



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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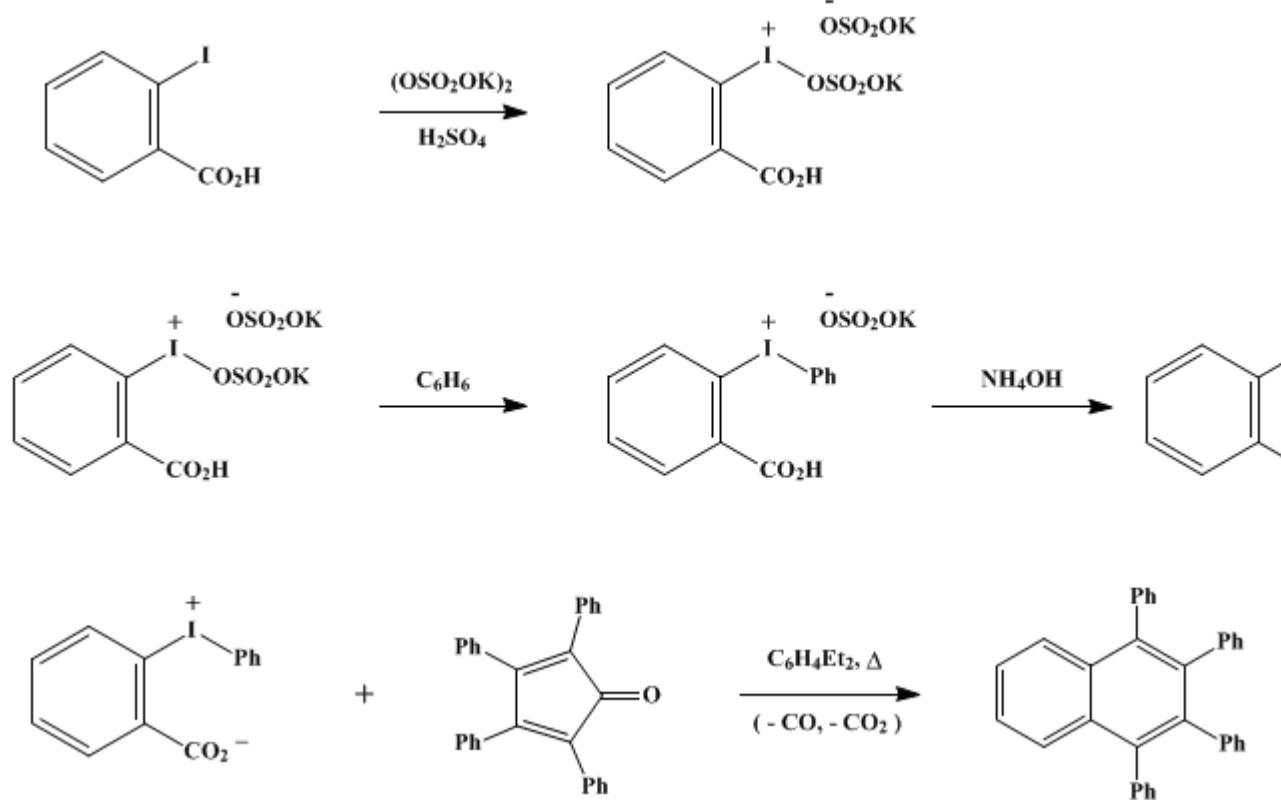
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## 1,2,3,4-TETRAPHENYLNAPHTHALENE

### [Naphthalene, 1,2,3,4-tetraphenyl-]



Submitted by Louis F. Fieser and Makhluf J. Haddadin<sup>1</sup>.

Checked by Joyce M. Dunston and Peter Yates.

### 1. Procedure

A. *Diphenyliodonium-2-carboxylate*. An Erlenmeyer flask containing 80 ml. of concentrated sulfuric acid (Note 1) is placed in an ice bath to cool. To a 2-l. three-necked flask are added (Note 2) 20 g. (0.081 mole) of lump-free *o*-iodobenzoic acid (Note 3) and 26 g. (0.096 mole) of potassium persulfate (Note 4). The flask is cooled in an ice bath, the chilled sulfuric acid is added, and the flask is swirled in an ice bath for 4–5 minutes to produce an even suspension and to control the initial exothermal reaction. The flask is then removed from the ice bath and the time is noted. The reaction mixture foams somewhat and acquires a succession of colors. The flask is mounted in a pan of acetone, a mechanical stirrer with a curved Teflon® blade is placed in the center neck of the flask and operated slowly, and a 250-ml. separatory funnel is mounted into a side neck. Three flasks are put in an ice bath to cool: one containing 190 ml. of distilled water, another 230 ml. of 29% ammonium hydroxide, and another 400 ml. of methylene chloride.

After the oxidation has proceeded for 20 minutes, the acetone bath is brought to 10° by addition of crushed dry ice, and the solution is stirred for 2–3 minutes. There is added 20 ml. of thiophene-free benzene (17.6 g., 0.226 mole), and stirring at 10° is continued for 1 hour (Note 5). The temperature of the acetone bath is lowered to –15° by addition of crushed dry ice and the bath kept at this temperature while the chilled 190 ml. of distilled water is added with efficient stirring to precipitate the potassium bisulfate salt of diphenyliodonium-2-carboxylic acid. The 400 ml. of chilled methylene chloride (Note 6) is added, and a 100° thermometer is mounted in a side neck in such a way that the 15–25° section is visible. With efficient cooling (bath at –15°) and stirring, the 230 ml. of chilled 29% ammonium

hydroxide (Note 7) is added at such a rate that the temperature of the reaction mixture remains between 15° and 25°. Approximately 10 minutes is required for the addition, and after the addition the aqueous layer should be alkaline to indicator paper (pH 9). The stirrer and the thermometer are removed and rinsed with water and **methylene chloride**. The bulk of the aqueous layer is decanted into a 500-ml. Erlenmeyer flask for temporary storage, and the reaction flask is emptied and rinsed into a 500-ml. separatory funnel. The pale tan lower **methylene chloride** layer is drained into a 1-l. Erlenmeyer flask, the decanted aqueous layer is added to the separatory funnel, and the combined aqueous layer is extracted with two 100-ml. portions of **methylene chloride**. The combined extract is dried over anhydrous **sodium sulfate**, filtered into a 1-l. Erlenmeyer flask, and the filtrate is evaporated on the steam bath until the product is left as a dry grayish cake. The cake is dislodged and broken up with a stainless steel spatula, and the bulk of the product is transferred to a paper. Material adhering to the flask and spatula is dissolved in boiling **methylene chloride** and the solution transferred to a tared 500-ml. flask and evaporated to dryness. The solid product is added to the flask and the combined solid is brought to constant weight at steam-bath temperature and water-aspirator pressure. The yield of crude product is 23.3–24.4 g. (Note 8).

Boiling water (275 ml.) is poured into the flask, the product brought into solution at the boiling point, and 0.4 g. of **Norit**® is added carefully to the slightly cooled solution. The solution is again heated to boiling, filtered, and allowed to stand for crystallization overnight, eventually at 0°. The colorless prisms of **diphenyliodonium-2-carboxylate monohydrate** (Note 9) are collected and air-dried to constant weight at room temperature. The yield of product, m.p. 220–222° (dec.), is 20–22 g. (72–79%, (Note 10).

B. **1,2,3,4-Tetraphenylnaphthalene**. To a 100-ml. round-bottomed flask equipped with an 11-cm. water-cooled condenser (Note 11) there is added 60 ml. of **diethylbenzene** (*meta* and *para* mixture) (Note 12), and the flask is heated in a fume hood with the free flame of a microburner until refluxing liquid rises well into the condenser. If a cloudy zone of condensate appears at the top of the condenser, the moisture is removed with an applicator stick wrapped with absorbent cotton (Note 13). The same technique is used later for removal of water of hydration which appears in the early stages of the reaction and causes hissing and eruption if allowed to drop back into the flask (Note 14). The flame is removed and 10 g. (0.026 mole) of **tetraphenylcyclopentadienone**<sup>2</sup> (Note 2) and 11.8 g. (0.035 mole) of **diphenyliodonium carboxylate monohydrate** are added to the flask. The mixture is heated over a microburner at a rate such as to maintain vigorous gas evolution and gentle refluxing. The water of hydration is eliminated in 8–10 minutes. The flask is then fitted with a normal reflux condenser and the heating is continued. After 30 minutes considerable undissolved **diphenyliodonium carboxylate** can still be seen, under illumination, at the bottom of the flask. In another 5 minutes the color changes to transparent red, and in a minute or two longer the solution becomes pale amber. Refluxing is continued until no solid remains (10–15 minutes) (Note 15). The flask is then fitted for distillation, and 55 ml. of liquid (**diethylbenzene** and **iodobenzene**, b.p. 188°) is removed by distillation. The residue is cooled and dissolved in 25 ml. of **dioxane**. The solution is rinsed into a 125-ml. Erlenmeyer flask and diluted with 25 ml. of 95% **ethanol**. The solution is heated to boiling, and water (6–7 ml.) is added gradually until a few shiny prisms remain undissolved on boiling. Crystallization is allowed to proceed at room temperature and then for several hours at 0°. The precipitate is removed by filtration, and the mother liquor upon further standing deposits a small second crop of crystals (0.3 g., m.p. 1° low). The main product melts initially in the range 196–199°, solidifies on cooling, and remelts sharply at 203–204° (Note 16). The total yield is 9.2–10.2 g. (82–90%).

## 2. Notes

1. The amount of acid is half that called for in previous procedures.<sup>3,4</sup>
2. The solids are added using a powder funnel or a rolled-up piece of glazed paper to prevent material from lodging on the neck or walls.
3. Obtained from Eastman Organic Chemicals.
4. The fine granular material supplied by Fisher Scientific Co. is satisfactory; any lumps present should be crushed. Persulfate in the form of large prisms should be ground prior to use.
5. If the reactants are mixed at room temperature, a rapid temperature rise of about 7° is noted. The reaction can then be brought to completion by swirling at 50° for 5 minutes or at room temperature for

20 minutes, but the product contains considerable brown pigment.

6. The **methylene chloride** is added for efficient extraction of the product as it is liberated on neutralization. The product is more soluble in this solvent than in **chloroform**.<sup>3,4</sup>

7. Neutralization with **sodium hydroxide**<sup>3,4</sup> leads to troublesome separation of sodium salts.

8. This crude product contains a little solid which will not redissolve in an organic solvent and it is unsuitable for procedure B. The checkers used a 500-ml. filter flask with sealed side arm for the evaporation and drying operation.

9. *Anal.* Calcd. for  $C_{13}H_{11}O_3I$  (342.13): C, 45.63; H, 3.24; I, 37.10. Found: C, 45.48; H, 3.19; I, 37.16.

10. Anhydrous material, m.p. 215–216° (dec.), can be obtained in quantitative yield by extracting 12 g. of the monohydrate in a Soxhlet extractor with 80 ml. of **methylene chloride** and evaporating to constant weight.

11. A convenient condenser is a water-cooled Ace Glass Bearing, No. 8244.

12. Obtained from Eastman Organic Chemicals, b.p. 175–181°. This solvent, in which the **benzyne** precursor is very sparingly soluble, seemed slightly superior to **trimethylene glycol dimethyl ether** (b.p. 222°) in which the solubility is considerably higher. ***o*-Dichlorobenzene** (b.p. 179°), a still better solvent for the dipolar salt, is less satisfactory than the **ether**. **Diethyl oxalate** (b.p. 184°) and **N,N-dimethylacetamide** (b.p. 195°) are unsatisfactory.

13. The checkers found it impossible to prevent water from dropping into the hot mixture and leading to its eruption through the top of the condenser. They found it convenient to eliminate the small condenser and use only a normal condenser where the prolonged reflux period is needed.

14. The yield was not improved by use of anhydrous material (Note 10).

15. Solid adhering to the walls of the flask can be dislodged by loosening the clamp supporting the flask and using the condenser as a lever to swirl the flask.

16. The double melting point has been observed in only one<sup>5</sup> of the previous studies. The initial melting point varies with the state of subdivision and is not a reliable index of purity. Several recrystallizations did not change the melting behavior or the remelt temperature. The checkers did not observe the double melting point with the product initially obtained, but did so with material recrystallized once.

### 3. Discussion

**1,2,3,4-Tetraphenylnaphthalene** has been isolated by Wittig and co-workers by generation of **benzyne** in the presence of excess **tetraphenylcyclopentadienone** as trapping agent. Yields of hydrocarbon isolated by chromatography and based upon the precursor are as follows: from ***o*-fluorobromobenzene**, 17%;<sup>6</sup> from either ***o*-iodophenylmercuric iodide** or **bis-(*o*-iodophenyl)-mercury**, 25%.<sup>7</sup> The hydrocarbon has also been obtained in low yield as one of two products resulting from the reaction of **diphenylacetylene** with **triphenylchromium**.<sup>5</sup> The present method is due to Le Goff,<sup>4</sup> who reports a 68% yield of hydrocarbon from **diphenyliodonium-2-carboxylate**. However, this investigator states in a private communication that he refluxed the **benzyne** precursor with a large excess of **tetraphenylcyclopentadienone** in **diethylene glycol dimethyl ether** and isolated the hydrocarbon by tedious **hexane** extraction and chromatography. In the experience of the submitters the solvent selected has too low a boiling point (161°) for efficient conversion.

### 4. Merits of the Preparation

The procedure demonstrates a safe and simple method for the generation of **benzyne** from a stable and easily prepared precursor and its use in the synthesis of a hitherto difficulty accessible hydrocarbon.

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### References and Notes

1. Department of Chemistry, Harvard University, Cambridge 38, Massachusetts.
2. J. R. Johnson and O. Grummitt, *Org. Syntheses, Coll. Vol. 3*, 806 (1955).
3. F. M. Beringer and I. Lillien, *J. Am. Chem. Soc.*, **82**, 725 (1960).
4. E. Le Goff, *J. Am. Chem. Soc.*, **84**, 3786 (1962).
5. H. Herwig, W. Metlesics, and H. H. Zeiss, *J. Am. Chem. Soc.*, **81**, 6203 (1959).
6. G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

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

potassium bisulfate salt of diphenyliodonium-2-carboxylic acid

ethanol (64-17-5)

sulfuric acid (7664-93-9)

Benzene,  
benzyne (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

acetone (67-64-1)

Norit (7782-42-5)

ammonium hydroxide (1336-21-6)

Iodobenzene (591-50-4)

o-iodobenzoic acid (88-67-5)

methylene chloride (75-09-2)

potassium persulfate (7727-21-1)

dioxane (123-91-1)

Diphenylacetylene (501-65-5)

hexane (110-54-3)

Tetraphenylcyclopentadienone (479-33-4)

diethyl oxalate (95-92-1)

diethylene glycol dimethyl ether (111-96-6)

diphenyliodonium-2-carboxylate,  
diphenyliodonium carboxylate (1488-42-2)

o-fluorobromobenzene (1072-85-1)

1,2,3,4-Tetraphenylnaphthalene,  
Naphthalene, 1,2,3,4-tetraphenyl- (751-38-2)

diphenyliodonium-2-carboxylate monohydrate,  
diphenyliodonium carboxylate monohydrate

diethylbenzene (135-01-3)

trimethylene glycol dimethyl ether (17081-21-9)

N,N-dimethylacetamide (127-19-5)

triphenylchromium

o-dichlorobenzene (95-50-1)

o-iodophenylmercuric iodide

bis-(o-iodophenyl)-mercury

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