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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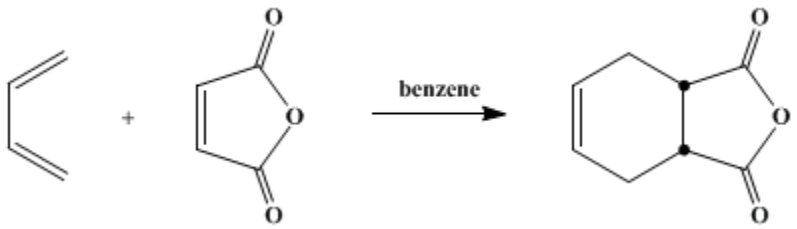
Organic Syntheses, Coll. Vol. 4, p.890 (1963); Vol. 30, p.93 (1950).

cis-Δ^4-TETRAHYDROPHTHALIC ANHYDRIDE

[4-Cyclohexene-1,2-dicarboxylic anhydride, *cis*-]



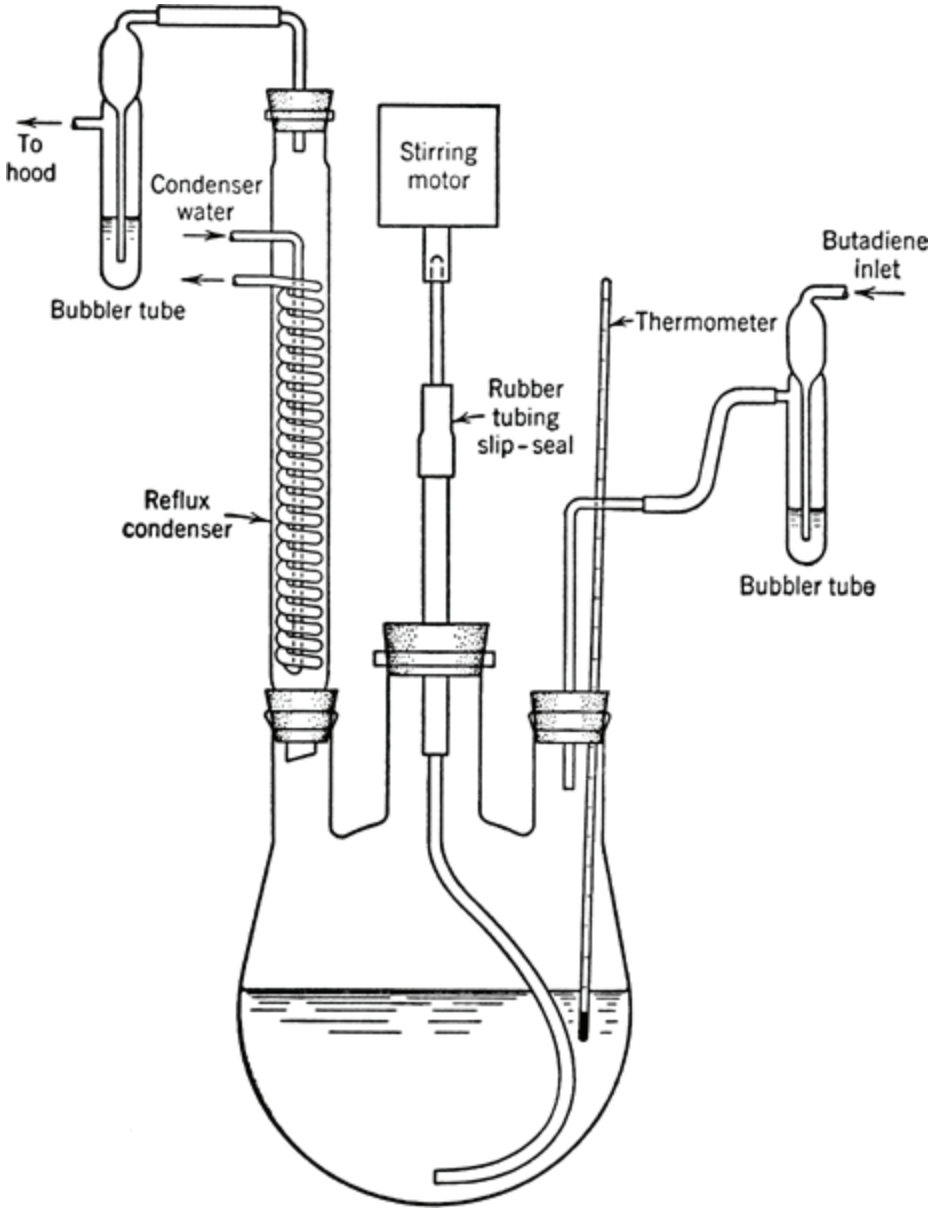
Submitted by Arthur C. Cope and Elbert C. Herrick[1].
Checked by Charles C. Price, Kenneth N. Campbell, and Robert P. Kane.

1. Procedure

The apparatus shown in Fig. 16, consisting of a 2-l. three-necked round-bottomed flask fitted with an efficient stirrer (Note 1), a gas-inlet tube, a thermometer, and a reflux condenser, is assembled in a ventilated hood. Bubbler tubes containing benzene are attached to the gas inlet tube and the top of the reflux condenser, and 500 ml. of dry benzene and 196 g. (2 moles) of maleic anhydride (Note 2) are placed in the flask. Stirring is begun, the flask is heated with a pan of hot water, and butadiene is introduced (from a commercial cylinder controlled by a needle valve) at a rapid rate (0.6–0.8 l. per minute). When the temperature of the solution has reached 50° (within 3–5 minutes) the pan of water is removed. The exothermic reaction causes the temperature to reach 70–75° in 15–25 minutes. The rapid stream of butadiene is nearly completely absorbed for 30–40 minutes, after which the rate is decreased until the reaction is completed (equal rates of bubbling in the two bubbler tubes) after 2–2.5 hours. The solution is poured into a 1-l. beaker at once to avoid crystallization of the product in the reaction flask. The beaker is covered and the mixture is kept at 0–5° overnight.

The product is collected on a large Büchner funnel and washed with 250 ml. of 35–60° petroleum ether. A second crop (5–15 g.) obtained by diluting the filtrate with an additional 250 ml. of petroleum ether is separated by filtration, combined with the first crop in a large crystallizing dish, and dried to constant weight (1–2 hours) in an oven at 70–80°. The yield of *cis*-Δ^4-tetrahydrophthalic anhydride is 281.5–294.5 g. (93–97%), m.p. 99–102° (Note 3).

Fig. 16. Assembly of apparatus for addition of butadiene to maleic anhydride.



2. Notes

1. Any stirrer that produces sufficiently vigorous agitation to disperse the gas through the liquid is satisfactory. It was found to be unnecessary to introduce the gas below the surface of the liquid.
2. A good grade of commercial maleic anhydride was used, m.p. 52–54°.
3. The product is analytically pure and suitable for use in preparing diethyl *cis*-Δ^4-tetrahydrophthalate (p. 304). Recrystallization from ligroin[2] or ether[3] raises the m.p. to 103–104°.

3. Discussion

cis-Δ^4-Tetrahydrophthalic anhydride has been prepared by the reaction of maleic anhydride and butadiene.[2,3,4,5,6] The procedure described is adapted from the one used by Kohler and Jansen.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 157
- Org. Syn. Coll. Vol. 4, 304

References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
2. Diels and Alder, *Ann.*, **460**, 113 (1928).
3. Jenkins and Costello, *J. Am. Chem. Soc.*, **68**, 2733 (1946).
4. Farmer and Warren, *J. Chem. Soc.*, **1929**, 903.
5. Kohler and Jansen, *J. Am. Chem. Soc.*, **60**, 2144 (1938); Cope and Herrick, *J. Am. Chem. Soc.*, **72**, 983 (1950).
6. Fieser and Novello, *J. Am. Chem. Soc.*, **64**, 806 (1942).

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

ligroin

petroleum ether

Diethyl cis-Δ^4-tetrahydrophthalate

cis-Δ^4-Tetrahydrophthalic anhydride

Benzene (71-43-2)

butadiene (106-99-0)

maleic anhydride (108-31-6)

4-Cyclohexene-1,2-dicarboxylic anhydride, cis- (935-79-5)