$K_5CoW_{12}O_{40}\cdot 3H_2O$: a novel cobalt polyoxometalate catalyst for conversion of epoxides to acetonides

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A mild and efficient preparation of 1,3-dioxolanes from epoxides and acetone has been carried out in high to excellent yields under catalysis of potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) (0.01 molar equiv.).

KEY WORDS: catalyst; cobalt polyoxometalate; epoxide; 1,3-dioxolane; acetonide

1. Introduction

Epoxides are important intermediates in organic synthesis [1] and their reactions with different nucleophiles under both nonsolvolytic [1,2] and solvolytic conditions have been the subject of extensive studies [3]. 1,3-dioxolanes are among the most widely used protecting groups for carbonyl compounds [4]. The formation of cyclic acetals starting from oxiranes and carbonyl compounds can occur in two ways: (a) by hydrolysis of the oxirane to the appropriate diol, followed by acetalization [5,6], and (b) by direct condensation of the oxirane with a carbonyl compound. In the latter reaction no water is formed, which makes direct condensation, in some cases, a more suitable method than other procedures involving removal of water to shift the equilibrium. The direct conversion of an epoxide to 1,3-dioxolane instead of adding water to form diol with subsequent elimination in the presence of acetone has been studied with only a few reagents [7]. A Lewis acid such as boron trifluoride is a good catalyst in the condensation of oxiranes and carbonyl compounds; anhydrous copper sulfate in acetone converts many oxiranes to acetals [8]. Aromatic and aliphatic aldehydes, which are substituted in the α-position and oxiranes react in the presence of a catalyst amount of tetraethyl ammonium bromide to produce 1,3-dioxolanes in good yields. Photochemical cycloaddition of aldehydes and 1-ethoxy-carbonyl-2-methyl-3-phenyl oxirane (ethyl-2-methyl-3-phenylglycidate) has been described [5].

The use of KSF clay [9], HBF_4 [10] and some Lewis acids has been studied for this transformation. Most of these Lewis acids failed to give the desired product [11–13]. Among Lewis acids, $BF_3\cdot OET$ has been successfully used for conversion of different types of carbonyl compounds to their corresponding 1,3-dioxolane derivatives with only ethylene and propylene oxides [14]. Recently the use of $RuCl_3$ [7], $TiCl_3(OTf)$ [15] and TiO(TFA) [5], bismuth(III) salts [16] and iron(III) trifluoroacetate [17], was reported for preparation of 1,3-dioxolanes from acetone and epoxides.

Heteropoly compounds provide a good basis for the molecular design of mixed oxide catalysts and they have high capability in practical uses. The catalytic function of heteropoly compounds has attracted much attention and they are used in solution as well as in the solid state as acid and oxidation catalysts. The reason why heteropoly catalysts are attractive is their variety and high potential as catalysts [18–21]. In this paper, during the course of our studies we present the conversion of epoxides to their 1,3-dioxolanes with acetone in the presence of potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) as a very efficient and reusable catalyst.

2. Experimental

2.1. Preparation of the catalyst

The synthesis of potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) starts with the preparation of sodium tungstodicobalt(II)ate from cobaltous acetate (2.5 g, 0.01 mol) and sodium tungstate (19.8 g, 0.06 mol) in acetic acid and water at pH 6.5–7.5. The sodium salt is then converted to potassium salt by treatment with potassium chloride (13 g). Finally, the cobalt(II) complex is oxidized to the cobalt(III) complex by potassium persulfate (10 g) in 40 ml of 2 M H_2SO_4. The crystals of $K_5CoW_{12}O_{40}\cdot 20H_2O$ were dried at 200 °C, after recrystalization with methanol, potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) was obtained. The structure of catalyst was confirmed by IR, UV-Vis, magnetic susceptibility, thermal gravimetric analysis (TGA), and elemental analysis [22–25].

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2.2. Typical procedure

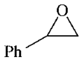
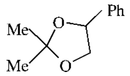
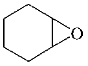
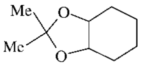
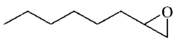
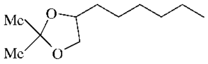
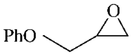
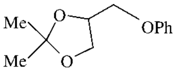
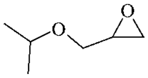
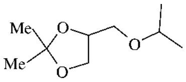
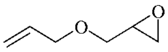
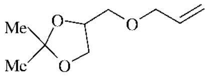
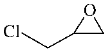
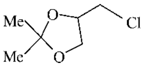
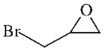
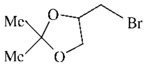
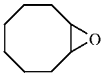
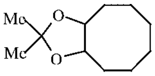
This procedure is performed by refluxing a mixture of the epoxides (1 mmol) in acetone (2 ml) in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$ (0.01 mmol) for the selected reaction time. The 1,3-dioxolanes were purified by distillation or by flash chromatography over silica gel and fully charactterized.

3. Results and discussion

Initial studies on cobalt polyoxometalate as a new catalyst for conversion of epoxides to acetonides showed $K_5CoW_{12}O_{40}\cdot 3H_2O$ to be an effective catalyst. As summarized in table 1, high to excellent yields of 1,3-dioxolanes were obtained in all cases. Various epoxides with both electron withdrawing and releasing groups were reacted with acetone in the presence of catalytic amounts (0.01 molar equiv.) of $K_5CoW_{12}O_{40}\cdot 3H_2O$. Reactions were followed by GC or TLC and the best result for this methodology was found for acetal formation with styrene epoxide (table 1, entry 1). Steric hindrance about the epoxide and electron withdrawing groups strongly inhibits acetal formation (table 1, entries 4 and 7–9).

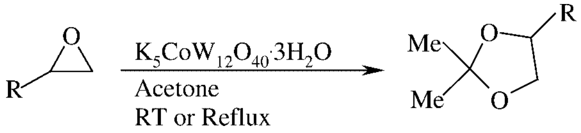
Table 1

Conversion of epoxides to 1,3-dioxolanes catalyzed by $K_5CoW_{12}O_{40}\cdot 3H_2O$.

Entry	Epoxide	1,3-dioxolane[a]	Time (min) (Condition)	Yield[b] (%)
1			5 (RT)	95
2			15 (RT)	94
3			60 (Reflux)	90
4			240 (Reflux)	75
5			180 (Reflux)	94
6			120 (Reflux)	85
7			420 (Reflux)	75
8			420 (Reflux)	70
9			420 (Reflux)	25

[a] The products were characterized by comparison of their physical and spectral data with those of authentic samples.

[b] Isolated yield.



Scheme 1.

The use of epoxides for acetal formation offers the advantage of being extremely gentle, operating at room temperature or reflux condition. In addition, preliminary isolation of the products simply involves removal of catalyst. In addition, we have found that cobalt polyoxometalate, $K_5CoW_{12}O_{40}\cdot 3H_2O$, can be reused several times without loss of activity, simply by filtering the catalyst, washing with acetone, drying and immediately reusing. The yield of the acetonide of styrene oxide promoted by the recovered catalyst for four times remained 95% and after seven times was about 85%.

Synthesis of 1,3-dioxolane of styrene oxide was performed with other polyoxometalates and the catalytic activities of these catalysts appear to be in the following order: $H_4SiW_{12}O_{40}\cdot xH_2O$ (21%), $K_5PMnW_9Mo_2O_{39}\cdot 3H_2O$ (20%), $Na_3PW_{12}O_{40}\cdot 12H_2O$ (18%), α-$K_7PW_9Mo_2O_{39}\cdot 12H_2O$ (12%), α_2-$K_7P_2W_{17}O_{62}(Mn^{2+}\cdot H_2O)\cdot 12H_2O$ (11%), β-$Na_8HPW_9O_{34}\cdot 18H_2O$ (9%). Since publication of Chester's work in 1970, $CoW_{12}O_{40}^{5-}$ and related polyoxometalate anions have been used as well-defined outer-sphere electron transfer agents in over 50 published studies [26]. Meanwhile, the potential utility of numerous polyoxometalate anions as electron transfer agents in the selective catalytic oxidations of organic substrates of practical importance has been fully recognized [27–30]. We suggest that ring opening of the epoxides followed by acetal formation is potentially performed through an electron transfer mechanism. This suggestion was confirmed by selective ring opening of different epoxides with alcohols, water and acetic acid by this catalyst. The possibility of concerted electron transfer mechanism was strongly supported by a large decrease of the reaction rate with addition of small amount of acrylonitrile (as a radical scavenger) in the reaction of epoxides with acetone in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$.

In summary, $K_5CoW_{12}O_{40}\cdot 3H_2O$ mediates the reaction of epoxides with acetone. This property leads to a gentle method for acetal formation (scheme 1). The approach is applicable to both large- and small-scale reactions. The selectivity of acetal formation is under study.

4. Conclusion

In conclusion we have shown the synthesis of 1,3-dioxolanes in a new and efficient way using a reusable catalyst, which can be used without activation. Moreover, our procedure compared with the previously reported methods, generally shows a mild and simple method for preparation of acetonides from epoxides and acetone.

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