# Metal Hydrogen Sulfates Catalyzed Methoxymethylation of Alcohols under Solvent-Free Conditions

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Methoxymethylation of a variety of alcohols was performed by using formaldehyde dimethoxy acetal in the presence of metal hydrogen sulfate $M(HSO_4)_n$ at room temperature and solvent-free conditions. The methoxymethyl ethers (MOM-ethers) were obtained with high yields and purity.

**Keywords:** Metal hydrogen sulfates; $M(HSO_4)_n$; Methoxymethylation; Alcohols; Formaldehyde dimethoxy acetal; Solvent-free conditions.

## INTRODUCTION

Acids are widely used as catalysts in industry for producing more than $1 \times 10^8$ mt/year of products.[1] The most commonly used are HF, $H_2SO_4$, $HClO_4$, and $H_3PO_4$ (in liquid form or supported on Keiselguhr). Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal in different chemical processes. Also, wastes and by-products can be minimized or avoided by using solid acids in developing cleaner synthesis routes. On the other hand, any reduction in the amount of liquid acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage and environmental protection.[2] On the other hand, using an applicable industrial catalyst that is safe and eco-friendly, green and simply recycled in the reaction mixtures, has received attention. Thus, green chemistry has been defined as a set of principles that reduces or eliminate the use or generation of hazardous substances throughout the entire life of chemical materials. Inorganic solid acidic salts such as metal hydrogen sulfates play a prominent role in organic synthesis under heterogeneous conditions.[3] Along this line, using $Al(HSO_4)_3$,[4] $Fe(HSO_4)_3$,[5] $Mg(HSO_4)_2$,[6] $NaHSO_4.H_2O$,[7] Oxone® ($2KHSO_5.KHSO_4.K_2SO_4$)[8] which are low in toxicity, highly stable towards humidity, recyclable and air stable have received more attention. The importance of these solid acid catalysts is growing because of their safe and eco-friendly nature as attention is directed toward the development of clean and green technologies for important organic molecules to promote environmental safety.

Protection of the hydroxyl functional group is an important process in multi-step syntheses. One of the popular methods for this purpose is to transform hydroxyl groups to their corresponding methoxymethyl ethers (MOM-ethers). The methoxymethyl protecting group is thus superior to the tetrahydropyranyl group, especially in the cases of polyols, because it is easier to distinguish mono-protection from multi-protection and to estimate impurity by NMR spectroscopy.[9] Methoxymethylation has usually been done with chloromethyl methyl ether under basic conditions.[10] The formaldehyde dimethoxy acetal (FDMA) is a cheap and commercially available compound that can be used for the preparation of MOM-ethers from hydroxyl compounds. Even though handling this reagent is easy, its main drawback is its poor methoxymethylating power that needs forceful conditions.[11] For the activation of FDMA, a variety of catalysts have been reported, but these methods have their own limitations as well as merits. For example, $MoO_2(acac)_2$ has been reported as an excellent catalyst for the methoxymethylation of different kinds of alcohols, but it is not a cheap and commercial catalyst for this purpose.[12] Patney has also reported anhydrous iron(III) chloride dispersed on molecular sieves (3 Å) for the methoxymethylation of primary and secondary alcohols by using FDMA at room temperature and with excellent yields. However, this procedure

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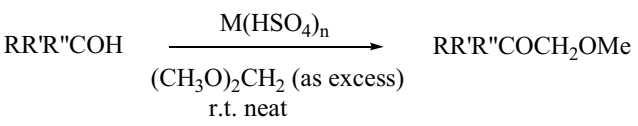
is not suitable for methoxymethylation of tertiary alcohols.[13] Very recently $Sc(OTf)_3$ and $Bi(OTf)_3$ have also been used as effective catalysts for methoxymethylation of alcohols.[14]

## RESULTS AND DISCUSSION

In connection with our recent interest in the direct methoxymethylation of alcohols with FDMA in the presence $H_3PMo_{12}O_{40}.xH_2O$[15] and silica sulfuric acid[16] as solid acid catalysts, and also in continuation of our studies on the use of inorganic hydrogen sulfate acidic salts in organic transformation,[4-8] we have found that metal hydrogen sulfates $[M(HSO_4)_n]$ are suitable for direct methoxymethylation of alcohols with FDMA at room temperature under solvent-free conditions (Scheme I).

**Scheme I**




R, R', R"= Alkyl, Aryl, H

M: Al, Fe, Mg, Ca

Methoxymethylation reaction of 2-phenylethanol was performed with different molar ratios of solid acids in order to optimize the reaction conditions. In a preliminary study, the effect of various solid acids on the yields and times of methoxymethylation was investigated with the above mentioned substrate as a model compound. As shown in Table 1, $Al(HSO_4)_3$ is the best solid acid catalyst for this purpose under solvent-free conditions.

Also, $Mg(HSO_4)_2$, $Ca(HSO_4)_2$, and $Fe(HSO_4)_3$ catalyze this protection with a longer reaction time. Such a reaction did not proceed in the presence of oxone®, $KHSO_4$, $HIO_3$, $H_5IO_6$, and silica zirconium hydrogen phosphate (Table 1, entries 7-11). The required molar ratio, 1:10:0.2, was applied for alcohol, FDMA, and catalyst $Al(HSO_4)_3$, respectively, under the abovementioned conditions. The molar ratio of other metal hydrogen sulfates (Fe, Mg, Ca) is 0.25 (Table 1, entries 15, 18, 20). Although ethyl acetate, acetonitrile, and $CH_2Cl_2$ afforded the product in high yields, we chose the solvent-free conditions for green and environmental acceptability. Entries 6 and 20 of Table 1, describe the times and yields of four consecutive protections leading to MOM-ethers. In these experiments the product was isolated by filtration and washing the solid residues with $CH_2Cl_2$ and the remaining catalyst being reloaded with fresh reagents for further runs. No decrease in the yield was observed; therefore, the described metal hydrogen sulfates $[Al(HSO_4)_3$ and $Ca(HSO_4)_2]$ could be reused as a catalyst in methoxymethylation reactions. It should be mentioned that $Fe(HSO_4)_3$ and $Mg(HSO_4)_2$ could not be recycled and reused again.

Both primary and secondary alcohols can be smoothly converted into the corresponding MOM-ethers in excellent yields. Benzylic alcohols bearing electron withdrawing groups such as nitro and halogens (Table 2, entry 2-5) or electron releasing groups (Table 2, entry 6) are converted into the corresponding methoxymethylated products with excellent yields.

During our investigation, we also found that hindered tertiary alcohols such as 1-adamantanol and 1-methyl-2-phenyl-2-propanol were also methoxymethylated in refluxing $CH_3CN$ with good to excellent yields. Fortunately, in the case of tertiary alcohols, an elimination reaction was not observed (Table 2, entries 14 and15). Results are tabulated in Table 2. Furthermore, our examination showed that this method is not applicable for protection of phenolic hydroxyl groups, and the starting material was recovered intact after 24 h. Therefore we observed the competitive methoxymethylation of alcohols in the presence of phenol. In a control experiment, when an equimolar mixture of benzyl alcohol (1 mmol) and phenol (1 mmol) with FDMA (10 mmol) in the presence of metal hydrogen sulfates [for $Al(HSO_4)_3$ (0.2 mmol) and another hydrogen sulfates Fe, Mg, and Ca (0.25 mmol)] under solvent-free conditions, the benzyl alcohol underwent chemoselectively methoxymethylation and gives benzyl methoxymethyl ether (80-86%), whereas the phenol remained intact (Scheme II).

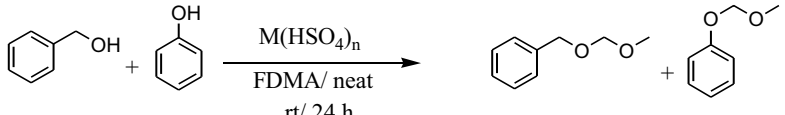
In this regard, we decided to use a molecule containing both phenolic and alcoholic hydroxyl groups such as 2,6-bis-hydroxymethyl-4-chloro-phenol. Therefore, in another experiment we also refluxed 2,6-bis-hydroxymethyl-4-chloro-phenol, FDMA(60 mmol) and $Al(HSO_4)_3$ (0.5 mmol) in acetonitrile for 18 h (Table 3). As shown in Scheme III, only the two non-phenolic hydroxy groups were converted into their corresponding methoxymethylated forms. The low yield of the obtained product concerned the sensitive two non-phenolic hydroxyl groups of

Table 1. The reaction of 2-phenylethanol (1 mmol) with formaldehyde dimethoxy acetal (10 mmol) in the presence of solid acids at room temperature under various conditions

| Entry | Catalyst | Amounts of cat. | Conditions | Time (Conversion) h (%) |
|---|---|---|---|---|
| 1 | $Al(HSO_4)_3$ | 0.2 mmol | $Me_3C$-O-Me | 24.0 (71) |
| 2 | $Al(HSO_4)_3$ | 0.2 mmol | $CH_2Cl_2$ | 7.0 (100) |
| 3 | $Al(HSO_4)_3$ | 0.2 mmol | $CH_3CN$ | 3.5 (100) |
| 4 | $Al(HSO_4)_3$ | 0.2 mmol | $CH_3COOEt$ | 2.75 (100) |
| 5 | $Al(HSO_4)_3$ | 0.1 mmol | Solvent-free | 5.5 (70) |
| 6 | $Al(HSO_4)_3$ | 0.2 mmol | Solvent-free | 0.42 (90), 2.5 (88), 3.33 (88), 4.5[a] (85)[a,b] |
| 7 | Oxone® | 0.3 mmol | Solvent-free | 13.0 (-[c]) |
| 8 | $SiO_2$-$ZrPO_4H$ | 1.5 g | Solvent-free | 10.0 (-[c]) |
| 9 | $HIO_3$ | 0.25 mmol | Solvent-free | 10.0 (-[c]) |
| 10 | $H_5IO_6$ | 0.4 mmol | Solvent-free | 13.0 (-[c]) |
| 11 | $KHSO_4$ | 0.4 mmol | Solvent-free | 16.0 (-[c]) |
| 12 | $NaHSO_4.H_2O$ | 0.5 mmol | Solvent-free | 16.0 (30[c]) |
| 13 | $Fe(HSO_4)_3$ | 0.1 mmol | Solvent-free | 8.0 (15) |
| 14 | $Fe(HSO_4)_3$ | 0.2 mmol | Solvent-free | 4.0 (45) |
| 15 | $Fe(HSO_4)_3$ | 0.25 mmol | Solvent-free | 2.0 (100) |
| 16 | $Mg(HSO_4)_2$ | 0.15 mmol | Solvent-free | 5.0 (33) |
| 17 | $Mg(HSO_4)_2$ | 0.2 mmol | Solvent-free | 3.5 (53) |
| 18 | $Mg(HSO_4)_2$ | 0.25 mmol | Solvent-free | 2.0 (100) |
| 19 | $Ca(HSO_4)_2$ | 0.2 mmol | Solvent-free | 4.0 (55) |
| 20 | $Ca(HSO_4)_2$ | 0.25 mmol | Solvent-free | 2.0 (87), 4.0 (72), 4.45 (61), 6.0[a] (54)[a,b] |

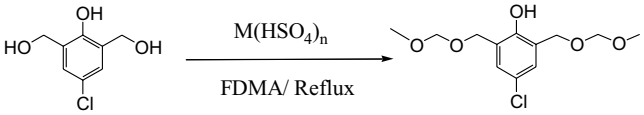
[a] The same recycled catalyst was used for each of the four runs. [b] Isolated yield. [c] No reaction.

**Scheme II**




| | Alcohol protected | Phenol protected |
|---|---|---|
| M= Al | 83% | 0% |
| M= Fe | 80% | 0% |
| M= Mg | 86% | 0% |
| M= Ca | 83% | 0% |

**Scheme III**

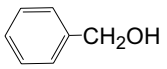
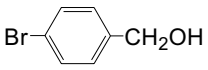
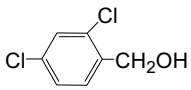
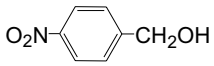
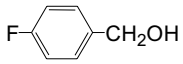
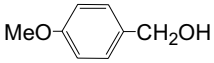
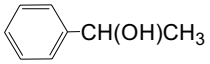
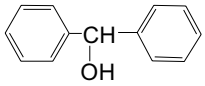
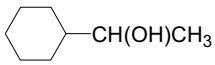
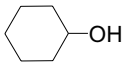
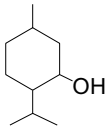
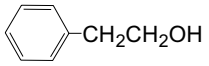
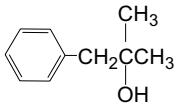
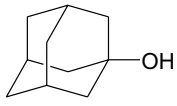



I II

4-substituted-2,6-dihydroxymethylphenol under acidic media;[19] when we used the protected phenolic hydroxyl group analogues (anisole derivatives) as starting materials the yields of reactions were increased (Table 3, entries 2 and 3).

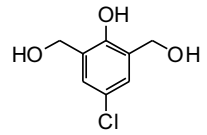
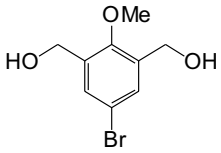
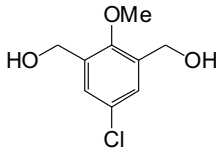
In conclusion, we have demonstrated that $M(HSO_4)_n$ can be used for the methoxymethylatoin of primary, secondary, and tertiary alcohols by formaldehyde dimethoxy acetal. We hope that $Al(HSO_4)_3$ will be superior to the other inorganic acidic metal hydrogen sulfates analogues due to a combination of Lewis and protic acidity.[3] The notable advantages of this method are mild reaction conditions, high yields, cheapness, safety and eco-friendliness, and recyclablity of the catalysts.

Table 2. Preparation of MOM-ethers from alcohols (1 mmol) and formaldehyde dimethoxy acetal (10 mmol) in the presence of $M(HSO_4)_n$ (M = Al, 0.2 mmol; M = Fe, Mg, Ca, 0.25 mmol) at room temperature and solvent-free conditions

| Entry | Substrate | $Al(HSO_4)_3$ Time (Yield) h (%)[a,b] | $Fe(HSO_4)_3$ Time (Yield) h (%)[a,b] | $Mg(HSO_4)_2$ Time (Yield) h (%)[a,b] | $Ca(HSO_4)_2$ Time (Yield) h (%)[a,b] |
|---|---|---|---|---|---|
| 1 |  | 1.67 (83) | 2.25 (80) | 2.5 (86) | 2.5 (83) |
| 2 |  | 4.0 (90) | 3.5 (89) | 4.0 (85) | 2.5 (83) |
| 3 |  | 0.67 (85) | 4.5 (90) | 5.0 (88) | 2.5 (89) |
| 4 |  | 12.0 (75[c]) | 10.0 (78[c]) | 11.0 (75[c]) | 17.0 (75[c]) |
| 5 |  | 0.86 (85) | 3.5 (80) | 4.0 (75) | 3.5 (85) |
| 6 |  | 0.33 (89) | 2.0 (82) | 2.0 (80) | 0.75 (83) |
| 7 |  | 3.0 (88) | 3.75 (72) | 2.75 (75) | 4.0 (77) |
| 8 |  | 0.33 (90) | 2.5 (90) | 2.5 (91) | 2.5 (90) |
| 9 |  | 1.5 (73) | 2.5 (74) | 2.25 (70) | 3.5 (72) |
| 10 |  | 1.0 (78) | 2.5 (81) | 3.0 (83) | 2.0 (80) |
| 11 |  | 17.5 (85) | 18 (77) | 20.0 (75) | 21.0 (72) |
| 12 | $CH_3(CH_2)_6CH_2OH$ | 4.5 (61) | 3.25 (63) | 3.0 (57) | 4.5 (60) |
| 13 |  | 0.42 (95) | 2.0 (91) | 2.0 (85) | 2.0 (87) |
| 14 |  | 14.0 (78) | 9.5 (80) | 12.0 (80) | 13.0 (72) |
| 15 |  | 8.5 (75[d]) | 9.0 (70[d]) | 9.0 (75[d]) | 9.5 (70[d]) |

[a] Isolated yield. [b] All of the isolated products are known compounds and their spectra and physical data have been reported in the literature.[17,18] [c] FDMA (30 mmol) was used. [d] Reaction conditions: to the mixture of alcohol (1 mmol), FDMA (30 mmol), and $CH_3CN$ (3 mL) $M(HSO_4)_n$ (0.3 mmol) were added at reflux conditions.

Table 3. Preparation of bis-MOM-ethers from bis-alcohols (1 mmol) and formaldehyde dimethoxy acetal (40 mmol) in the presence of $M(HSO_4)_n$ (M = Al, 0.6 mmol; M = Fe, Mg, Ca, 0.75 mmol) under reflux conditions

| Entry | Substrate | $Al(HSO_4)_3$ Time (Yield) h (%)[a] | $Fe(HSO_4)_3$ Time (Yield) h (%)[a] | $Mg(HSO_4)_2$ Time (Yield) h (%)[a] | $Ca(HSO_4)_2$ Time (Yield) h (%)[a] |
|---|---|---|---|---|---|
| 1 |  | 18 (30[e]) | 17 (28[e]) | 17.5 (25[e]) | 16.5 (32[e]) |
| 2 |  | 12.5 (76) | 13 (77) | 15.0 (85) | 16.0 (70) |
| 3 |  | 13.0 (74) | 13 (75) | 15.5 (82) | 16.5 (70) |

[a] Isolated yield. [e] Reaction conditions: to the mixture of alcohol (1 mmol), FDMA (60 mmol), and $M(HSO_4)_n$ [Al: (0.5 mmol), Fe, Mg, Ca: (0.75 mmol)] were added in reflux conditions.

## EXPERIMENTAL SECTION

### General

Substrates were purchased from Fluka, Merck and Aldrich chemical companies. $Al(HSO_4)_3$, $Fe(HSO_4)_3$, $Mg(HSO_4)_2$, $Ca(HSO_4)_2$,[4-6] and 2,6-bis-hydroxymethyl-4-chloro-phenol and 4-substituted-2,6-dihydroxymethyl anisole were prepared according to our previously reported procedures.[19,20]

### General Procedure

To a solution of alcohol (1 mmol) and FDMA (10 mmol), $M(HSO_4)_n$ (M = Al, 0.2 mmol; M = Fe, Mg, Ca, 0.25 mmol) was added, and the suspension was stirred for an appropriate time. After completion of the reaction, the excess of FDMA was removed by distillation. Then, t-butyl methyl ether (10 mL) was added and the mixture was filtered off. Water (10 mL) was added and neutralized with $NaHCO_3$ (10%) and extracted with t-butyl methyl ether (2 × 10 mL). The organic layer was dried over anhydrous $Na_2SO_4$ (3 g) and evaporation of the solvent on a rotary evaporator afforded a residue, which was passed through a short pad of silica gel using a mixture of ethyl acetate and *n*-hexane as eluent to afford the highly pure MOM-ether.

### Typical Procedure for the Preparation of 4-Chloro-2,6-bis-methoxymethoxy-methyl-phenol (II)

To a solution of 2,6-bis-hydroxymethyl-4-chloro-phenol (**I**), (0.188 g, 1 mmol) and FDMA (4.56 g, 60 mmol), $M(HSO_4)_n$ [Al: (0.159 g, 0.5 mmol), Fe, Mg, Ca: (0.75 mmol, 0.260 g, 0.163 g, 0.175 g respectively)] was added, and the suspension was refluxed. The progress of the reaction was monitored by TLC; after completion of the reaction (Table 3, entry 1) the mixture was filtered, and the remaining metal hydrogen sulfate was washed with methanol (2 × 10 mL) and distilled; the solvent afforded a residue, which was passed through a column of silica gel using a mixture of ethyl acetate and *n*-hexane as eluent to afford white crystals (mp 99 °C), 0.132 g, 30% of the product (**II**).

IR (KBr): 3195, 2916, 2852, 1599, 1463, 1377, 1229, 1082, 992, 852, 737, 577 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 90 MHs): δ 4.545 (s, 6H), 4.767 (s, 4H), 5.170 (s, 4H), 6.800 (s, 2H), 7.675 (b, 1H).

$^{13}C$ NMR ($CDCl_3$, 22.5 MHz): δ 65.782, 91.360, 95.983, 124.036, 127.301, 128.301, 152.525.

### 4-Chloro-2,6-bis-methoxymethoxy-methyl-anisol

To a solution of 2,6-bis-hydroxymethyl-4-chloro-anisol (0.202 g, 1 mmol) and FDMA (3.04 g, 40 mmol),

$M(HSO_4)_n$ [Al: (0.159 g, 0.5 mmol), Fe, Mg, Ca: (0.75 mmol, 0.260 g, 0.163 g, 0.175 g, respectively)] was added and the suspension was refluxed. The progress of the reaction was monitored by TLC; after completion of the reaction (Table 3, entry 3) the excess of FDMA removed by distillation, and the remaining metal hydrogen sulfate washed with methanol (2 × 10 mL) and distilled the solvent afforded a residue, which was passed through a column of silica gel using a mixture of ethyl acetate and *n*-hexane as eluent to afford white crystals (mp 45-47 °C), of the product.

IR (KBr): 3019, 2959, 2837, 1592, 1463, 1377, 1292, 1247, 1093, 1037, 825, 590.

$^1$H-NMR ($CDCl_3$, 90 MHs): δ 3.90 (s, 3H), 4.33 (s, 6H), 4.82 (s, 4H), 5.25 (s, 4H), 7.08 (s, 2H).

$^{13}$C-NMR ($CDCl_3$, 22.5 MHz): δ 66.35, 92.76, 97.08, 102.65, 127.36, 132.55, 134.42, 152.12.

**4-Bromo-2,6-bis-methoxymethoxy-methyl-anisol**

To a solution of 2,6-bis-hydroxymethyl-4-bromo-anisol (0.247 g, 1 mmol) and FDMA (3.04 g, 40 mmol), $M(HSO_4)_n$ [Al: (0.159 g, 0.5 mmol), Fe, Mg, Ca: (0.75 mmol, 0.260 g, 0.163 g, 0.175 g respectively)] was added and the suspension was refluxed. The progress of the reaction was monitored by TLC; after completion of the reaction (Table 3, entry 2) the excess of FDMA was removed by distillation, and the remaining metal hydrogen sulfate washed with methanol (2 × 10 mL) and distilled the solvent afforded a residue, which was passed through a column of silica gel using a mixture of ethyl acetate and *n*-hexane as eluent to afford white crystals (mp 64-66 °C), of the product.

IR (KBr): 3059, 2945, 2828, 1584, 1461, 1290, 1248, 1075, 1041, 825, 606.

$^1$H-NMR ($CDCl_3$, 90 MHs): δ 3.90 (s, 3H), 4.33 (s, 6H), 4.82 (s, 4H), 5.27 (s, 4H), 7.25 (s, 2H).

$^{13}$C-NMR ($CDCl_3$, 22.5 MHz): δ 66.35, 92.76, 97.08, 101.45, 126.65, 128.65, 132.32, 153.67

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