

Efficient and Regioselective Alcoholysis of Styrene Oxide by Aluminium Phosphotungstate Nanocatalyst; on the Temperature Dependence Aspect

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Abstract: In the presence of alcohols and a very low amount of the aluminium dodecaphosphotungstate $\text{AlPW}_{12}\text{O}_{40}$, styrene oxide efficiently leads to β -alkoxy alcohols at low temperatures.

Key words: heteropolyacid • Catalysis • Styrene oxide • Alcoholysis • β -alkoxy alcohols

INTRODUCTION

Epoxides are valuable compounds because their easy transformation into an array of functional organic intermediates [1-2]. Ring-opening of epoxides with alcohols leads to β -alkoxy alcohols [3-4] which are widely applied in pharmaceutical [5-6] and natural chemistry [7]. Various systems have been used to catalyze the alcoholysis [8-15]. Given our research topic on the heteropolyacids as catalysts [16-19], we became interested on their use for the alcoholysis of styrene oxide (**1**). According to the literature, this reaction, at room temperature, can be mediated by 1-2 mol% of $\text{AlPW}_{12}\text{O}_{40}$ [15]. We now disclose that such a reaction occurs efficiently with lower amounts of the catalyst and is effective with a more variety of alcohols (Eq. 1). Also the reactions carried out at three different temperatures.

Experimental: $\text{AlPW}_{12}\text{O}_{40}$ was prepared by small modifications of the reported procedure [20]. Aluminium foil (160 mg) and 12-tungstophosphoric acid (16 g) [21]

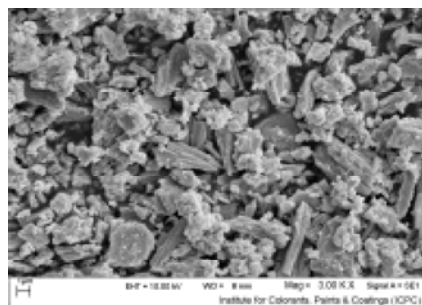
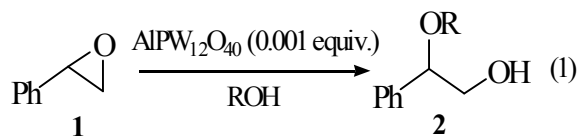
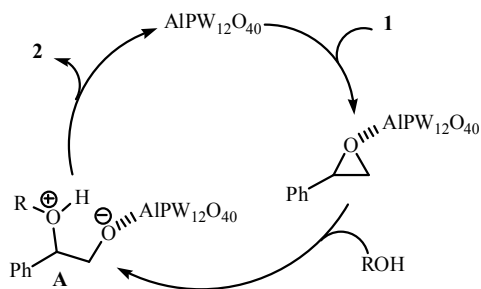


Fig. 1: SEM of aluminium phosphotungstate

were added to distilled water (30 mL). After stirring at room temperature for 14 days, the mixture was filtered. The recovered crystals were recrystallized three times in water to obtain colorless crystals, which were identified by ICP, FT-IR and SEM (Fig. 1). They were heated at 100°C for a night before use.

Typical methanolysis procedure, $\text{AlPW}_{12}\text{O}_{40}$ (0.003 g, 0.001 mmol) was added to the solution of styrene oxide (124 mg, 1 mmol) in MeOH (5 mL). The mixture was heated to 40°C for 5 min, then cooled and filtered through the short pad of alumina. Chromatography on silica eluted with petroleum ether/ethyl acetate (85/15) led to 2-methoxy-2-phenylethanol (152 mg) which was identified from the comparison of its ¹HNMR data with those of literature.

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Scheme 1

RESULTS AND DISCUSSIONS

Experiments have been firstly carried out using an alcoholic solution of **1** containing 0.001 equiv. of $\text{AIPW}_{12}\text{O}_{40}$ which was heated at 40°C for 5 min (Table 1). Under these conditions, conversions of at least 97% were obtained with an array of alcohols. Primary and secondary saturated alcohols afforded the corresponding 2-alkoxy-2-phenyl ethanol (**2**) in high yields (Runs 1-3), whereas the efficiency slightly decreased with allyl alcohol (Run 4) and secondary alcohols (Runs 5 and 6).

The production of **2** could be explained by coordination of the oxygen of **1** to the catalyst (Scheme 1). This favors the regioselective nucleophilic attack of ROH at the benzylic position to afford the ionic species **A**, which evolves towards **2** in liberating the starting catalyst.

The alcoholysis occur also at room temperature but the reaction times, especially for allyl alcohol and secondary alcohols, have to be increased to reach the full conversion (Table 2). Under these conditions, yields higher than 98% were again obtained with primary alcohols except allyl alcohol Runs 7-10, whereas improved yields were obtained with secondary alcohols (Runs 11 and 12).

According to the results assembled in Table 3, the increase of the reaction temperature to 60°C did not improve the alcoholysis process.

Table 1: Alcoholysis of styrene oxide (0.124 g, 1 mmol) using $\text{AIPW}_{12}\text{O}_{40}$ (0.003 g, 0.001 mmol) in alcohol (5 mL) at 40°C for 5 min.

Run	R	Conversion%	Yield%	Ref.
1	Me	100	99	10, 12, 13
2	Et	100	100	10, 12
3	<i>n</i> -Pr	97	100	10, 12, 16
4	$\text{CH}_2=\text{CHCH}_2$	100	83	13, 16
5	<i>i</i> -Pr	97	70	10
6	MeCHEt	100	71	16

Table 2: Alcoholysis of styrene oxide (0.124 g, 1 mmol) using $\text{AIPW}_{12}\text{O}_{40}$ (0.003 g, 0.001 mmol) in alcohol (5 mL) at RT.

Run	R	Time (min)	Yield%
7	Me	10	98
8	Et	10	100
9	<i>n</i> -Pr	25	100
10	$\text{CH}_2=\text{CHCH}_2$	25	68
11	<i>i</i> -Pr	125	94
12	MeCHEt	40	77

Table 3: Alcoholysis of styrene oxide (0.124 g, 1 mmol) using $\text{AIPW}_{12}\text{O}_{40}$ (0.003 g, 0.001 mmol) in alcohol (5 mL) at 60°C .

Run	R	Time (min)	Yield%
13	<i>n</i> -Pr	5	93
14	$\text{CH}_2=\text{CHCH}_2$	5	73
15	<i>i</i> -Pr	10	70
16	MeCHEt	10	56

CONCLUSION

The catalysis by very low amounts of Aluminum 12-Tungstophosphate of the alcoholysis of styrene oxide efficiently occurs with a variety of alcohols to regioselectively affords the corresponding 2-alkoxy-2-phenylethanol.

ACKNOWLEDGEMENTS

We thank Chemistry & Chemical Engineering Research Center of Iran (CCERCI) for the support of these studies.

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