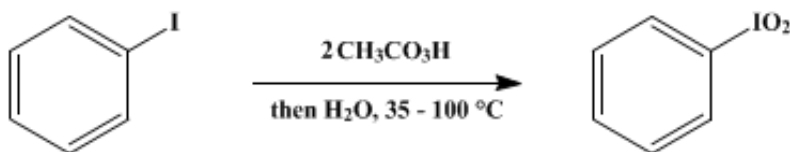


## IODOXYBENZENE

[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 iodobenzene<sup>2</sup> 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 titration<sup>3</sup> 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.<sup>3</sup>

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

## 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,  $\text{Ar}_2\text{I}^+\text{X}^-$ .<sup>15</sup>

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## References and Notes

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**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