



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.

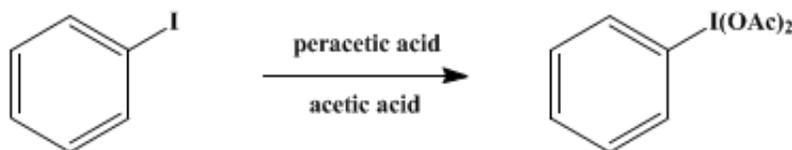
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior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

IODOSOBENZENE DIACETATE

[Benzene, iodoso-, diacetate]



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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).

The apparatus consists of a 200-ml. beaker equipped with a magnetic stirrer or any other type suitable for stirring a small volume of liquid. The flask is charged with 20.4 g. (0.10 mole) of iodobenzene² and is immersed in a water bath maintained at 30° (Note 2). Thirty-six grams (31 ml., 0.24 mole) of commercial 40% peracetic acid (Note 3) is added dropwise to the well-stirred iodobenzene over a period of 30–40 minutes. Stirring is continued for another 20 minutes at a bath temperature of 30°, during which time a homogeneous yellow solution is formed. Crystallization of iodosobenzene diacetate may begin during this period.

The beaker is chilled in an ice bath for 1 hour. The crystalline diacetate that separates is collected on a Büchner funnel and washed with three 20-ml. portions of cold water. After drying for 30 minutes on the funnel with suction, the diacetate is dried overnight in a vacuum desiccator containing calcium chloride (Note 4). The dried diacetate weighs 26.7–29.3 g. (83–91%) and melts at 158–159° with decomposition. The purity of the diacetate, determined by the titration method of Lucas, Kennedy, and Formo,³ is 97–98%, which is good enough for most purposes. The purity can be increased to 99–100% by a recrystallization from 5M acetic acid.

2. Notes

1. Rubber gloves should be worn when handling vessels containing peracetic acid, for traces of the liquid can cause severe irritation. Skin that has come into contact with peracetic acid should be washed

immediately and treated with sodium bicarbonate. Details for the safe handling of peracetic acid are found in Bulletin 4 supplied by Buffalo Electrochemical Corp.

2. Appreciable amounts of iodoxybenzene are formed if the temperature of the bath is allowed to go above 30° or if the addition of peracetic acid is faster than indicated.

3. Satisfactory 40% peracetic acid is obtainable from Buffalo Electrochemical Corp., Food Machinery and Chemical Corp., Buffalo, New York. The specifications given by the manufacturer for its composition are: peracetic acid, 40%; hydrogen peroxide, 5%; acetic acid, 39%; sulfuric acid, 1%; water, 15%. Its density is 1.15 g. per ml.

A fresh sample of this 40% peracetic acid contains about 1.54 equivalents, or 0.77 mole, of peroxide per 100 ml. of solution, corresponding to 1.34 equivalents per 100 g. The concentration can be determined by treating the peroxide solution with potassium iodide and titrating the liberated iodine with standard sodium thiosulfate. The concentration of peroxide in peracetic acid decreases somewhat on long standing and should be checked before the peracetic acid is used. The yield of diacetate is lowered if the concentration of the peroxide is less than 1.0 equivalent per 100 g. of peracetic acid. The total amount of peroxide used should be 2.4 moles, or 4.8 equivalents, for each mole of iodobenzene.

4. The surface of the diacetate may become yellow during the drying, but this does not affect its usefulness for most purposes.

3. Discussion

Willgerodt⁴ prepared iodosobenzene diacetate by adding chlorine to iodobenzene and hydrolyzing the dichloride to iodosobenzene, which was then reacted with acetic acid. Pausacker⁵ used this method to synthesize a number of analogs but found it inferior to his modification of the method of Böeseken and Schneider⁶ in which iodobenzene is treated with 30% hydrogen peroxide and acetic anhydride. Arbusov⁷ obtained the diacetate in 79% yield by the action of a mixture of peracetic and acetic acids on iodobenzene. Quantitative yields of the diacetate have been claimed for the reaction of iodobenzene dichloride with lead tetraacetate in glacial acetic acid containing 10% acetic anhydride, followed by precipitation of the lead as the chloride.⁸

4. Merits of the Preparation

Iodosobenzene diacetate is best prepared by the action of peracetic acid and acetic acid on iodobenzene. The present procedure is superior to earlier ones^{5,6,7,8} because it uses inexpensive, commercially available peracetic acid, is faster, and gives higher yields. The procedure seems general for aryl iodides with electron-releasing substituents, for the submitters have obtained good yields of diacetates from *o*-, *m*- and *p*-iodotoluene, 2- and 4-iodo-*m*-xylene, 2-iodo-*p*-xylene, *o*-iodophenetole, and 4-iodobiphenyl.

Iodosobenzene diacetate is used as a reagent for the preparation of glycol diacetates from olefins,⁹ for the oxidation of aromatic amines to corresponding azo compounds,¹⁰ for the ring acetylation of *N*-arylamides,¹¹ for oxidation of some phenols to phenyl ethers,¹² and as a coupling agent in the preparation of iodonium salts.¹³ Its hydrolysis to iodosobenzene constitutes the best synthesis of that compound.¹⁴

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 658
- Org. Syn. Coll. Vol. 5, 665
- Org. Syn. Coll. Vol. 8, 132

References and Notes

1. Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn, New York.

2. H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, Coll. Vol. **2**, 351 (1943).
 3. H. J. Lucas, E. R. Kennedy, and M. W. Formo, *Org. Syntheses*, Coll. Vol. **3**, 483 (1955).
 4. C. Willgerodt, *Ber.*, **25**, 3495 (1892).
 5. K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).
 6. J. Böeseken and G. C. C. Schneider, *J. Prakt. Chem.*, **131**, 285 (1931).
 7. B. A. Arbusov, *J. Prakt. Chem.*, **131**, 351 (1931).
 8. R. Neu, *Ber.*, **72B**, 1505 (1939).
 9. R. Criegee and H. Beucker, *Ann.* **541**, 218 (1939).
 10. K. H. Pausacker, *J. Chem. Soc.*, 1989 (1953).
 11. G. B. Barlin and N. V. Riggs, *J. Chem. Soc.*, 3125 (1954).
 12. K. H. Pausacker and A. R. Fox, *J. Chem. Soc.*, 295 (1957).
 13. F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *J. Am. Chem. Soc.*, **81**, 342 (1959).
 14. H. Saltzman and J. G. Sharefkin, *this volume*, p. 658.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

o-, m- and p-iodotoluene
2- and 4-iodo-m-xylene
sulfuric acid (7664-93-9)
acetic acid (64-19-7)
acetic anhydride (108-24-7)
sodium bicarbonate (144-55-8)
potassium iodide (7681-11-0)
sodium thiosulfate (7772-98-7)
iodine (7553-56-2)
chlorine (7782-50-5)
hydrogen peroxide,
peroxide (7722-84-1)
Iodobenzene (591-50-4)
iodobenzene dichloride (2401-21-0)
peracetic acid (79-21-0)
Iodosobenzene (536-80-1)
Iodoxybenzene (696-33-3)
Iodosobenzene diacetate,
Benzene, iodoso-, diacetate (3240-34-4)

[4-iodobiphenyl \(1591-31-7\)](#)

[2-Iodo-p-xylene \(1122-42-5\)](#)

[o-iodophenetole \(614-73-3\)](#)

[lead tetraacetate \(546-67-8\)](#)