



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.

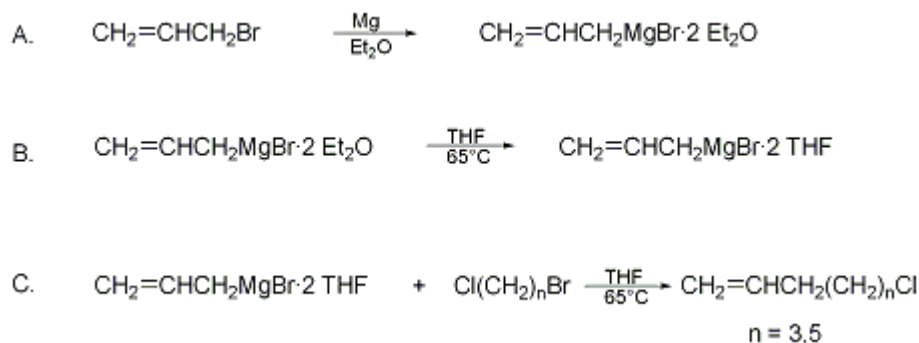
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 10, p.222 (2004); Vol. 76, p.221 (1999).

6-CHLORO-1-HEXENE AND 8-CHLORO-1-OCTENE

[1-Hexene, 6-chloro- and 1-Octene, 8-chloro-]



Submitted by Pierre Mazerolles, Paul Boussaguet, and Vincent Huc¹.

Checked by Frédéric Denonne and Léon Ghosez.

1. Procedure

A. Allylmagnesium bromide (ethereal complex solution). A dry, 3-L, three-necked, round-bottomed flask is equipped with a sealed mechanical stirrer (Note 1), 500-mL, pressure-equalizing, dropping funnel and a reflux condenser, the top of which is connected to a calcium chloride drying tube. The flask is charged with a large excess of magnesium turnings (90.00 g, 3.75 g-atom) (Note 2) and 150 mL of dry diethyl ether. To the stirred mixture is added dropwise a solution of allyl bromide (Note 3) (181.60 g, 1.50 mol) in 1.5 L of dry diethyl ether. At the end of the addition (8 hr) the mixture is stirred for 1 hr, whereupon the Grignard reagent solution is transferred under nitrogen, with a cannula, into a 2-L, two-necked, round-bottomed flask equipped with a 500-mL dropping funnel and a reflux condenser fitted with a swan neck (distillation) adapter connected with a descending condenser (Note 4).

B. Allylmagnesium bromide (THF complex solution). After removal of the water in the vertical reflux condenser, the solution of the Grignard reagent is heated with a water-bath (45°C, then progressively up to 65°C) with stirring to remove the uncomplexed diethyl ether (2 hr). Dry tetrahydrofuran (THF, 500 mL) is added rapidly (10 min) to the gray pasty residue. A vigorous reaction occurs, and the decomplexed diethyl ether is easily removed by distillation. The reaction is completed by heating the mixture with stirring for 1 hr to give a fluid gray THF solution of allylmagnesium bromide (Note 5).

C. 6-Chloro-1-hexene. The swan neck and the descending condenser are removed, the vertical reflux condenser is fitted with a drying tube, and water is again circulated through the condenser. To the stirred mixture heated at 50-60°C, pure 1-bromo-3-chloropropane (Note 6) (150.00 g, 0.95 mol) is added at a rate sufficient to maintain a good reflux in the condenser. At the end of the addition (0.5 hr), the mixture is boiled for 1 hr and then cooled. Excess Grignard reagent is destroyed by slow addition of water, while cooling the mixture, to produce two clear layers. The aqueous phase is extracted with pentane (3 × 300 mL each), and the organic phase is dried over calcium chloride. Removal of the solvent (water bath at 45°C, then progressively to 95°C, Vigreux column 2") gives 183.40 g of oily residue. The remainder of the solvent is removed under vacuum (up to 45°C/147 mm). Distillation of the residue in a Claisen flask gives the following fractions: Head fraction, from 50°C to 74°C/130 mm (21.16 g) containing 60% of chlorohexene (Note 7); central fraction, 74-75°C/130 mm (93.00 g, 0.78 mol, 82% yield) consisting of almost pure chlorohexene (Note 8); residue, clear yellow, about 1 mL.

8-Chloro-1-octene. Similarly, the reaction of 1-bromo-5-chloropentane (Note 9) (88.37 g, 0.47 mol) with a solution of allylmagnesium bromide prepared as above from allyl bromide (90.75 g, 0.75 mol) and magnesium turnings (45.00 g, 1.87 mol), gives, after the usual treatment, 60.14 g of 8-chloro-1-octene (86% yield), bp 75-76°C/20 mm (Note 10).

2. Notes

1. Stirring with a large magnetic bar and an efficient magnetic stirrer (IKA mod. MAG. RET) is possible, but the magnetic bar turns with some difficulty at the beginning of the reaction.
2. A large excess of [magnesium turnings](#) is necessary to prevent the formation of biallyl (1,5-hexadiene) by a Würtz-coupling reaction. Small [magnesium turnings](#) (3-4-mm size, 0.5-mm thickness) were obtained with a lathe from a pure magnesium bar (A. Weber Métaux). The checkers used Aldrich [magnesium turnings](#) (98%).
3. The reaction starts easily; the addition of a crystal of [iodine](#) is not necessary. To minimize the formation of [hexadiene](#), the addition of [allyl bromide](#) must be slow enough to maintain the temperature of the flask below the boiling point of ether. [Allyl bromide](#) (Fluka "purum") even when stored in the dark in the presence of [silver](#) wool contains some high-boiling material and must be purified by distillation. Pure product (bp 71°C) is used just after distillation.
4. Unreacted [magnesium](#), washed with water, alcohol and ether and dried in an oven, weighs 56.16 g (94% of the theoretical yield).
5. Such a large amount of THF is not necessary to remove the complexed [ether](#), but if a smaller quantity is used, the mixture solidifies on cooling.
6. [1-Bromo-3-chloropropane](#) (Fluka "purum") was dried and distilled before use (bp 56°C/ 34 mm).
7. The amount was estimated by VPC. As the principal impurity is THF, the yield of [chlorohexene](#) may be increased to 90% by careful distillation.
8. The product obtained contains traces of THF and a small amount (3-5%) of [6-bromo-1-hexene](#) (identified by mass spectroscopy). Usually this by-product is not an impurity, especially when [6-chloro-1-hexene](#) is used to prepare the corresponding Grignard reagent. The spectral data are as follows: ¹H NMR (80 MHz, CDCl₃) δ: 1.79 (m, 6 H), 3.51 (t, 2 H, J = 8.0), 4.98 (m, 2 H), 5.71 (m, 1 H) ; ¹³C NMR (20 MHz, CDCl₃) δ: 26.1, 32.0, 32.9, 44.8, 114.8, 136.1 .
9. [1-Bromo-5-chloropentane](#) is easily prepared from [tetrahydropyran](#) according to the process described by Newman and Wotiz,² bp 89°C/17 mm; n_D²⁰ 1.4842. The checkers purchased [1-bromo-5-chloropentane](#) from Aldrich Chemical Company, Inc.
10. Like [6-chloro-1-hexene](#), [8-chloro-1-octene](#) contains a small amount (3-5%) of the corresponding bromide ([8-bromo-1-octene](#)), which is not a problem in some reactions.

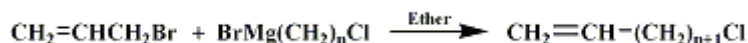
Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

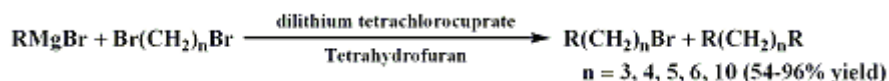
3. Discussion

Haloalkenes, CH₂=CH-(CH₂)_nX (n = 3-7; × X = Cl, Br), are interesting synthons for use: in the preparation of long chain alkenols and alkenoic acids;³ in cyclization reactions,^{4,5,6,7,8,9,10} as intermediates in the synthesis of pheromones;^{11,12} in the preparation of silica gel having a functional surface;¹³ and for the synthesis of ω-iodochloroalkanes,¹⁴ and organogermanium dendrimers.¹⁵ They are usually prepared from the corresponding alkenols.

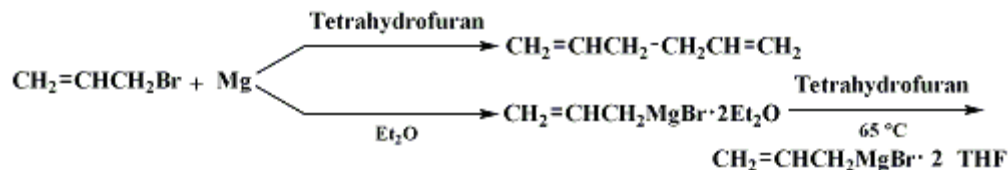
An interesting synthesis of this type of compound is the reaction of [allyl bromide](#) with a mono Grignard reagent of a dihalide, especially a chlorobromide.¹⁶ However this synthesis is only suitable for long chains, n ≥ 4: n = 4, 45% yield; n = 6, 60% yield.



On the other hand, bromoalkanes react with saturated¹⁷ or ethylenic¹⁸ Grignard reagents in [tetrahydrofuran](#) in the presence of a suitable catalyst (dilithium tetrachlorocuprate^{19,20}):

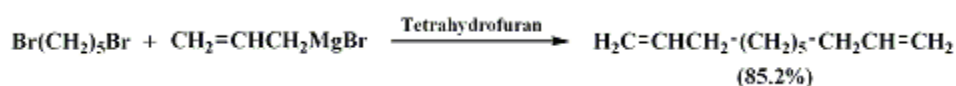


It was shown that alkyl bromides react *without a catalyst* with allylmagnesium bromide in THF. However, because allyl bromide reacts quantitatively with magnesium in THF to give 1,5-hexadiene by a Würtz-coupling reaction, allylmagnesium bromide can be obtained in this solvent only by solvent exchange:

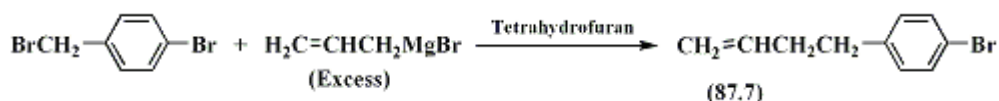


The reaction with the readily available 1-bromo-3-chloropropane is a direct, inexpensive method for preparing of 6-chlorohexene in high yields (80-90%); this reaction may be readily extended to 1-bromo-5-chloropentane² and to other accessible ω-bromochloroalkanes.²¹

With dibromoalkanes the corresponding dienes are formed in good yield:



With aralkyl dibromides, only alkyl bromides react:



References and Notes

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

6-Chloro-1-hexene:

1-Hexene, 6-chloro- (8,9); (928-89-2)

8-Chloro-1-octene:

1-Octene, 8-chloro- (8,9); (871-90-9)

Allylmagnesium bromide:

Magnesium, bromo-2-propenyl- (8,9); (1730-25-2)

Magnesium (8,9); (7439-95-4)

Allyl bromide:

1-Propene, 3-bromo- (8,9); (106-95-6)

1-Bromo-3-chloropropane:

Propane, 1-bromo-3-chloro- (8,9); (109-70-6)

1-Bromo-5-chloropentane:

Pentane, 1-bromo-5-chloro- (9); (54512-75-3)

6-Bromo-1-hexene:

1-Hexene, 6-bromo- (8,9); (2695-47-8)