Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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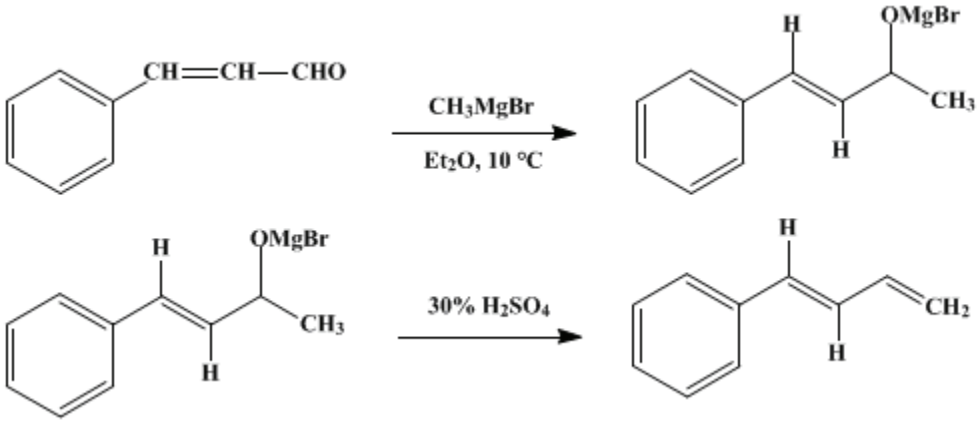
trans-1-PHENYL-1,3-BUTADIENE

[1,3-Butadiene, 1-phenyl-, *trans*-]



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1. Procedure

In a 1-l. three-necked flask equipped with a mercury-sealed stirrer, a reflux condenser protected with a calcium chloride drying tube, a separatory funnel, a nitrogen inlet tube, and a thermometer is placed 0.515 mole of methylmagnesium bromide in 250–350 ml. of ether (a 1.5–2.0*N* solution). The mixture is cooled to a temperature below 10° by means of an ice-water bath, the stirrer is started, and a solution of 66.1 g. (0.50 mole) of cinnamaldehyde (Note 1) in 60 ml. of absolute ether is added, the rate of addition being controlled so that the temperature is kept below 10°. Throughout the addition, which takes about 1 hour, a slow stream of dry nitrogen is passed through the flask (Note 2).

The flask is detached from the condenser and stirrer, and its contents are transferred to a 500-ml. separatory funnel. The apparatus is then reassembled, without the nitrogen inlet tube or the drying tube, and 175 ml. of 30% sulfuric acid (by weight) is placed in the flask. Without cooling, but with efficient stirring with a Hershberg Nichrome wire stirrer at 1500–1700 r.p.m. (Note 3),[2] the ethereal solution of the cinnamaldehyde-methylmagnesium bromide adduct is added rapidly to the acid. The time for this addition (5–7 minutes) is limited by the efficiency of the condenser. Heat then is applied to maintain gentle reflux until the *total* time elapsed from the initiation of hydrolysis is 20 minutes. The contents of the flask are *immediately* transferred to a 1-l. separatory funnel, the lower aqueous layer is discarded, and the ether layer is washed successively with 50 ml. of water, a mixture of 50 ml. of 5% aqueous sodium hydroxide and 50 ml. of saturated ammonium chloride solution, and 50 ml. of water. Before each of the washings the air in the separatory funnel is displaced with nitrogen. When the second wash solution is added, 0.3 g. of phenyl-β-naphthylamine is dissolved in the ether layer. The washed solution is dried with 20 g. of anhydrous sodium sulfate for 30 minutes and then with 15 g. of anhydrous potassium carbonate for 12 hours.

The ethereal solution is filtered and concentrated by distillation from a steam bath to a residual volume of 80–100 ml. Some water separates at this time, and the mixture is cooled and then dried with about 15 g. of anhydrous potassium carbonate. The concentrated solution is filtered into a 125-ml. modified Claisen flask[3] and distilled under reduced pressure in a nitrogen atmosphere into a receiver containing 0.3 g. of phenyl-β-naphthylamine. In this manner 52–54 g. (80–83%) of crude *trans*-1-phenyl-1,3-butadiene is obtained, b.p. 81–85°/10–11 mm.; n_D^{25} 1.606–1.608, which may contain some methylstyrylcarbinol and water. This material is dried with 5 g. of anhydrous potassium carbonate, filtered, and distilled as before. The yield of *trans*-1-phenyl-1,3-butadiene is 47–49 g. (72–75%), b.p. 78–81°/8 mm.; n_D^{25} 1.607–1.608. This product is satisfactory for most purposes (Note 4) and (Note 5).

2. Notes

1. Cinnamaldehyde obtained from the Eastman Kodak Company was purified by washing a solution in an equal volume of ether with aqueous sodium carbonate and then with water, dried, and distilled under nitrogen; b.p. 101–102°/2–3 mm.; n_D^{20} 1.6195.

2. The procedure may be altered at this point so that *trans*-methylstyrylcarbinol is obtained. It is necessary, however, to observe the precaution that all apparatus coming in contact with the *trans*-methylstyrylcarbinol be free from traces of acid.

The solution is stirred for 30 minutes after the addition is complete. Then 125 ml. of a saturated solution of ammonium chloride (about 28%), which has been neutralized to litmus with concentrated ammonium hydroxide, is added dropwise, the temperature being held at 5–10°. This addition takes from 1 to 1.5 hours. After decanting the ether layer, breaking up the precipitate and extracting it with two 60-ml. portions of absolute ether, and adding the extracts to the main solution, the solution is distilled from a steam bath until the residual volume is about 100 ml. The solution is transferred to a Claisen flask, and the residual ether is removed by evacuation with a water pump. After the discard of a small fore-run, the product is collected at 93–94°/1.5 mm.; yield, 65–67 g. (88–90%).

Upon cooling at 0–10° the *trans*-methylstyrylcarbinol forms a mass of white crystals melting at 30–34°. These may be purified by crystallization from petroleum ether (b.p. 30–35°) -methylene chloride (6:1). For each 30 g. of the carbinol, 350 ml. of the solvent mixture is used. The solution is cooled to −75° to −80° in Dry Ice and kept at that temperature for about 3 hours. The solution is filtered quickly by suction through a chilled funnel, washed with the cold solvent mixture, and dried in a vacuum desiccator. The yield of pure *trans*-methylstyrylcarbinol is 28.5 g., m.p. 33.5–34.5°; n_D^{35} 1.5598; d_4^{35} 0.9995.

3. The stirring must be vigorous in order to mix the ether and aqueous layers. This is absolutely essential for the production of reasonable yields. Slower stirring necessitates a longer time for the hydrolysis with consequent longer contact time between the 1-phenyl-1,3-butadiene and the sulfuric acid, which results in extensive polymerization of the product and corresponding decrease in yield.

4. Pure *trans*-1-phenyl-1,3-butadiene was obtained by distillation of the twice-distilled product under nitrogen through a 12-plate column of the total reflux-variable takeoff type[2] after adding 0.5% of phenyl-β-naphthylamine. The packed section of the column was an 18-in. section of Pyrex tubing (10 mm. o.d.) filled with 4-mm. single-turn glass helices. Insulation was provided by means of a vacuum jacket, and heat losses were compensated by resistance wire wound on the jacket.

About 50% of the sample taken was collected, b.p. 86°/11 mm.; n_D^{25} 1.6086–1.6090; d_4^{25} 0.9235–0.9239.

5. Present evidence indicates that 1-phenyl-1,3-butadiene[4] prepared by this method is the *trans* isomer.[5]

3. Discussion

1-Phenyl-1,3-butadiene has been prepared by the decarboxylation of allocinnamylideneacetic acid[6] and of cinnamylidenemalonic acid;[7] the dehydration of methylstyrylcarbinol from the Grignard addition of methylmagnesium halide to cinnamaldehyde;[8] the rearrangement and dehydration of the alcohol intermediate formed by the Grignard addition of phenylmagnesium bromide to crotonaldehyde;[9] the formation of methylstyrylcarbinol, its conversion to methylstyrylcarbinyl chloride, and dehydrohalogenation;[10] a modified Wurtz reaction in which benzyl chloride is coupled with allyl chloride by means of sodium in liquid ammonia;[11] the condensation of styrene and acetaldehyde and dehydration of the intermediate in the presence of sulfuric acid in acetic acid;[12] and by the dehydrochlorination of 4-chloro-1-phenyl-2-butene (prepared by the condensation of butadiene with benzenediazonium chloride).[13] Reference [12] describes the preparation of 1-phenyl-1,3-butadiene by pyrolysis of 1-phenyl-1,3-butyleneglycol diacetate and 2,6-dimethyl-4-phenyl-1,3-dioxane. The present method is a modification of the procedure of von der Heide.[8]

trans-Methylstyrylcarbinol has been prepared by several methods: the hydrolysis of the addition product formed from methylmagnesium halide and cinnamaldehyde in a variety of ways;[10,14] hydrolysis of the addition compound formed from styrylmagnesium bromide and acetaldehyde;[4] hydrolysis and hydrogenation of the product formed in the Grignard reaction of phenylethynylmagnesium bromide and acetaldehyde;[15] the addition of hypobromous acid to 1-phenyl-1,3-butadiene followed by reduction with

sodium amalgam in acetic acid;[16] the allylic rearrangement of 1-phenyl-1-acetoxy-3-butene to 1-phenyl-3-acetoxy-1-butene followed by saponification;[17] and the reduction of benzalacetone by means of aluminum isopropoxide.[18] The method employed here is essentially that of Kenyon, Partridge, and Phillips.[14]

References and Notes

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

petroleum ether

phenyl-β-naphthylamine

cinnamaldehyde-methylmagnesium bromide

allocinnamylideneacetic acid

acetaldehyde (75-07-0)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ammonia (7664-41-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

allyl chloride (107-05-1)

benzenediazonium chloride

Benzalacetone (122-57-6)

sodium (13966-32-0)

aluminum isopropoxide

benzyl chloride (100-44-7)

hypobromous acid (13517-11-8)

ammonium hydroxide (1336-21-6)

cinnamaldehyde

methylene chloride (75-09-2)

styrene (100-42-5)

butadiene (106-99-0)

styrylmagnesium bromide

methylmagnesium bromide (75-16-1)

crotonaldehyde (123-73-9)

methylstyrylcarbinol

1-phenyl-1,3-butadiene (31915-94-3)

cinnamylidenemalonic acid (4472-92-8)

methylstyrylcarbinyl chloride

4-chloro-1-phenyl-2-butene

1-phenyl-1,3-butyleneglycol diacetate

2,6-dimethyl-4-phenyl-1,3-dioxane

phenylethynylmagnesium bromide

1-phenyl-1-acetoxy-3-butene

1-phenyl-3-acetoxy-1-butene

trans-1-Phenyl-1,3-butadiene,
1,3-Butadiene, 1-phenyl-, trans- (16939-57-4)

trans-Methylstyrylcarbinol (17488-65-2)