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Reductive Etherification of Aromatic Aldehydes with Decaborane

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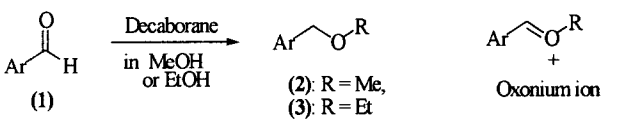
Abstract: Aromatic aldehydes were easily converted to the corresponding ethers in methanol or ethanol using decaborane at r.t. under nitrogen in high yields.

Acetals, a protected form of aldehyde compounds, have been reported to be reduced to ethers. A number of reagents have been known to effect reductive cleavage of acetals and ketals to ethers. These are $LiAlH_4$-Lewis acid (BF_3 or $AlCl_3$),[1,2] diisobutyl aluminum hydride,[3] H_2 with Rh on alumina-HCl,[4] diborane in tetrahydrofuran,[5] decaborane in refluxing toluene,[6] $NaCNBH_3$-HCl(gas) in methanol,[7] trimethylsilane in methylene chloride,[8] and $(Et)_3SiH$ in CF_3COOH.[9] Although several reductive etherifications of carbonyl compounds using trimethylsilane in methylene chloride[10], zeolite MCM-22 in refluxing alcohol[11] or trimethylsilane and trimethylsilyl iodide in pentane at - 78℃- r.t.[12] have already been developed, there are no widely applicable methods which involve a simple and efficient process using air stable reagents.

Here, we report the efficient and direct reductive method of aromatic aldehydes in methanol or ethanol to the corresponding ethers. The treatment of aromatic aldehydes in methanol or ethanol with decaborane at r.t. under nitrogen gave the corresponding ethers in high yields. The reaction seemed to proceed by the formation of an acetal or hemiacetal *in situ* followed by the reduction. The decaborane seemed to be worked as catalyst[13] for the formation of the acetal or hemiacetal in solution and a reducing agent. The intermediate for this reaction seemed to be oxonium ion formed from the acetal or hemiacetal. The reaction condition is mild and the method is direct way from aromatic aldehydes to the corresponding ethers.

Scheme 1.



The following experimental procedure is representative. To a solution of 5-iodosalicylaldehyde (100 mg, 0.40 mmol) in 5 ml of methanol was added decaborane (25 mg, 0.2 mmol) at r.t. under nitrogen.

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The resulting solution was stirred for 3.5 h. Acetone and silica gel were added to the solution and then chromatographed on short pad silica gel using a solution of ethyl acetate and n-hexane (1:4) to give methyl ether (quantitative) as a colorless syrup.

In conclusion, aromatic aldehydes in methanol or ethanol were converted efficiently and conveniently to the corresponding ethers using decaborane at r.t. under nitrogen in high yields.

Table 1. Reductive Etherifications of Aromatic Aldehydes with Decaborane

Entry	Substrate(1)	Time (h)	Product (2)[b] (%)[a]	Time (h)	Product (3)[b] (%)
1	Benzaldehyde	22	96	24	95
2	*o*-Anisaldehyde	6	99	6.5	99
3	*m*-Anisaldehyde	7	99	6.5	98
4	*p*-Anisaldehyde	4.5	99	6	99
5	5-Nitrosalicylaldehyde	12	97	12	98
6	Salicylaldehyde	30	98	30	97
7	5-Iodosalicylaldehyde	3.5	99	2.5	99

a) All yields are isolated ones. b) All products gave spectra consistent with the assigned structures.

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13. Electon deficient decaborane or decomposed decaborane seemed to act as catalyst for the formation of acetal and for the formation of oxonium ion.