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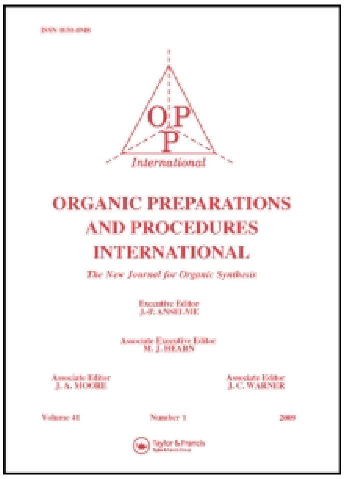

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3-METHYL-3-BUTEN-1-OL AND 3-BUTEN-1-OL

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3-METHYL-3-BUTEN-1-OL AND 3-BUTEN-1-OL

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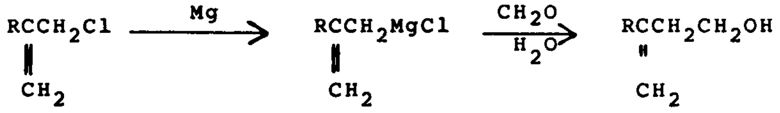

$$\underset{\substack{\| \\ CH_2}}{RCCH_2Cl} \xrightarrow{Mg} \underset{\substack{\| \\ CH_2}}{RCCH_2MgCl} \xrightarrow[H_2O]{CH_2O} \underset{\substack{\| \\ CH_2}}{RCCH_2CH_2OH}$$

$R = CH_3, H$

While Grignard reactions are often relatively simple to carry out, those involving formaldehyde require special attention. Procedures using gaseous formaldehyde or s - trioxane are frequently employed[5]· paraformaldehyde is usually avoided because of its water content. Special attention must also be given to preparation of Grignard reagents from allylic or benzylic halides to reduce or eliminate coupling of the newly formed Grignard reagent with unreacted halide.

We wish to report a well-tested procedure for the preparation of 3-methyl-3-buten-1-ol and 3-buten-1-ol which illustrates these precautions.[6] Although both of these compounds are available commercially in research quantities, their cost is prohibitive for many research groups. The procedure reported below uses inexpensive starting materials and the solvent (tetrahydrofuran) may be recovered for repeated use.

EXPERIMENTAL

3-Methyl-3-buten-1-ol.- A 3-l., three-necked flask was charged with magnesium (145.5 g., 6.0 g-atoms) and equipped with a Trubore stirrer, a dropping funnel with an equilibrating sidearm, a double-jacketed reflux condenser topped with a nitrogen inlet[7] and the entire apparatus was flame-dried under a dry nitrogen stream. The apparatus was cooled and tetrahydrofuran (1.4 l.) was distilled from lithium aluminum hydride[8] into the reaction flask. The mixture was stirred and heated to reflux and a small crystal of iodine was added followed by a solution of 135.5 g. (1.5 moles) of freshly distilled methallyl chloride in 100 ml. of tetrahydrofuran over a period of six to eight hours. Back titration of an aliquot that had been added to standard hydrochloric acid indicated an 85% yield of Grignard reagent.

The dropping funnel was replaced by an addition flask for solids[9,10] containing 38.2 g. (1.27 moles) of paraformaldehyde which had been dried at 0.02 mm over phosphorus pentoxide for more than 48 hours. The paraformaldehyde was added in portions over a period of thirty minutes to the refluxing solution. The reaction was quite exothermic and little heating was required once the paraformaldehyde had begun to depolymerize. The reaction mixture was heated at reflux for an additional 2 hours and then it was cooled to 0°. Approximately 180 ml. of saturated ammonium chloride solution[11] was added dropwise and the mixture was stirred for 30 minutes to effect complete hydrolysis. Magnesium sulfate (185 g.) was added and, after it was stirred for an hour, the mixture was filtered and the cake was washed well with ether. The filtrate and washings were distilled through a 24-in. spinning band column to give 78 g. (71%) of 3-methyl-3-buten-1-ol, bp. 131-133°, n_D^{25} 1.4312, lit.[12] bp. 130°, n_D^{20} 1.4311. Gas chromatographic analysis on a 7.5 ft. x ¼ in. 15% Craig polysuccinate column at 84° indicated greater than 99% purity.

<u>3-Buten-1-ol</u>.- The above procedure was carried out on twice the scale using redistilled allyl chloride to give 3-buten-1-ol in 66% yield, bp. 116-118°, $n_D^{25.5}$ 1.4190, lit.[13-15] bp. 115°, n_D^{26} 1.4182; bp. 113-114°, n_D^{21} 1.4206; bp. 112.5 - 113.5/748 mm., n_D^{20} 1.4424.

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2. Present address: Lilly Research Laboratories, Eli Lilly and Co., Indianapolis, Indiana 46206.

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4. Present address: Department of Chemistry, Texas A & M University, College Station, Texas 77843.

5. M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Constable (London, 1954).

6. The experiments reported herein were conducted in the laboratories of Professor W. S. Johnson. We gratefully acknowledge his advice and encouragement.

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8. Calcium hydride is also an effective drying agent.

9. L. F. Fieser, "Experiments in Organic Chemistry," Third Edition, D. C. Heath and Co., Boston (1955), page 265. It was found helpful to use a male standard taper joint cooled by a coil of condenser tubing as an extension.

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