Organic Syntheses

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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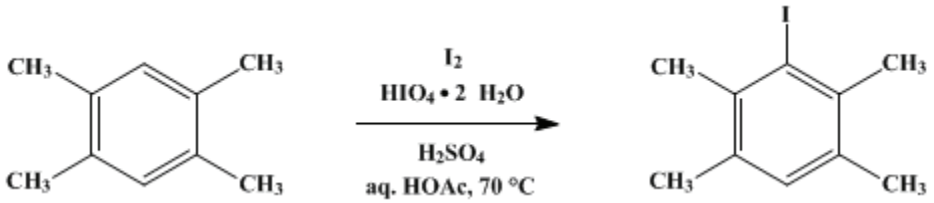
Organic Syntheses, Coll. Vol. 6, p.700 (1988); Vol. 51, p.94 (1971).

DIRECT IODINATION OF POLYALKYLBENZENES: IODODURENE

[Benzene, 3-iodo-1,2,4,5-tetramethyl-]



Submitted by H. Suzuki[1]
Checked by Robert E. Ireland and Robert Czarny.

1. Procedure

A 200-ml., three-necked flask equipped with a reflux condenser, a thermometer, a glass stopper, and a magnetic stirring bar is charged with 13.4 g. (0.101 mole) of durene (Note 1), 4.56 g. (0.0215 mole) of periodic acid dihydrate, and 10.2 g. (0.0402 mole) of iodine. A solution of 3 ml. of concentrated sulfuric acid and 20 ml. of water in 100 ml. of glacial acetic acid is added to this mixture. The resulting purple solution is heated at 65–70° with stirring for approximately 1 hour until the color of iodine disappears. The reaction mixture is diluted with approximately 250 ml. of water, and the white-yellow solid that separates (Note 2) is collected on a Büchner funnel and washed three times with 100-ml. portions of water. The product is dissolved in a minimum amount of boiling acetone (about 125 ml. is required); the solution is cooled to room temperature and subsequently stored overnight in a refrigerator. The product is collected by rapid filtration through a Büchner funnel, yielding 20.8–22.6 g. (80–87%) of iododurene as colorless, fine needles, m.p. 78–80°.

2. Notes

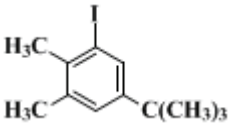
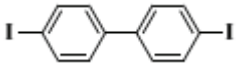
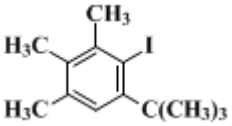
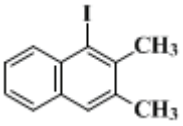
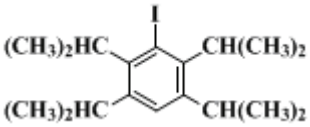
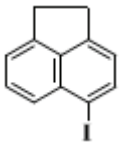
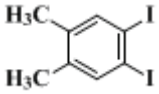
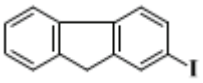
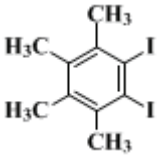
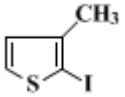
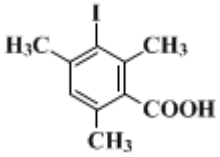
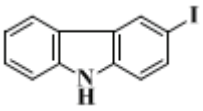
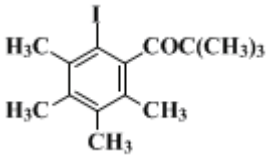
1. Durene (m.p. 79–80°), prepared according to the procedure in *Org. Synth.*, **Coll. Vol. 2**, 248 (1943), was used by the submitter. Commercially available durene, which melted at 79–80° after purification by the *Org. Synth.* procedure above, was used by the checkers.
2. Some crystals of iododurene that have formed during the heating period tend to take on a purple coloration because of occluded iodine. This impurity is readily removed by the recrystallization procedure.

3. Discussion

The present procedure is the most convenient method for the direct, high-yield preparation of mono-, di-, or triîodo derivatives from various polyalkylbenzenes and their derivatives. It is also applicable to some moderately activated heteroaromatic systems. However, the reaction fails with compounds bearing strongly deactivating substituent groups. Shorter reaction times and higher degree of product purity are assured by the use of periodic acid as an oxidizing agent. A feature of the reagent is that iodine is oxidized by periodic acid and periodic acid is reduced by iodine, both forming an active iodinating species which reacts with an aromatic compound, eventually leading to the formation of only the desired iodination product and water. A brief review of the iodine/periodic acid reagent has recently appeared.[2] The preparation of tetraiodo and more highly iodinated derivatives of alkylbenzenes by this procedure is difficult, and the Jacobsen reaction for the disproportionation of diîodo compounds by the action of sulfuric acid is preferred.[3] Polyiodo derivatives are useful for the characterization of polyalkylbenzenes and their derivatives, liquids available only in a small quantities, since the introduction of iodine atoms increases the molecular weight and converts a liquid hydrocarbon into a highly crystalline solid with a moderate melting range.[4] Table I illustrates the iodoarenes prepared from

the corresponding arenes by conditions similar to that described herein.

TABLE I
IODOARENES PREPARED FROM THE CORRESPONDING ARENES

Iodoarenes	Ref.	Yield, %	Iodoarenes	Ref.	Yield, %
	5	81		6	94
	5	89		6	84
	5	85[a]		6	69
	5	85		6	86
	5	84		7	72
	8	86		6	85[b]
	9	85			

[a]Based on unrecovered hydrocarbon. The reaction proceeds quite slowly.
[b]A solution of periodic acid in acetic acid is added dropwise, with stirring, to a mixture of carbazole, iodine, and 80% (v/v) acetic acid. It is necessary to separate the product from colored substance by chromatography over alumina, using benzene as the eluant.

Iododurene has been prepared by treatment of durene with iodine and mercury(II) oxide,[10] sulfur iodide and nitric acid,[11] iodine and zinc chloride[12] or copper(II) chloride,[13] or iodoanisole and sulfuric acid.[14]

References and Notes

1. Department of Chemistry, Kyoto University, Kyoto 606, Japan. [Present address: Department of Chemistry, Ehime University, Matsuyama 790, Japan.]
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

nitric acid (7697-37-2)

mercury(II) oxide (21908-53-2)

iodine (7553-56-2)

acetone (67-64-1)

zinc chloride (7646-85-7)

copper(II) chloride (7758-89-6)

carbazole (86-74-8)

Durene (95-93-2)

periodic acid

Iododurene

Benzene, 3-iodo-1,2,4,5-tetramethyl- (2100-25-6)

periodic acid dihydrate

sulfur iodide

iodoanisole