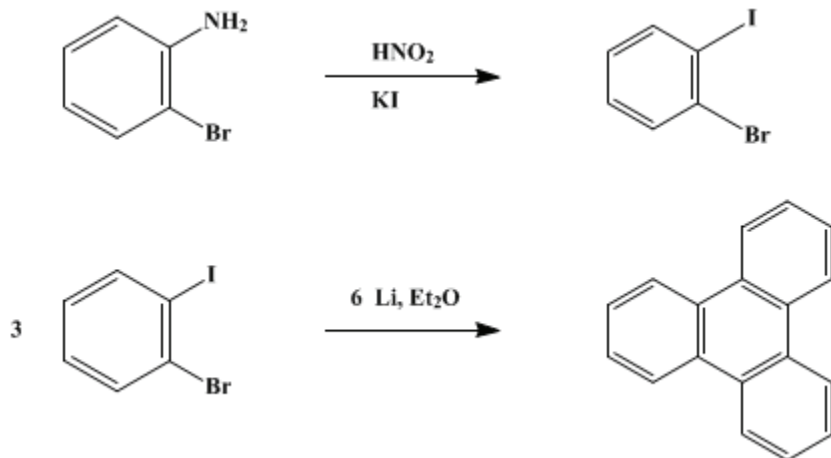


TRIPHENYLENE



Submitted by H. Heaney and I. T. Millar¹.
Checked by John D. Roberts and L. K. Montgomery.

1. Procedure

(Note 1)

In a 600-ml. beaker fitted with a thermometer and mechanical stirrer are placed 150 ml. of concentrated hydrochloric acid and 55 g. (0.32 mole) of *o*-bromoaniline. After brief stirring, 100 g. of ice is added and the beaker is surrounded by an ice-salt bath. The solution is then diazotized by the dropwise addition with stirring of a solution of 24.3 g. (0.35 mole) of sodium nitrite in 100 ml. of water, the temperature being kept at 0–5°.

After stirring the diazotized solution for 15 minutes, it is slowly poured through a glass-wool filter into a solution of 180 g. (3.4 moles) of potassium iodide in 600 ml. of water. After standing overnight, the heavy dark oil is separated, washed successively with 10% aqueous sodium hydroxide, water, 5% aqueous sodium bisulfite and water, and then dried over magnesium sulfate.

Distillation under reduced pressure gives *o*-bromoiodobenzene as a nearly colorless liquid, b.p. 120–121° at 15 mm. Yield 65–75 g. (72–83%).

A 1-l. flask is fitted with a reflux condenser, dropping funnel, and a sealed mechanical stirrer. A nitrogen atmosphere is maintained in the flask during the entire reaction period.

In the flask is placed 150 ml. of anhydrous ether, and 5.7 g. (4.1 atomic equivalents) of lithium foil is then added (Note 2). A solution of 56.6 g. (0.2 mole) of *o*-bromoiodobenzene in 300 ml. of anhydrous ether is added dropwise (Note 3). When a vigorous reaction commences, the stirrer is started and the flask is cooled in ice water to maintain the temperature at about 10°. The reflux condenser is replaced by a thermometer, and the remainder of the *o*-bromoiodobenzene solution is added at a rate such that the temperature in the flask remains at about 10° (about 1.5 hours). When this addition is complete, 200 ml. of dry benzene is added; the mixture is stirred at 10° for 1 hour and finally at room temperature for 1 hour. The mixture is then poured through a glass-wool filter on 200 g. of ice.

The organic layer is separated, evaporated on a steam bath, and the dark semicrystalline residue is distilled with steam to remove biphenyl. The contents of the steam-distillation flask are then extracted with ether (Note 4), and the ethereal layer is separated, dried over magnesium sulfate, and percolated through a short column of chromatographic alumina (Note 5) and (Note 6). Evaporation of the ethereal solution gives crude triphenylene which is sublimed at 175–180° and 0.1 mm. pressure. After rejection of an initial sublimate of impure biphenyl, the sublimed material forms nearly colorless crystals, m.p. 186–194° (Note 7). Yield 8–9 g. (53–59%). It may be further purified by recrystallization from a

mixture of methylene chloride and pentane yielding colorless crystals, m.p. 199° (Note 8).

2. Notes

1. Although the procedure described here is still a useful method of preparing triphenylene, it is in the opinion of the submitters no longer the best available. In their opinion a more nearly pure product and a higher yield (85%) may be obtained by the reaction of *o*-bromofluorobenzene and magnesium in tetrahydrofuran² (private communication from H. Heaney).
 2. Slugs of lithium, coated with paraffin oil, are hammered into thin foil. They are washed free of oil with dry ether and cut by scissors into slips which are allowed to fall directly into the ether in the reaction flask.
 3. By adding 10–20 ml. of the *o*-bromiodobenzene solution to the metal before stirring is started, high local concentrations of the dihalo compound which initiate reaction are built up. An induction period of about 10 minutes is usually observed before the vigorous reaction commences.
 4. The checkers found that, in view of the limited solubility of triphenylene in ether (about 1 g. per 100 ml.), care must be exercised in the extraction to ensure that all the product is removed.
 5. The volume of ether solution must be reduced to approach the solubility limit of the triphenylene in ether before the chromatographic procedure.
 6. The checkers used a 30-mm. (I.D.) chromatographic column charged with approximately 250 g. of activated (400° for 12 hours), acid-washed, chromatographic aluminum oxide (Merck and Co., Inc.).
 7. The contaminant in the product of m.p. 186–194° is present in low concentration and is very probably *o*-terphenyl. It is characterized by an absorption near 695 cm.⁻¹ in the infrared which is absent in the spectrum of pure triphenylene.
- The submitters report that the purity of the product is rather dependent upon the purity of the lithium used and that results can vary from batch to batch. In addition, they state that side reactions may be catalyzed by traces of heavy metals, that the degree of vigor in the initial reaction may influence the purity of the product owing to local overheating, and that increase in scale of this reaction is deleterious.
8. The checkers carried out this recrystallization by dissolving triphenylene in a minimum of methylene chloride maintained at reflux. Pentane was slowly added to this solution; up to 90% recovery was achieved.

3. Discussion

Triphenylene has been prepared by self-condensation of cyclohexanone using sulfuric acid³ or polyphosphoric acid⁴ followed by dehydrogenation of the product, dodecahydrotriphenylene, using copper,³ palladium-charcoal,⁴ or selenium;⁵ by electrolytic oxidation of cyclohexanone;⁶ from chlorobenzene and sodium⁷ or phenyllithium;⁸ from 2-cyclohexyl-1-phenylcyclohexanol⁹ or 2-(1-cyclohexene-1-yl)-1-phenylcyclohexanol^{4,10} by dehydrogenation; from 9-phenanthryl magnesium bromide and succinic anhydride followed by reduction, cyclization, and dehydrogenation;¹¹ by the action of lithium on *o*-diiodobenzene¹² or magnesium on *o*-bromofluorobenzene,² and by the dehydrogenation of *o*-terphenyl.¹³

References and Notes

1. University College of North Staffordshire, Keele, Staffordshire, England.
2. K. D. Bartle, H. Heaney, D. W. Jones, and P. Lees, *Tetrahedron*, **21**, 3289 (1965).
3. C. Mannich, *Ber.*, **40**, 153 (1907).
4. P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, 4479 (1955); see also J. Plesek and P. Munk, *Chem. Listy*, **51**, 980 (1957), and C. C. Barker, R. G. Emmerson, and J. D. Periam, *J. Chem. Soc.*, 1077 (1958).
5. O. Diels and A. Karstens, *Ber.*, **60**, 2323 (1927).
6. F. Pirrone, *Gazz. Chim. Ital.*, **66**, 244 (1936).
7. W. E. Bachmann and H. T. Clarke, *J. Am. Chem. Soc.*, **49**, 2089 (1927).
8. G. Wittig and W. Merkle, *Ber.*, **75**, 1493 (1942).
9. C. D. Nenitzescu and D. Curcaneanu, *Ber.*, **70**, 346 (1937).

10. W. S. Rapson, *J. Chem. Soc.*, **15** (1941).
 11. E. Bergmann and O. Blum-Bergmann, *J. Am. Chem. Soc.*, **59**, 1441 (1937).
 12. H. Heaney, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, **1** (1956).
 13. P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.*, **1687** (1960).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

polyphosphoric acid

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

Cyclohexanone (108-94-1)

potassium iodide (7681-11-0)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

sodium bisulfite (7631-90-5)

copper (7440-50-8)

chlorobenzene (108-90-7)

sodium (13966-32-0)

palladium (7440-05-3)

Biphenyl (92-52-4)

Pentane (109-66-0)

methylene chloride (75-09-2)

Phenyllithium (591-51-5)

lithium (7439-93-2)
magnesium sulfate (7487-88-9)
Succinic anhydride (108-30-5)
selenium
aluminum oxide (1344-28-1)
Tetrahydrofuran (109-99-9)
9-phenanthryl magnesium bromide
o-terphenyl (84-15-1)
o-bromofluorobenzene (1072-85-1)
Triphenylene (217-59-4)
dodecahydrotriphenylene
2-cyclohexyl-1-phenylcyclohexanol
2-(1-cyclohexene-1-yl)-1-phenylcyclohexanol
o-bromoaniline (615-36-1)
o-bromiodobenzene (583-55-1)
o-diiodobenzene (615-42-9)