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Synthesis of Benzyl/Allyl Alkyl Ethers from Corresponding Magnesium Alkoxides

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Abstract: In the presence of iodine, alcohols react with magnesium to produce magnesium alkoxides which are then treated with benzyl chloride or allyl bromide to produce benzyl alkyl ethers or allyl alkyl ethers. Copyright © 1996 Elsevier Science Ltd

Benzyl/allyl alkyl ethers can be synthesized by the Williamson synthesis,[1] by phase-transfer catalysis,[2] by the bis [acetylacetonato] nickel method,[3] or by the Grignard route.[4] We now report a new method for the synthesis of benzyl alkyl ethers and allyl alkyl ethers from corresponding magnesium alkoxides. In the presence of iodine and hexane, alcohols readily react with magnesium to produce corresponding magnesium alkoxides.[5] By the simplified method used in this paper, the preparation of magnesium alkoxides was carried out in the absence of hexane or any other saturated hydrocarbons. The formed magnesium alkoxides are then treated with benzyl chloride or allyl bromide to produce the ethers.

$$2ROH + Mg \xrightarrow[-H_2]{I_2} \underset{1}{Mg(OR)_2} \xrightarrow[\Delta]{R'X} \underset{2}{2ROR'} + MgX_2$$

Magnesium is safer than sodium used in Williamson synthesis and stable in the air. Because the reaction is carried out in non-aqueous systems, no hydrolysis by-products were formed. The yields are good/ excellent (Table 1).

Table 1. Yields of Benzyl alkyl Ethers and Allyl alkyl Ethers from Corresponding Magnesium Alkoxides

Compd.	R	R'X	ROH:Mg:R'X (mol)	Time	Yield (%)
2a	C_2H_5	$C_6H_5CH_2Cl$	0.9:0.1:0.1	24h	82
2b	n- C_3H_7	$C_6H_5CH_2Cl$	0.6:0.1:0.1	24h	87
2c	n-C_4H_9	$C_6H_5CH_2Cl$	0.6:0.1:0.1	12h	92
2d	n-C_5H_{11}	$C_6H_5CH_2Cl$	0.6:0.1:0.1	12h	93
2e	n-C_6H_{13}	$C_6H_5CH_2Cl$	0.6:0.1:0.1	12h	94
2f	CH_2CH_2OH	$C_6H_5CH_2Cl$	2.4:0.2:0.1	10h	72
2g	CH_3	CH_2=$CHCH_2Br$	1.6:0.1:0.1	2d	78
2h	C_2H_5	CH_2=$CHCH_2Br$	1.3:0.1:0.1	2d	91
2i	n- C_3H_7	CH2=$CHCH_2Br$	0.8:0.1:0.1	2d	94
2j	n-C_4H_9	CH2=$CHCH_2Br$	0.8:0.1:0.1	2d	95

Magnesium alkoxides are prepared by heating 0.1 mol of magnesium powder, 0.002 mol of iodine, 0.2 mol of alcohol at 60 ℃ until the iodine color disappeared. The rest of the alcohol (Table 1) was then added and the mixture was refluxed until all magnesium powder was digested. The resulting magnesium alkoxides in alcohol can be used directly to react with 0.1 mol of benzyl chloride or allyl bromide at reflux. By distillation of the reaction mixture, steam distillation of the solid residue, diethyl ether extraction (25 mL × 2) of the steam distillate, and finally fractional distillation, the benzyl alkyl ethers were obtained. The allyl alkyl ethers are recovered by double fractional distillation of reaction mixture, mixing crude products with 60 ml of xylene, washing with water, drying with calcium chloride, and finally fractional distillation again.

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