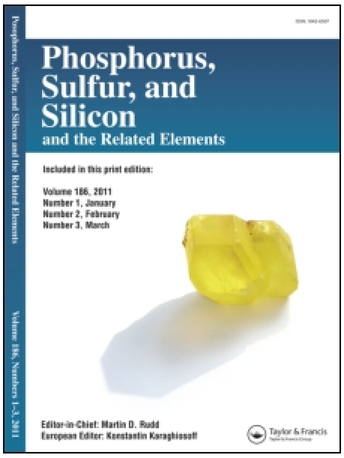

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Catalytic Conversion of Epoxides to 1,3-Dioxolanes with Phosphomolybdic Acid (PMA) in Solution and under Solvent-Free Conditions

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To cite this Article Zeynizadeh, Behzad and Sadighnia, Leila(2008) 'Catalytic Conversion of Epoxides to 1,3-Dioxolanes with Phosphomolybdic Acid (PMA) in Solution and under Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 9, 2274 — 2279

To link to this Article: DOI: 10.1080/10426500801960554

URL: http://dx.doi.org/10.1080/10426500801960554

Phosphorus, Sulfur, and Silicon, 183:2274–2279, 2008
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500801960554

Catalytic Conversion of Epoxides to 1,3-Dioxolanes with Phosphomolybdic Acid (PMA) in Solution and under Solvent-Free Conditions

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The fast and efficient conversion of epoxides into 2,2-dimethyl-1,3-dioxolanes was studied with catalytic amounts of phosphomolybdic acid (PMA) (0.1-0.2 mol %) at room temperature in solution and under solvent-free conditions. The products were obtained in high to excellent yields within 1–2 min.

Keywords 1,3-Dioxolanes; catalytic; epoxides; phosphomolybdic acid; solvent-free

INTRODUCTION

Direct conversion of an epoxide to a 2,2-dimethyl-1,3-dioxolane with acetone instead of adding water to form a diol and the subsequent protection with a carbonyl compound is subject of interest due to the importance of 1,3-dioxolanes as widely used protecting groups for diols particularly for carbohydrates and steroid chemistry.[1,2] In addition, 1,3-dioxolanes are very suitable derivatives of diols for GC, GLC and mass spectrometry.[3] The literature review shows that direct transformation of epoxides into 1,3-dioxolanes has been carried out with some reagents or catalysts including $CuSO_4$,[3] HBF_4,[4] $BF_3.OEt_2$,[5] $SnCl_2$,[6] $SnCl_4$,[7] $TiCl_4$,[8] $TiO(TFA)_2$ and $TiCl_3(OTf)$,[9] $BiCl_3$, $Bi(TFA)_3$ and $Bi(OTf)_3$,[10] zeolite,[11] KSF clay,[12] montmorillonite K10,[13] 2,4,4,6-tetrabromo-2,5-cyclohexadienone,[14] $Sn^{II}(TPP)(ClO_4)$,[15] and *N*-benzyl-2-cyanopyridinium hexafluoroantimonate.[16] Among these reagents, $BF_3.OEt_2$ has been used for conversion of different types of carbonyl compounds into 1,3-dioxolanes with ethylene and propylene oxides. Transition metal catalysts such as $[C_5Me_5Ir(NCCH_3)_3]$,[17] CH_3ReO_3,[18]

Received 12 July 2007; accepted 4 February 2008.

The authors gratefully acknowledge the Research Council of Urmia University for financial support of this work.

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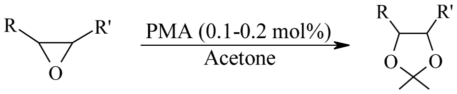


SCHEME 1

$RuCl_3^{19}$ and $Er(OTf)_3^{20}$ can also catalyze the title reaction. Recently, polyoxometalates such as $(NH_4)_8[CeW_{10}O_{36}] \cdot 20\ H_2O$,[21] $K_5CoW_{12}O_{40} \cdot 3\ H_2O$[22] and Wells-Dawson heteropolyacid $H_7P_2Mo_{17}VO_{62}^{23}$ were also effectively used for the direct conversion of epoxides into 1,3-dioxolanes. Although the direct transformation of epoxides into 1,3-dioxolanes has been studied with various reagents/catalysts, new effective catalysts for both academic and practical applications are still of interest.

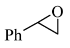
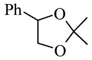
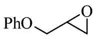
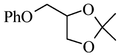
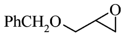
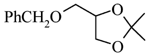
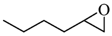
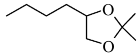
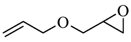
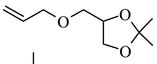
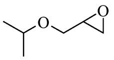
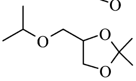
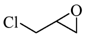
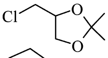
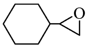
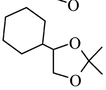
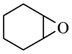
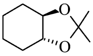
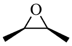
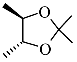
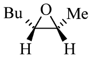
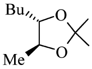
Herein, we report the immediate and direct conversion of epoxides into 2,2-dimethyl-1,3-dioxolanes with 0.1—0.2 mol% of phosphomolybdic acid, $H_3[PMo_{12}O_{40}] \cdot x\ H_2O$, at room temperature in solution and under solvent-free conditions (Scheme 1).

RESULTS AND DISCUSSION

Heteropolyacids and their salts have many advantages as catalysts which make them economically and environmentally attractive both in academic and industrial chemistry. These compounds are effective catalysts for various reactions and have high capability in practical uses because their redox and acidic properties can be controlled at the atomic and molecular levels by changing the constituent elements according to the needs of the chemical process.[24] The homogenous catalysts and fine organic synthesis products catalyzed by heteropoly compounds have been extensively reviewed.[25] Environmental and economical considerations prompt an urgent need to redesign commercially important processes.

The literature review shows that phosphomolybdic acid (PMA) as a commercially available reagent has found useful applications in organic synthesis.[26] In one example, it was reported that the reaction of methyloxirane and acetone with 1 wt.% of PMA takes place with the formation of the corresponding 1,3-dioxolane and 32% polymeric product within 3 h.[13] The lack of systematic study in the direct conversion of structurally different epoxides into 2,2-dimethyl-1,3-dioxolanes with PMA and our research interest in this subject encouraged us to study this transformation. In a preliminary experiment styrene oxide in acetone solution and in the presence of 0.2 mol% of PMA was easily and efficiently converted to 2,2-dimethyl-4-phenyl-1,3-dioxolane without formation of any polymeric product. The reaction was completed within 2 min at room

TABLE I Conversion of Epoxides to 1,3-Dioxolanes with PMA in Solution and under Solvent-free Conditions[a]

Epoxide	1,3-Dioxolane	Solution[b] Mol % (cat.)	Solution[b] Yield (%)[d]	Solvent-free[c] Mol % (cat.)	Solvent-free[c] Yield (%)[d]	Ref.
		0.2	98	0.1	97	6
		0.2	98	0.1	98	20
		0.2	95	0.1	95	6
		0.2	90	0.1	93	20
		0.2	97	0.1	98	6
		0.2	95	0.1	94	10
		0.2	75	0.1	78	10
		0.2	89	0.1	86	6
		0.2	85	0.1	85	6
		0.2	78	0.1	77	20
		0.2	80	0.1	83	6

[a]All reactions were carried out at room temperature within 1–2 min. [b]Acetone (2 mL) was used as a solvent. [c]The reactions were carried out with 2 mmol of acetone. [d]Yields refer to isolated pure products.

temperature. This achievement prompted us to study the applicability of this synthetic method for conversion of epoxides bearing electron-releasing or withdrawing groups into the corresponding 1,3-dioxolanes in solution. Table I shows the general trend and versatility of this protocol. The reactions were carried out under mild conditions and completed within 2 min at room temperature. The corresponding 1,3-dioxolanes were obtained in high to excellent yields.

We also found that the direct conversion of styrene oxide to the corresponding 1,3-dioxolane with 2 molar equivalents of acetone in the presence of 0.1 mol% of phosphomolybdic acid takes place efficiently at room temperature without using any solvent. Based on this result we carried out the reactions of other epoxides with 2 molar equivalents of acetone in the presence of 0.1 mol% of phosphomolybdic acid without solvent. All reactions were completed within 1 min at room temperature with the formation of the corresponding 1,3-dioxolanes in high to excellent yields. The results are also summarized in Table I.

In conclusion, we have shown that structurally different epoxides were rapidly and efficiently converted into the corresponding 1,3-dioxolanes with catalytic amounts of phosphomolybdic acid at room temperature. The reactions were carried out either in solution or under solvent-free conditions. Due to the efficiency, mild reaction conditions, availability of phosphomolybdic acid and the easy work-up procedure this protocol could be considered a useful contribution to the present methodologies.

EXPERIMENTAL

All reagents and substrates were purchased from commercial sources with the best quality, and they were used without further purification. NMR spectra were recorded with a 300 MHz Bruker Avance spectrometer. The products were characterized by ^1H and ^{13}C NMR spectroscopy. All yields refer to isolated pure products. TLC was applied for purity determination of the substrates, products and reaction monitoring using silica gel 60 F_{254} aluminum sheets.

General Procedure for Conversion of Epoxides to 1,3-Dioxolanes with Phosphomolybdic Acid in Acetone Solution

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of the epoxide (1 mmol) in acetone (2 mL) was prepared and then phosphomolybdic acid (0.0036 g, 0.002 mmol) was added. The reaction mixture was stirred for 2 min and the progress of the reaction was monitored by TLC (CCl_4/Et_2O: 5/2). After completion of the reaction, water (4 mL) was added and the reaction mixture was stirred for 2 min. The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and the combined extracts were then dried over anhydrous Na_2SO_4. Evaporation of the solvent gives the pure 1,3-dioxolane in 75–98% yield.

General Procedure for Conversion of Epoxides to 1,3-Dioxolanes with Phosphomolybdic Acid under Solvent-free Conditions

To a round-bottomed flask (10 mL) equipped with a magnetic stirrer and charged with the epoxide (1 mmol), acetone (0.116 g, 2 mmol) and then phosphomolybdic acid (0.0018 g, 0.001 mmol) was added. The mixture was stirred for 1 min and the progress of the reaction was monitored by TLC (CCl_4/Et_2O: 5/2). Water (4 mL) was then added and the reaction mixture was stirred for 2 min. The mixture was extracted with CH_2Cl_2 (3×5 mL) and the combined extracts were then dried over anhydrous Na_2SO_4. Evaporation of the solvent affords the pure 1,3-dioxolane in 77−98% yield.

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