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.

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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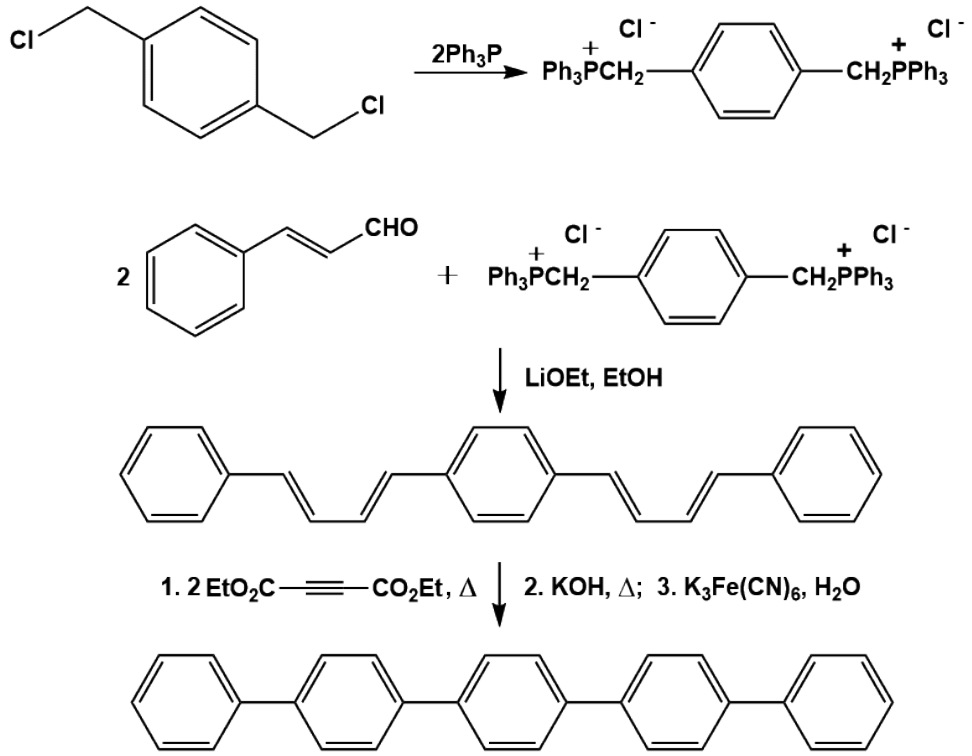
p-QUINQUEPHENYL



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Checked by Virgil Boekelheide and Richard E. Partch.

1. Procedure

A. *p-Xylylene-bis(triphenylphosphonium chloride)*. A mixture of 262 g. (1.0 mole) of triphenylphosphine (Note 1) and 84 g. (0.48 mole) of *p*-xylylene dichloride (Note 2) in 1 l. of dimethyl formamide is heated at reflux with stirring for 3 hours (Note 3). The mixture is then allowed to cool to room temperature with stirring, and the white crystalline solid is collected, washed with 100 ml. of dimethylformamide followed by 300 ml. of ether, and dried in a vacuum oven at 20 mm. pressure and 80°. The dry weight is 313–329 g. (93–98%).

B. *1,4-Bis-(4-phenylbutadienyl)benzene*. To a solution of 70 g. (0.10 mole) of *p*-xylylene-bis (triphenylphosphonium chloride) and 35 g. (0.26 mole) of cinnamaldehyde in 250 ml. of ethanol (Note 4) is added a solution of 0.25*M* lithium ethoxide in ethanol (Note 5). After being allowed to stand overnight at room temperature the yellow solid is collected by filtration, washed with 300 ml. of 60% ethanol, and dried in a vacuum oven at 20 mm. and 70°. The dry weight is 29–32 g. (87–95%). The solid is then dissolved in the minimum amount (about 2 l.) of boiling xylene, treated with decolorizing charcoal, and filtered. The filtrate is reduced in volume to about 1.2 l. and digested at the boiling point with a trace of iodine for 3 hours (Note 6). After the solution has stood overnight at room temperature, the yellow plates are collected by filtration, washed with benzene, and dried in a vacuum oven at 20 mm. pressure at 70°. The weight of crystals, m.p. 285–287° (Note 7), is 23–25 g. (69–75%).

C. *p-Quinquephenyl*. A mixture of 3.40 g. (0.020 mole) of diethyl acetylenedicarboxylate[2] and 3.34 g. (0.010 mole) of 1,4-bis-(4-phenylbutadienyl)benzene is refluxed with 20 ml. of *o*-dichlorobenzene for 3 hours. It is allowed to cool to about 80°, then 100 ml. of ethanol and 5 g. of potassium hydroxide are added, and the mixture is refluxed for about 2 hours. The solvent is evaporated on a steam bath under a nitrogen atmosphere (Note 8), and the damp solid is extracted with 200 ml. of water. The intense yellow or yellow-orange aqueous layer is filtered, then extracted twice with 75-ml. portions of ether, charcoal is

added and then filtered to separate water-insoluble matter. The filtrate is just neutralized with dilute hydrochloric acid (Note 9) and then made basic with 5 g. of sodium carbonate. To this is added a solution of 30 g. of potassium ferricyanide in 200 ml. of water. The mixture rapidly becomes milky and is allowed to stand overnight (Note 10). The suspended solid is centrifuged and washed with water twice by centrifugation. It is dried in a vacuum oven to give 3.1–4.2 g. of a green-tinged solid (Note 11). The combined material from five runs (18 g.) is sublimed to give 10 g. (52%) of pure quinquephenyl, m.p. 385–390°. This can be recrystallized from dimethylsulfoxide to give well-defined leaflets.

2. Notes

1. Commercial triphenylphosphine was used without further purification.
2. A sample of this compound was obtained from Hooker Electrochemical Co. and used without further purification.
3. The salt begins to precipitate after about 30 minutes.
4. Commercial anhydrous ethanol was used throughout.
5. Prepared by dissolving 1.74 g. of lithium wire in 1 1. of ethanol.
6. After the volume is reduced, a small crystal of iodine is added whereupon large yellow leaflets of product begin to separate.
7. The product can be recrystallized readily from dimethylformamide to give yellow leaflets, m.p. 290–293°. However, it is pure enough to be used in the next step. This synthesis has also been applied to the preparation of 1,4-bis-[4-(*p*-tolyl)butadienyl]benzene (100%), 1,4-bis-[4-(3-nitrophenyl)butadienyl]-benzene (56%), and 1,4-bis-(3-methyl-4-phenylbutadienyl)benzene (87%).
8. Nitrogen is used both for rapid removal of the solvent and to maintain an inert atmosphere.
9. The acid is added slowly with stirring until a trace of permanent precipitate is formed.
10. All the steps to this point can be completed in 1 day.
11. This procedure has been applied to the synthesis of 4,4"" dimethylquinquephenyl and 2',3'"-dimethylquinquephenyl from 1,4-bis-[4-(*p*-tolyl)butadienyl]benzene and 1,4-bis-(3-methyl-4-phenylbutadienyl)benzene, respectively.

3. Discussion

1,4-Bis-(4-phenylbutadienyl)benzene has been obtained by condensation of cinnamaldehyde and *p*-phenylenediacetic acid with lead oxide.[3] *p*-Quinquephenyl has been prepared by the reaction of biphenyllithium with 1,4-cyclohexanedione, followed by dehydration and air oxidation of the dihydroquinquephenyl;[4] by the Gatterman coupling reaction of benzenediazonium formate with copper;[5] by the Ullmann coupling of 4-iodoterphenyl and 4-iodobiphenyl with silver;[5] by the catalytic reduction of *p*-di-bromobenzene;[6] and the Friedel-Crafts reaction of cyclohexene with terphenyl followed by dehydrogenation.[7] The procedure described represents the best route to both the 1,4-bis-(4-arylbutadienyl)benzenes and quinquephenyls that has been reported.[8] The details of the oxidative decarboxylation step for reactions of the type described here have been established by Fieser and Haddadin.[9]

References and Notes

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

Cyclohexene (110-83-8)

lead oxide

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

copper (7440-50-8)

iodine (7553-56-2)

potassium hydroxide (1310-58-3)

xylene (106-42-3)

cinnamaldehyde

silver (7440-22-4)

potassium ferricyanide (13746-66-2)

Lithium wire (7439-93-2)

dimethylformamide,
dimethyl formamide (68-12-2)

dimethylsulfoxide (67-68-5)

1,4-Bis-(4-phenylbutadienyl)benzene (10162-88-6)

quinquephenyl

1,4-bis-[4-(3-nitrophenyl)butadienyl]-benzene

1,4-bis-(3-methyl-4-phenylbutadienyl)benzene

biphenyllithium

dihydroquinquephenyl

benzenediazonium formate

4-iodoterphenyl

terphenyl (84-15-1)

diethyl acetylenedicarboxylate (762-21-0)

triphenylphosphine (603-35-0)

1,4-Cyclohexanedione (637-88-7)

lithium ethoxide

4-iodobiphenyl (1591-31-7)

o-dichlorobenzene (95-50-1)

p-di-bromobenzene (106-37-6)

p-phenylenediacetic acid (7325-46-4)

4,4"" dimethylquinquephenyl

2',3'"-dimethylquinquephenyl

p-Quinquephenyl (3073-05-0)

p-Xylylene-bis(triphenylphosphonium chloride) (1519-47-7)

p-xylylene dichloride (623-25-6)

1,4-bis-[4-(p-tolyl)butadienyl]benzene