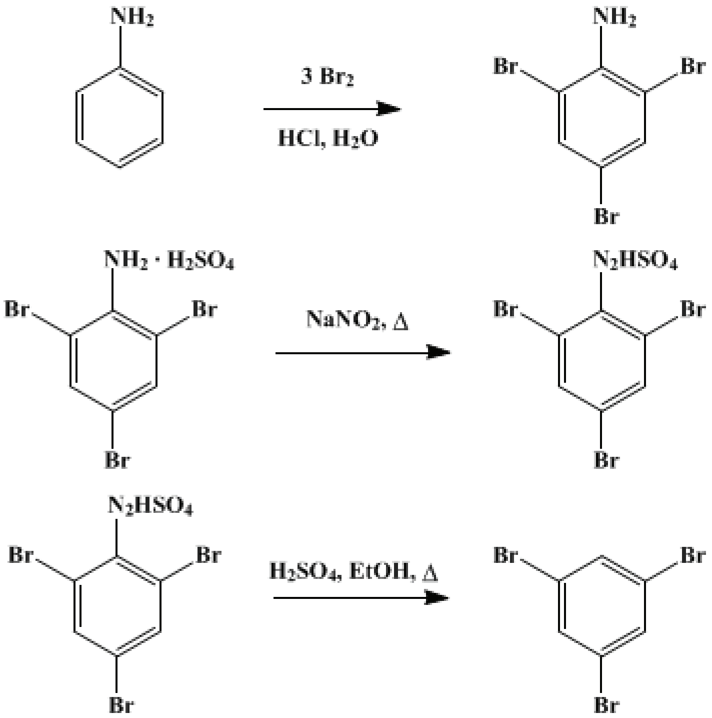
***sym*.-TRIBROMOBENZENE**

[Benzene, 1,3,5-tribromo-]

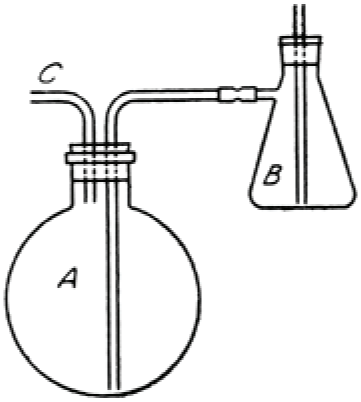


Submitted by G. H. Coleman and William F. Talbot.
Checked by Reynold C. Fuson and Charles F. Woodward.

1. Procedure

The apparatus consists of a 12-l. round-bottomed flask and a 250-cc. suction flask provided with stoppers and glass tubes as shown in Fig. 19. After the flasks have been charged, A is surrounded by an ice bath and B by a water bath heated to 40–50°. In flask A are placed 100 g. (1.1 moles) of aniline, 1 l. of water, and 100 cc. (1.2 moles) of concentrated hydrochloric acid; when the aniline has dissolved, sufficient water is added to bring the volume of the solution to 5 l. Flask B is charged with 577 g. (185 cc., 3.6 moles) of bromine; the baths are adjusted, and a rapid stream of air saturated with bromine vapor is drawn into A by applying suction at C (Note 1) and (Note 2).

Fig. 19



The introduction of bromine is continued until the solution assumes a distinctly yellow color; approximately three to four hours is required, and the reaction is then complete. The tribromoaniline is filtered on a Büchner funnel, thoroughly washed with water to remove hydrobromic acid, sucked as dry as possible, and taken without further drying to the next step.

The moist tribromoaniline, together with 2.1 l. of 95 per cent alcohol and 525 cc. of benzene, is placed in a 5-l. two-necked flask. One neck of the flask bears a reflux condenser; the other is closed with a stopper that can be removed momentarily for the addition of reagents. The tribromoaniline is brought into solution by heating the flask on a steam bath. To this solution is added 140 cc. of concentrated sulfuric acid, and then 140 g. (2.03 moles) of powdered sodium nitrite as rapidly as the violence of the reaction will permit. When the reaction has moderated, the solution is brought to boiling and maintained there as long as gas is evolved. It is then allowed to stand in a warm place for three hours more.

After the mixture has been cooled (preferably in an ice bath), the mother liquor is removed from the solid by decantation through a Büchner funnel; if necessary, a wire gauze is used to retain the solid in the flask. To the solid is then added a solution of 150 cc. of concentrated sulfuric acid in 1.5 l. of water. When the excess sodium nitrite has been decomposed, the solid is transferred to a Büchner funnel and washed first with water and then with a small amount of alcohol. The yield of crude, dry tribromobenzene is 250–260 g. (74–77 per cent of the theoretical amount). The product is reddish brown and melts at 112–116°.

For further purification, 100 g. of the crude product is dissolved in a boiling mixture of 1560 cc. of glacial acetic acid and 350 cc. of water; the solution is boiled for a few minutes with 25 g. of decolorizing carbon, filtered hot, and allowed to cool. The crystals are washed on a Büchner funnel with a small amount of chilled 95 per cent alcohol to remove the acetic acid. The whole of the crude product crystallized in this way furnishes 216–240 g. (64–71 per cent of the theoretical amount) of slightly colored tribromobenzene, melting at 121.5–122.5° (corr.).

The yield of crude product may be increased 50–60 g.—making a total of 300–320 g. (89–95 per cent of the theoretical amount)—by working up the mother liquors. The alcoholic liquors and washings are diluted to 6 l., and the aqueous layer is separated from the heavy oil at the bottom. The benzene is then distilled from the oil in a distilling flask, care being taken not to overheat the product after the benzene has been removed. The residual tribromobenzene may be recrystallized in the manner described above.

2. Notes

1. Considerable heat is generated by the reaction, and it is necessary to cool A to prevent the loss of bromine. Flask B must be kept at 40–50° to ensure a high concentration of bromine vapor in the air stream; the violent agitation produced by air saturated at lower temperatures whips the reaction mixture into a light foam that is likely to overflow the flask.
2. It is well to interpose a safety flask between the reaction flask and the aspirator. The safety flask is partially filled with water through which the air stream passes after the bromine vapor has been removed. This device has a double purpose; it enables one to gauge the rate of aspiration by the rate at which the air current bubbles through the water, and it serves to detect the escape of bromine vapors from the reaction flask. A small amount of bromine will impart to the water a distinctly yellow color. In case bromine does escape into this trap a momentary release of the suction will cause the wash water to be drawn into the reaction flask, thus returning the bromine to the reaction mixture.

3. Discussion

Sym.-tribromobenzene has been prepared from 3,5-dibromoaniline by the replacement of the amino group by bromine;[1] from bromoacetylene by the action of light;[2] by the decomposition of 2,4,6-tribromophenylhydrazine;[3] by the reduction of 2,4,6-tribromobenzenediazonium sulfate;[4], [5] and as a by-product in the preparation of 2,4,6-tribromobenzonitrile.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 947

References and Notes

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3. Chattaway and Vonderwahl, J. Chem. Soc. **107**, 1508 (1915).
4. Jackson and Moore, Am. Chem. J. **12**, 167 (1890).
5. Jackson and Bentley, ibid. **14**, 335 (1892).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sym.-TRIBROMOBENZENE

alcohol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

aniline (62-53-3)

HYDROBROMIC ACID (10035-10-6)

bromine (7726-95-6)

sodium nitrite (7632-00-0)

carbon (7782-42-5)

TRIBROMOBENZENE

Benzene, 1,3,5-tribromo- (626-39-1)

tribromoaniline

3,5-dibromoaniline

bromoacetylene (593-61-3)

2,4,6-tribromophenylhydrazine

2,4,6-tribromobenzenediazonium sulfate

2,4,6-tribromobenzonitrile