



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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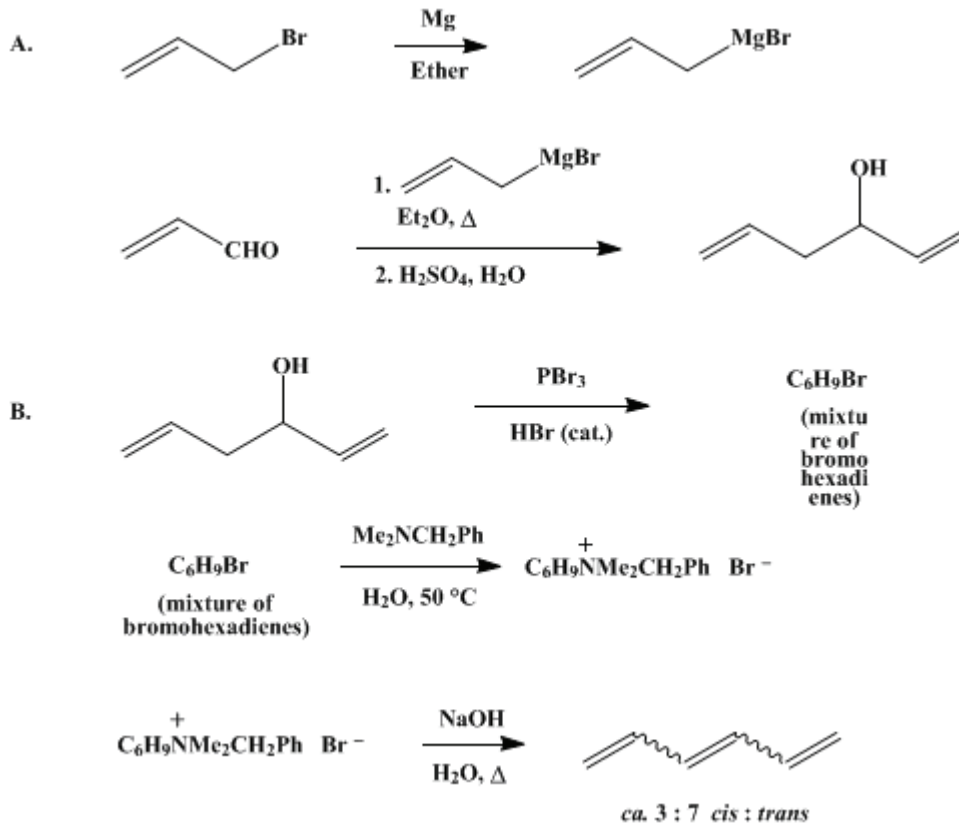
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1,3,5-HEXATRIENE



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1. Procedure

A. *1,5-Hexadien-3-ol* (Note 1). In a 5-l. three-necked flask fitted with a stirrer, a dropping funnel and an ice-water condenser are placed 153.0 g. (6.28 g. atoms) of [magnesium turnings](#), 360 ml. of anhydrous [ether](#) (Note 2), and a few crystals of [iodine](#). A solution of 351.0 g. (2.90 moles) of [allyl bromide](#) (Note 3) in 2.6 l. of [ether](#) is added in small portions until the reaction begins, and then at such a rate as to maintain gentle refluxing of the [ether](#). The addition requires about 3 hours, after which the reaction mixture is refluxed on a steam bath for an additional hour. [Acrolein](#) (Note 4) (104.0 g., 1.86 moles) is added during 2 hours, and this causes gentle refluxing. After an additional hour at room temperature the reaction mixture is poured slowly into 2 l. of ice water. The precipitate is dissolved by adding slowly a solution of 120 ml. of concentrated [sulfuric acid](#) (sp. gr. 1.84) in 400 ml. of water (Note 5). The organic layer is separated and the water layer extracted with three 200-ml. portions of [ether](#). The combined oil and [ether](#) extracts are dried over 8–10 g. of anhydrous [magnesium sulfate](#). After removal of the [ether](#), the residue is distilled through a 6-in. column packed with glass helices to yield 104–108 g. (57–59%, based on [acrolein](#)) of *1,5-hexadien-3-ol*; b.p. 62–65/50 mm., n_D^{25} 1.4440.

B. *1,3,5-Hexatriene*. In a 500-ml., three-necked, round-bottomed flask fitted with a mechanical stirrer, a thermometer, and a graduated dropping funnel are placed 114 g. (0.42 mole) of [phosphorus tribromide](#) (Note 6) and 2 drops of 48% [hydrobromic acid](#). As the contents of the flask are stirred and maintained at 10–15° by means of an ice-water bath, 98 g. (1.00 mole) of *1,5-hexadien-3-ol* is added in the course of 1.5 to 1.75 hours. The mixture is allowed to stir at 10–15° for 40 minutes and then to stand at room temperature overnight. The flask is cooled in an ice-salt bath for 20 minutes, and the upper organic layer is decanted from the residue while still cold. The organic layer is successively washed

with three 40-ml. portions each of ice water, 5% sodium bicarbonate, and water. The crude bromohexadiene weighs 147–153 g. (91–95%) (Note 7).

In an assembly similar to that used for the previous reaction, 90 g. (0.67 mole) of dimethylbenzylamine (Note 8), 0.13 g. of hydroquinone, and 500 ml. of water are stirred and heated at 50°. The crude bromohexadiene (107 g., 0.67 mole) is added in the course of 20–40 minutes, and stirring and heating are maintained at 50° for 2–2.5 more hours. The flask is then fitted for downward distillation, and the mixture is distilled at about 40–50° and 30 mm. until no more oil distils with the water. A total of 133–200 ml. of distillate is collected. This is discarded.

A solution of sodium hydroxide (106 g., 2.7 moles) in 535 ml. of water is placed in a 2-l. flask equipped with a sealed mechanical stirrer and an outlet arranged for downward distillation into an ice-cooled receiver. The aqueous solution of the quaternary bromide is added dropwise to the boiling solution of sodium hydroxide during a period of 2.5–4 hours (Note 9). The hexatriene and dimethylbenzylamine which form are distilled with the water. Distillation is continued for 10–15 minutes after the final addition of quaternary bromide solution. The clear upper layer of the distillate is separated, cooled to 5–10°, washed with three 170-ml. portions each of cold 2*N* hydrochloric acid and water, and dried over anhydrous sodium sulfate. The oil is then distilled, a spinning-band column being used to give 32.0–34.0 g. (54–60%) of 1,3,5-hexatriene; b.p. 80–80.5°, n_D^{20} 1.5103–1.5119 (Note 10).

2. Notes

1. This method is essentially that of Butz, Butz, and Gaddis² except for modified charge ratios to increase the output per batch at some sacrifice in per cent yield.
2. Baker and Adamson, reagent grade.
3. Matheson, Coleman and Bell, b.p. 70–71°.
4. Shell Chemical Co., commercial grade, inhibited.
5. When the magnesium complex is dissolved, the solution may be decanted from the excess magnesium metal.
6. Dow Chemical Co., practical grade.
7. The moist crude bromohexadiene is quaternized in water without further purification. The submitters report that, if desired, the crude mixture may be dried over anhydrous calcium chloride and fractionally distilled through a 10-in. stainless-steel-packed column at reduced pressure. Crude bromohexadiene (220–230 g.) from 147 g. (1.50 moles) of 1,5-hexadiene-3-ol was found to give the fractions listed in Table I. The yield of the total distillate is 174.9 g. of which fractions 1–4 amount to 155.7 g. (64.5%). The 1-bromo isomer has been reported in the literature,^{3,4} and the infrared spectrum suggests that fraction 1 is 3-bromo-1,5-hexadiene. Both isomers when treated separately in this procedure yield hexatriene.

TABLE I

Fraction	Wt., g.	B.P./mm.	n_D^{20}	Product
1	43.2	55–56°/34	1.4829	3-Bromo-1,5-hexadiene
2	31.7	57–72°/34	1.4923	Mixture of the 3- and 1-bromo isomers
3	70.7	72–73°/36	1.4981	1-Bromo-2,5-hexadiene
4	10.1	56–59°/18	1.4996	Mostly 1-bromo-2,5-hexadiene
5	19.2	64–103°/141	1.5196	—

8. The amine should be freshly distilled.
9. This time, although not critical, was chosen to prevent accumulation of unreacted quaternary base or of hexatriene in the reaction vessel.
10. The faintly yellow product obtained before distillation is quite pure. The infrared absorption spectra of the liquid before and after distillation are identical and have, in addition to all the bands shown in the published spectrum of Woods and Schwartzman,⁵ weak absorption bands, notably at 820, 989, 1187, and 1452 cm^{-1} . The differences between the two spectra are due to various ratios of *cis* and *trans* isomers in these hexatriene samples. The ratio of *cis*- to *trans*-1,3,5-hexatriene in this preparation is

estimated at 3:7. This is based on studies using vapor-phase chromatography, ultraviolet absorption spectra, and refractive indices.⁶ The **hexatriene** is stored under **nitrogen** at -5° . Although no visible change is observed after 1 week of storage, the liquid is partially polymerized to the consistency of glycol after 3 weeks. **Hexatriene** can be removed from the thin syrup by distillation at 40 mm., and when redistilled at atmospheric pressure under **nitrogen** has b.p. 80.5° , n_D^{20} 1.5101. Its infrared absorption spectrum is then identical with that of freshly prepared **hexatriene**.

3. Discussion

1,3,5-Hexatriene has been prepared by many workers. The more successful methods are the catalytic pyrolyses (alumina, $260-325^{\circ}$) of **1,3-hexadien-5-ol**^{5,7,8} and **2,4-hexadien-1-ol**.⁹ Other methods which give **hexatriene** of questionable purity or involve less convenient laboratory methods are dehydration of **1,5-hexadien-3-ol** by **sodium bisulfate** at 170° ,¹⁰ or by **phthalic anhydride** at $160-200^{\circ}$,² and by catalytic hydrogenation of **divinylacetylene**.¹¹ Additional methods are listed in footnote ⁵. The present procedure is a practical laboratory method of preparing pure **hexatriene** in satisfactory yields.

References and Notes

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Appendix

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

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium hydroxide (1310-73-2)

Acrolein (107-02-8)

hydroquinone (123-31-9)

sodium bicarbonate (144-55-8)

magnesium,
magnesium turnings (7439-95-4)

HYDROBROMIC ACID (10035-10-6)

Allyl bromide (106-95-6)

sodium sulfate (7757-82-6)

phosphorus tribromide (7789-60-8)

nitrogen (7727-37-9)

phthalic anhydride (85-44-9)

iodine (7553-56-2)

sodium bisulfate (7681-38-1)

magnesium sulfate (7487-88-9)

dimethylbenzylamine (103-83-3)

1,3,5-Hexatriene,
hexatriene (2235-12-3)

1,5-Hexadien-3-ol,
1,5-hexadiene-3-ol (924-41-4)

bromohexadiene

3-Bromo-1,5-hexadiene

1-Bromo-2,5-hexadiene

1,3-hexadien-5-ol

2,4-hexadien-1-ol (17102-64-6)

divinylacetylene (31014-03-6)

trans-1,3,5-hexatriene