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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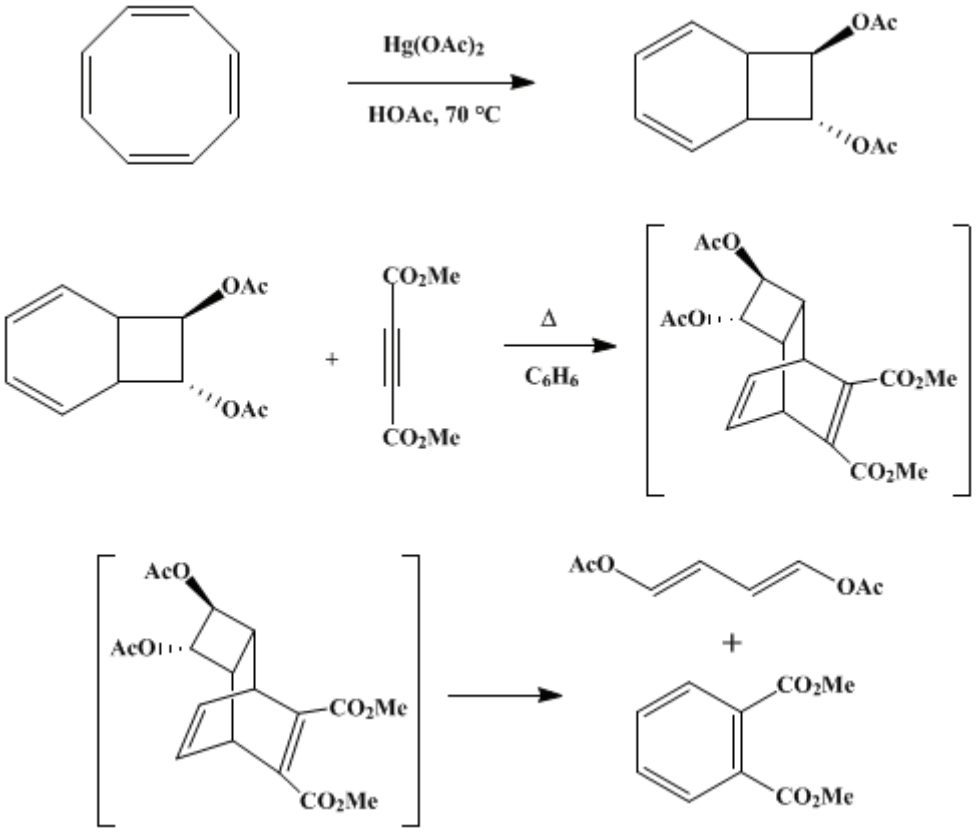
trans,trans-1,3-BUTADIENE-1,4-DIYL DIACETATE

[1,3-Butadiene-1,4-diol, diacetate, *E,E*-]



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1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A. trans-7,8-*Diacetoxybicyclo*[4.2.0]*octa*-2,4-*diene*. A 1-l., three-necked flask fitted with a reflux condenser, an efficient stirrer, and a thermometer dipping well into the solution is charged with a suspension of mercury(II) acetate (Note 1) (160 g., 0.502 mole) in glacial acetic acid (400 ml). While the suspension is stirred, 52.0 g. of cycloöctatetraene (0.500 mole) (Note 2) is added rapidly. The white addition compound that separates after 10–15 minutes is decomposed by careful heating of the reaction mixture at 70–75° for 2 hours (Note 3). While still warm, the mixture is poured through funnels containing glass wool plugs into two, 4-l. beakers, each containing 2 l. of water (Note 4). The mixture is allowed to stand for several hours, and the solid that separates is collected on a Büchner funnel and pressed as dry as possible on the funnel. The moist, yellow solid is spread out on a large piece of filter paper and allowed to dry overnight, yielding 83–86 g. (75–77.5%) of *trans*-7,8-diacetoxybicyclo[4.2.0] octa-2,4-diene, m.p. 52–55° (Note 5); it may be used in the next step without further purification (Note 6).

B. trans,trans-1,3-*Butadiene*-1,4-*diyl diacetate*. A solution of the diacetate (83.0 g., 0.373 mole) and

dimethyl acetylenedicarboxylate [*Org. Synth.*, **Coll. Vol. 4**, 329 (1963); 54.0 g., 0.380 mole] in benzene (250 ml.) is placed in a 500-ml. flask and refluxed for 6 hours (Note 7). The solution is filtered to remove the remaining mercury and mercury salts, and the benzene is distilled under reduced pressure. The residual viscous yellow oil is distilled under reduced pressure (Note 8). A mixture of 1,3-butadiene-1,4-diyl diacetate and dimethyl phthalate is collected at 140–155° (18–20 mm.), bath temperature 170–200°, from which the diene crystallizes as colorless needles in the cooled receiver. The solid is broken up, washed onto a Büchner funnel with petroleum ether (b.p. 60–70°), pressed between sheets of filter paper to remove excess dimethyl phthalate, and recrystallized from *ca.* 1:2 acetone–petroleum ether (b.p. 60–70°) (Note 9), yielding 26–31 g. (41–49%) of *trans,trans*-1,3-butadiene-1,4-diyl diacetate, as colorless needles, m.p. 102–104° (Note 10),(Note 11), and (Note 12).

2. Notes

1. "Baker analyzed" mercury(II) acetate was used as obtained from J. T. Baker Chemical Company.
2. Cycloöctatetraene was used as obtained from Badische Anilin- und Soda-Fabrik, 67 Ludwigshafen, Rhein, Germany.
3. Temperatures in excess of 75° cause darkening of the reaction mixture. The submitters found that adequate temperature control could be maintained with a Bunsen flame; the checkers used a heating mantle.
4. This operation should be carried out in a well-ventilated hood. Scratching the sides of the beakers at the surface of the water promotes crystallization. The beakers are stirred occasionally to promote rapid crystallization and to minimize the formation of a solid cake on the bottom.
5. The checkers obtained 92–93 g. (83–84%); m.p. 58–61°.
6. Melting points of 61–62°, 61.4–62.5°, 64–65°, and 66° have been reported.[3,4,5] The diacetate may be recrystallized from aqueous acetic acid,[3,4,5] ligroin,[3] or ethanol.[4]
7. A longer reflux period, *e.g.*, overnight, did not affect the yield.
8. The submitters used a 500-ml. distilling flask with a 250-ml. distilling flask as receiver. The side arm of the distilling flask was extended, if necessary, with a Tygon joint into the bulb of the receiver. The receiver was cooled with a stream of cold water. The distillation was continued until about three-fourths of the material in the flask had distilled. The checkers used standard-taper glassware for the distillation and found it necessary to heat the distillation adapter with a microburner from time to time in order to prevent plugging by solidified product. They continued the distillation until no further solid product distilled.
9. The checkers found that it was essential to conduct the recrystallization rapidly in order to obtain maximum yields.
10. The checkers obtained a yield of 40.8 g. (64%) when distillation of the product mixture was continued until no additional solid product distilled (*cf.* (Note 8) and (Note 9)).
11. A satisfactory alternative to recrystallization of the diene is the following. The crude solid is placed in a 100-ml. beaker containing 40–50 ml. of a 15% solution of acetone in petroleum ether (b.p. 60–70°). The lumps are broken up, and the colorless solid is filtered from the pale-yellow solution. A final wash with 20 ml. of ice-cold acetone leaves 31–32 g. of diene, m.p. 99–102°, pure enough for many purposes.
12. The IR and UV spectra of the product have been reported.[6]

3. Discussion

This method is essentially that described by Reppe, Schlichting, Klager, and Toepel,[3] although the correct structures were assigned by others.[4,7] 7,8-Diacetoxybicyclo[4.2.0]octa-2,4-diene has also been prepared by oxidation of cycloöctatetraene with lead tetraäcetate,[5] and by chlorination of cycloöctatetraene with sulfuryl chloride followed by displacement with potassium acetate.[3,7] The two other geometric isomers of the diene have been prepared by another method.[6] *trans,trans*-1,3-Butadiene-1,4-diyl diacetate is a reactive diene in the Diels-Alder reaction. It has been used as the starting material in stereospecific syntheses of conduritol-D[8] and shikimic acid,[9,10] and in simple, general methods of preparation of benzene derivatives, especially unsymmetrical biphenyls.[11,12]

References and Notes

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

ligroin

petroleum ether

conduritol-D

ethanol (64-17-5)

acetic acid (64-19-7)

Benzene (71-43-2)

mercury(II) acetate (1600-27-7)

mercury (7439-97-6)

acetone (67-64-1)

sulfuryl chloride (7791-25-5)

potassium acetate (127-08-2)

Dimethyl acetylenedicarboxylate (762-42-5)

1,3-butadiene-1,4-diyl diacetate

dimethyl phthalate (131-11-3)

7,8-Diacetoxybicyclo[4.2.0]octa-2,4-diene

shikimic acid

cyclooctatetraene

trans,trans-1,3-BUTADIENE-1,4-DIYL DIACETATE

1,3-Butadiene-1,4-diol, diacetate, E,E- (15910-11-9)

trans-7,8-Diacetoxybicyclo[4.2.0]octa-2,4-diene (42301-50-8)

lead tetraacetate (546-67-8)