



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.

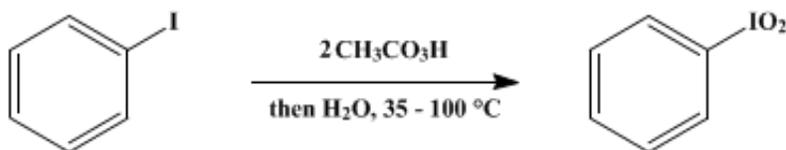
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior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

IODOXYBENZENE

[Benzene, iodoxy-]



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1. Procedure

*Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. Peroxy compounds should be added to the organic material, never the reverse. For relatively fast reactions, the rate of addition of the peroxy compound should be slow enough so that it reacts rapidly and no significant unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peroxy compound is being added, and cooling should generally be provided since many reactions of peroxy compounds are exothermic. New or unfamiliar reactions, particularly those run at elevated temperatures, should be run first on a small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds (including unreacted peroxy compounds) have been destroyed. Decomposition of active oxygen compounds may be accomplished by the procedure described in Korach, M.; Nielsen, D. R.; Rideout, W. H. *Org. Synth.* 1962, 42, 50 (*Org. Synth.* 1973, Coll. Vol. 5, 414). [Note added January 2011].*

Caution! Avoid inhaling the vapor of peracetic acid or allowing the liquid to come into contact with the skin. The reaction is best carried out in a hood (Note 1). Iodoxybenzene explodes if heated to 230°.

A 500-ml. three-necked flask fitted with reflux condenser, stirrer, and dropping funnel and containing 20.4 g. (0.10 mole) of iodobenzene² is immersed in an oil bath maintained at 35°. Seventy-five grams (65 ml., 0.50 mole) of commercial 40% peracetic acid (Note 1) is added with vigorous stirring over a 30-minute period. Solid may begin to form before all the peracetic acid has been added, but, although this may slow down the stirring, it does not decrease the yield or cause a rise in temperature.

After all the peracetic acid has been added, the reaction mixture is diluted with 80 ml. of water and heated from 35° to 100° over a 20-minute period (Note 2). It is then kept at 100° for 45 minutes. The flask is cooled to 0–5° in an ice bath, and the solid iodoxybenzene is collected on a Büchner funnel and air-dried with suction for 1 hour. Additional material is obtained by concentrating the filtrate to one-fourth of its volume (*Caution! (Note 3)*). The two crops of crude iodoxybenzene are combined and dried overnight in a desiccator; weight 19.6–20.5 g.; m.p. 230° (*Caution! Explodes!*). Iodometric titration³ shows the purity to be about 94% (Note 4).

Purification of the crude iodoxybenzene is effected by grinding it to a powder in a mortar, macerating it with 70 ml. of chloroform, and separating the solid by filtration. The chloroform extraction is repeated and the solid is dried; weight 17–19 g. (72–80%); purity 99.0–99.9% by iodometric titration.³

2. Notes

1. For a source and the specifications of 40% [peracetic acid](#) and precautions in handling it, see [Note 3](#) and [Note 1](#) under the preparation of [iodosobenzene diacetate](#), p. 661.
2. If the temperature of the bath is not raised slowly, foaming is difficult to control. Although the gradual rise in temperature causes considerable foaming, the reaction mixture remains within the flask.
3. The filtrate must not be evaporated to dryness because [iodoxybenzene](#) explodes when heated.
4. The major by-products in this reaction are [iodobenzene](#) and [iodosobenzene diacetate](#). An excess of 20 ml. of [peracetic acid](#) over the 65 ml. recommended results in an increase in the amount of [iodobenzene](#). Both impurities are removed from the product by washing with [chloroform](#).

3. Discussion

[Iodoxybenzene](#) has been prepared by the disproportionation of [iodosobenzene](#),^{4,5,6} by oxidation of [iodosobenzene](#) with [hypochlorous acid](#) or bleaching powder,⁷ and by oxidation of [iodobenzene](#) with [hypochlorous acid](#) or with [sodium hydroxide](#) and [bromine](#).⁸ Other oxidizing agents used with [iodobenzene](#) include air,³ [chlorine](#) in [pyridine](#),⁹ Caro's acid,^{10,11} concentrated [chloric acid](#),¹² and [peracetic acid](#) solution.¹³ Hypochlorite oxidation of [iodobenzene dichloride](#) has also been employed.¹⁴

4. Merits of the Preparation

This one-step method of preparing [iodoxybenzene](#) is preferable to earlier methods because it is simpler and the yield is substantially higher. The procedure seems general for iodoxyarenes, at least those with electron-releasing substituents, for the submitters have used it to obtain good yields of *o*-, *m*- and *p*-iodoxytoluene, 2- and 4-[iodoxy-*m*-xylene](#), 2-[iodoxy-*p*-xylene](#), [*o*-iodoxyphenetole](#), [4-iodoxybiphenyl](#), and [*o*-iodoxybenzoic acid](#).

Iodoxyarenes are useful in the preparation of [iodonium](#) salts, $\text{Ar}_2\text{I}^+\text{X}^-$.¹⁵

References and Notes

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14. [M. W. Formo](#) and [J. R. Johnson](#), *Org. Syntheses*, Coll. Vol. **3**, 486 (1955).
15. [C. Hartman](#) and [V. Meyer](#), *Ber.*, **27**, 504 (1894).

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

o-, m- and p-iodoxytoluene
sodium hydroxide (1310-73-2)
chloroform (67-66-3)
bromine (7726-95-6)
pyridine (110-86-1)
chlorine (7782-50-5)
chloric acid (7790-93-4)
hypochlorous acid (7790-92-3)
Iodobenzene (591-50-4)
iodobenzene dichloride (2401-21-0)
peracetic acid (79-21-0)
Iodonium
Iodosobenzene (536-80-1)
Iodoxybenzene,
Benzene, iodoxy- (696-33-3)
Iodosobenzene diacetate (3240-34-4)
4-iodoxybiphenyl
4-iodoxy-m-xylene
2-iodoxy-p-xylene
o-iodoxyphenetole
o-iodoxybenzoic acid