



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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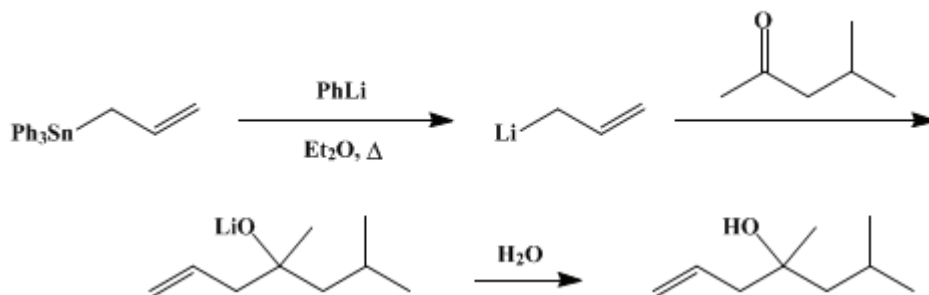
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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4,6-DIMETHYL-1-HEPTEN-4-OL

[1-Hepten-4-ol, 4,6-dimethyl-]



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1. Procedure

Caution! See p. 976.

A solution of 50 g (0.127 mole) of allyltriphenyltin (Note 1) and (Note 2) in 200 ml. of diethyl ether (Note 3) is prepared in a 1-l. three-necked flask fitted with a reflux condenser, a motor-driven glass sleeve-type stirrer, nitrogen-inlet tube, and a 250-ml. dropping funnel with pressure-equalizing side arm. After the system has been flushed thoroughly with prepurified nitrogen, 113 ml. of a 1.13*N* solution of phenyllithium (0.127 mole) in diethyl ether (Note 4) is added rapidly to the stirred allyltriphenyltin solution. Precipitation of tetraphenyltin occurs immediately, and the reaction mixture is stirred for 30 minutes in an atmosphere of prepurified nitrogen. Through the dropping funnel is then added 12.0 g. (0.12 mole) of 4-methyl-2-pentanone (Note 5) in 25 ml. of diethyl ether at such a rate that moderate reflux is maintained. Subsequently the reaction mixture is refluxed for 1 hour, allowed to cool to room temperature, and hydrolyzed by adding 100 ml. of distilled water (Note 6). The solid tetraphenyltin is filtered (53.5 g. = 98% yield), and the filtrate is transferred to a separatory funnel. The aqueous layer is separated and extracted with three 30-ml. portions of ether. The ethereal extracts and the organic layer are combined and dried over anhydrous magnesium sulfate. After removal of the ether by distillation at atmospheric pressure, the residue is filtered through a sintered-glass funnel into a 250-ml. distilling flask and fractionally distilled at reduced pressure using a vacuum-jacketed Vigreux column equipped with a still head of the total-condensing, partial-takeoff type. 4,6-Dimethyl-1-hepten-4-ol, b.p. 70–71°/20 mm., n_D^{20} 1.4403, is obtained in 70–75% yield (12.0–12.8 g.) (Note 7).

2. Notes

1. Allyltriphenyltin is prepared as follows. To a 3-l. three-necked flask fitted with a reflux condenser, a motor-driven stirrer, nitrogen-inlet tube, and a 1-l. dropping funnel with pressure-equalizing side arm are added 50 g. (2.1 g. atom) of magnesium turnings and 800 ml. of diethyl ether (Mallinckrodt reagent grade). The dropping funnel is charged with a solution of 120 g. (1.0 mole) of allyl bromide (Eastman Kodak white label) and 250 g. (0.65 mole) of triphenyltin chloride (Metal Thermit Corporation) in 600 ml. of tetrahydrofuran (Electrochemicals Department, E. I. du Pont de Nemours and Company, Inc.) which has been freshly distilled from lithium aluminium hydride. This solution is added to the vigorously stirred, refluxing magnesium suspension during 7 hours. After the addition is complete, 500 ml. of dry benzene is added and the reaction mixture is refluxed overnight at 60°. It is then hydrolyzed by careful addition of 150 ml. of a saturated ammonium chloride solution. The organic phase is decanted from the solids, and the latter are washed twice with ether. The combined organic layer and ethereal extracts are evaporated at reduced pressure with the aid of a rotary evaporator. The solid

residue is recrystallized from 350 ml. of ligroin. The yield of product, m.p. 73–74°, is 190–205 g. (75–80%).

Allyltriphenyltin can also be prepared by using the reaction of preformed allylmagnesium bromide with triphenyltin chloride.² However, the submitters prefer the simpler procedure described above for large-scale preparations of allyltin compounds.

2. Tetraallyltin, triallylphenyltin, and diallyldiphenyltin may be used in place of allyltriphenyltin.

3. The diethyl ether used is Mallinckrodt reagent grade and is distilled from lithium aluminum hydride before use.

4. Etheral phenyllithium, prepared from lithium and bromobenzene,³ may be standardized by adding an aliquot to water and titrating with standard sulfuric acid.

5. The 4-methyl-2-pentanone used is Eastman Kodak white label grade.

6. The first few milliliters of water should be added dropwise.

7. The reported⁴ physical constants for 4,6-dimethyl-1-hepten-4-ol are b.p. 68–69°/20 mm., n_D^{20} 1.4402.

3. Discussion

This procedure is essentially that reported previously.⁵ 4,6-Dimethyl-1-hepten-4-ol has also been prepared by the reaction between allylmagnesium bromide and 4-methyl-2-pentanone,⁴ by the treatment of magnesium with a mixture of allyl bromide and 4-methyl-2-pentanone,^{6,7} and by the treatment of zinc with a mixture of allyl iodide and 4-methyl-2-pentanone.⁸

4. Merits of Preparation

The present synthesis of 4,6-dimethyl-1-hepten-4-ol is an example of the preparation and use of allyllithium. The same general procedure may be used to prepare vinylithium from ether solutions of any of the compounds $(CH_2=CH)_nSn(C_6H_5)_{4-n}$ ($n = 1-4$),⁹ and benzylithium from any of the $(C_6H_5CH_2)_nSn(C_6H_5)_{4-n}$ ($n=1-4$) compounds.¹⁰

Allyllithium is of particular value in the preparation of allylmetal derivatives.⁵ Allyllithium may also be prepared by transmetalation between phenyllithium and tetraallyltin¹¹ or by cleavage of allyl phenyl ether with lithium in tetrahydrofuran.¹²

References and Notes

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Appendix

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

ligroin

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium (7439-95-4)

Allyl bromide (106-95-6)

nitrogen (7727-37-9)

allyl iodide (556-56-9)

zinc (7440-66-6)

bromobenzene (108-86-1)

4-methyl-2-pentanone (108-10-1)

Phenyllithium (591-51-5)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

lithium aluminum hydride,
lithium aluminium hydride (16853-85-3)

Allylmagnesium bromide (1730-25-2)

4,6-Dimethyl-1-hepten-4-ol,
1-Hepten-4-ol, 4,6-dimethyl- (32189-75-6)

Allyltriphenyltin (76-63-1)

tetraphenyltin (595-90-4)

triphenyltin chloride (639-58-7)

Tetraallyltin (7393-43-3)

triallylphenyltin

diallyldiphenyltin (10074-32-5)

Allyllithium

vinylolithium (917-57-7)

benzylolithium

allyl phenyl ether (1746-13-0)

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