



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](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.

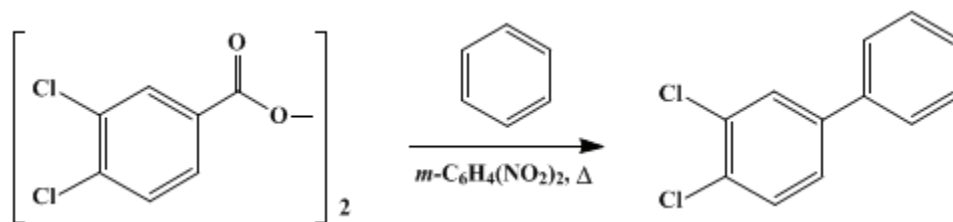
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## ARYLBENZENES: 3,4-DICHLOROBIPHENYL

### [Biphenyl, 3,4-dichloro-]



Submitted by D. H. Hey and M. J. Perkins<sup>1</sup>.

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### 1. Procedure

Thirty-eight grams (0.1 mole) of bis-3,4-dichlorobenzoyl peroxide (Note 1) is added to a boiling solution of 3 g. of *m*-dinitro-benzene in 800 ml. of dry reagent grade benzene contained in a 1-l. round-bottomed flask, and the resulting solution is boiled under reflux for 40 hours. The solvent is then distilled from the red solution until the residual volume is about 200 ml. (Note 2), and the mixture is allowed to cool. The 3,4-dichlorobenzoic acid which separates is removed by suction filtration, washed with a little cold benzene, and then with 100 ml. of petroleum ether (b.p. 80–100°). The combined filtrate and washings are further concentrated by distillation (Note 2) to about 60 ml., cooled, and a small second crop of 3,4-dichlorobenzoic acid is removed and washed with a little benzene followed by a little petroleum ether. The total yield of acid, m.p. 208–210° (Lit.<sup>2</sup> m.p. 208–209°), is 18.2 g. (95%) (Note 3). The filtrate and washings are combined (Note 4) and chromatographed on a column of basic alumina (30 cm. x 3.5 cm.) which is eluted with petroleum ether (b.p. 40–60°). Solvent is distilled from the eluate (Note 5), and the residual crude 3,4-dichlorobiphenyl is distilled under reduced pressure using a short air condenser and a receiver chilled in ice. There is obtained 17.3–18.0 g. (78–81%) of almost pure 3,4-dichlorobiphenyl (b.p. 146–150° at 2 mm.) which sets to a colorless solid, m.p. 44–47° (Note 6).

### 2. Notes

1. The bis-3,4-dichlorobenzoyl peroxide may be prepared as follows.<sup>3,4</sup> To a 2-l. beaker containing 400 ml. of water which is cooled to 0–5° in an ice bath is added slowly 40 g. (0.51 mole) of sodium peroxide. A dropping funnel containing 167.6 g. (0.8 mole) of 3,4-dichlorobenzoyl chloride in 400 ml. of dry toluene is supported over the beaker. The peroxide solution is cooled and stirred vigorously while the toluene solution is added drop-wise over a 1-hour period. The solution is stirred for an additional 2 hours. The precipitate is filtered using a suction funnel, washed with 600 ml. of cold water, and dried in air overnight. There is obtained 114 g. (75%) of bis-3,4-dichlorobenzoyl peroxide, m.p. 135° dec. The crude product is purified by dissolving it in chloroform and precipitating by the addition of methanol, m.p. 139° dec.
2. Solvent removal may conveniently be carried out with a rotary evaporator to obviate bumping caused by separation of the dichlorobenzoic acid from the boiling solution.
3. In syntheses of other arylbenzenes, in which the acid by-product is more soluble, it may be extracted from the reaction mixture with aqueous sodium bicarbonate or removed in the subsequent chromatography.
4. At this point the solvent is largely petroleum ether. Appreciable quantities of benzene in the mixture to be chromatographed tend to carry some of the dinitrobenzene through the alumina.
5. After removal of the solvent from the eluate, almost pure white 3,4-dichlorobiphenyl crystallizes, m.p. 44–48°. It may be purified by recrystallization from methanol as an alternative to vacuum distillation.
6. The product may be freed from a trace (≈1%) of biphenyl present as an impurity by recrystallization

from [methanol](#) which raises the melting point to 47–48°. The literature values range from 46<sup>5</sup> to 49–50°. <sup>6</sup>

### 3. Discussion

3,4-Dichlorobiphenyl has been prepared by the arylation of [benzene](#) using the Gomberg procedure starting with [3,4-dichloroaniline](#),<sup>5</sup> and using the acid-catalyzed decomposition of [1-\(3,4-dichlorophenyl\)-3,3-dimethyltriazene](#) in [benzene](#).<sup>6</sup> The arylation procedure given above, which utilizes a diaryl peroxide as the aryl radical source, provides a route arylbenzenes which involves simple operations and gives a good yield of pure product. In the absence of the nitro compound, the mode of action of which has been discussed in terms of two somewhat different mechanisms,<sup>7,8</sup> the yields of aronic acids and arylbenzenes are commonly below 50%,<sup>9</sup> and the arylbenzene may be contaminated with aryldihydrobenzenes.<sup>10</sup> The present procedure has been used to prepare a variety of simple arylbenzenes in isolated yields ranging from 70 to 90%. If a nitro substituent is present in the peroxide, high yields are obtained without the addition of further nitro compound.<sup>9</sup>

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### References and Notes

1. Department of Chemistry, King's College, University of London.
2. G. M. Kraay, *Rec. Trav. Chim.*, **49**, 1083 (1930).
3. A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York, 1954, p. 38.
4. A. I. Vogel, "Practical Organic Chemistry," 3rd. ed., Longmans, London, 1956, p. 808.
5. H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, 557 (1926).
6. U. S. Patent 2,280,504 (1942) [*Chem. Abstr.*, **36**, 5658 (1942)]; Ger. Patent 870,106 (1953) [*Chem. Abstr.*, **50**, 16863 (1956)].
7. G. B. Gill and G. H. Williams, *J. Chem. Soc.*, B, 880 (1966).
8. G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *J. Chem. Soc.*, (B), 233 (1971).
9. K. H. Pausacker, *Australian J. Chem.*, **10**, 49 (1957).
10. D. F. DeTar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

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### Appendix

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

petroleum ether

[Benzene](#) (71-43-2)

[methanol](#) (67-56-1)

[chloroform](#) (67-66-3)

[sodium bicarbonate](#) (144-55-8)

[toluene](#) (108-88-3)

[Biphenyl](#) (92-52-4)

[sodium peroxide](#)

3,4-Dichlorobiphenyl,  
Biphenyl, 3,4-dichloro- (2974-92-7)

bis-3,4-dichlorobenzoyl peroxide

3,4-dichlorobenzoic acid (51-44-5)

3,4-dichlorobenzoyl chloride (3024-72-4)

dichlorobenzoic acid (50-45-3)

dinitrobenzene (528-29-0)

3,4-dichloroaniline (95-76-1)

1-(3,4-dichlorophenyl)-3,3-dimethyltriazene

m-dinitro-benzene (99-65-0)