

Efficient Preparation of *vic*-Diacetates from Epoxides and Acetic Anhydride in the Presence of Iron(III)-substituted Polyoxometalate as Catalyst

Bahram Yadollahi* and Farhad Kabiri Esfahani

Institute for Advanced Studies in Basic Sciences (IASBS), Gava Zang, Zanjan 45138-79368, Iran

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Iron(III)-substituted polyoxometalate $(\text{TBA})_4\text{PFeW}_{11}\text{O}_{39} \cdot 3\text{H}_2\text{O}$, has been demonstrated as an efficient catalyst in the ring opening of 1,2-epoxides with acetic anhydride for the one-pot synthesis of 1,2-diol esters in high to excellent yields under solvent-free condition.

Because of their ease of formation and wide reactivity with nucleophiles, Lewis acids, radicals, reducing agents, oxidizing agents, acids, and bases, epoxides are often used as starting material and intermediates in organic synthesis.¹ The opening of epoxides to the corresponding alcohols is one of the most useful reactions in organic synthesis,² and O-acetylation of hydroxy group is one of the most important and widely used transformations in organic chemistry,³ especially in the construction of polyfunctional molecules such as nucleosides, carbohydrates, steroids, and natural products as a protection strategy.⁴ Thus, it is very important if we have epoxide which opens to yield corresponding 1,2-diol diacetate selectively, and for example if we need to 1,2-diol, this 1,2-diol diacetate can be hydrolyzed and used in other synthesis procedures.

As a part of our continued effort to explore unique reactivity of polyoxometalates,⁵ we try to use from transition metal-substituted polyoxometalates as catalyst in the ring-opening reaction of 1,2-epoxides with acetic anhydride. Transition metal-substituted polyoxometalates as oxidatively stable inorganic porphyrins have received much attention in the preceding two decades.⁶ The versatility of these catalysts has also been demonstrated by applications in various oxidation reactions. The possibility of working with these polyoxometalates in both polar and nonpolar solvents can lead to valuable applications in catalysis. However, there has been very little exploitation of their catalytic reactivity in nucleophilic ring-opening of epoxides.⁷

The tetrabutylammonium (TBA) salts of transition metal-substituted polyoxometalates, $(\text{TBA})_n[\text{PMW}_{11}\text{O}_{39}] \cdot x\text{H}_2\text{O}$, $\text{M} = \text{V}^{\text{III}}$, Cr^{III} , Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II} , used in this work have been prepared previously.⁸ In our work, the required catalysts were made by starting from an aqueous solution of the required anion prepared in situ, to which was added a solution of TBA bromide, and determined by spectroscopy methods like elemental and thermogravimetric analysis, IR and UV-vis spectroscopy, and powder X-ray diffraction method. The results indicated that the hydration numbers for all of these compounds are about 3.

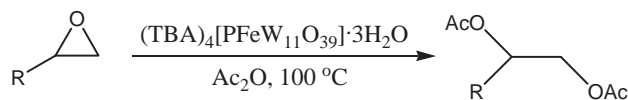
The reactions involving one-pot transformations of substrates to products are currently of interest because of potential applications in organic synthesis. As mentioned above, we used from tetrabutylammonium salts of transition metal-substituted kegglin-type polyoxometalates as a suitable and efficient catalyst in one-pot synthesis of 1,2-diol diacetates from 1,2-epoxides and acetic anhydride under solvent free condition.

At first, we examined the reaction of phenyl glycidyl ether (1 mmol) with acetic anhydride (net solvent) using catalytic amounts of various polyoxometalate complexes at 100 °C temperature to give the corresponding 1,2-diol esters. Although the reaction without a catalyst gave no product (below 3%), it proceeded catalytically upon addition of transition metal-substituted polyoxometalates. Among the catalysts tested, Fe^{III} -substituted polyoxometalate, $(\text{TBA})_4\text{PFeW}_{11}\text{O}_{39} \cdot 3\text{H}_2\text{O}$ was found to be highly active for the reaction (99%). The catalytic activity for other transition metal-substituted polyoxometalates, after 3 h reaction appears to be in the following order: $(\text{TBA})_5\text{PW}_{11}\text{MnO}_{39} \cdot 3\text{H}_2\text{O}$ (93%) > $(\text{TBA})_5\text{PW}_{11}\text{CoO}_{39} \cdot 3\text{H}_2\text{O}$ (78%) \approx $(\text{TBA})_4\text{PW}_{11}\text{VO}_{40} \cdot 3\text{H}_2\text{O}$ (78%) > $(\text{TBA})_5\text{PW}_{11}\text{ZnO}_{39} \cdot 3\text{H}_2\text{O}$ (57%) > $(\text{TBA})_4\text{PW}_{11}\text{CrO}_{39} \cdot 3\text{H}_2\text{O}$ (50%) > $(\text{TBA})_5\text{PW}_{11}\text{CuO}_{39} \cdot 3\text{H}_2\text{O}$ (30%) > $(\text{TBA})_5\text{PW}_{11}\text{NiO}_{39} \cdot 3\text{H}_2\text{O}$ (20%) > $(\text{TBA})_5\text{H}_2\text{PW}_{11}\text{O}_{39} \cdot 3\text{H}_2\text{O}$ (5%).

After studied the various amount of the catalyst, we found that the 0.05 equiv. from $(\text{TBA})_4\text{PFeW}_{11}\text{O}_{39} \cdot 3\text{H}_2\text{O}$ is the best, and the synthesis of 1,2-diol diacetate was efficiently achieved under this condition. To show the scope of the reaction, we extended it to a variety of epoxides, and in all cases a very clean reaction was observed. Thus 1,2-epoxides (1 mmol) were treated with acetic anhydride (2 mL) in the presence of $(\text{TBA})_4\text{PFeW}_{11}\text{O}_{39} \cdot 3\text{H}_2\text{O}$ (5 mol %) at 100 °C temperature (Scheme 1), and after appropriate time gave the corresponding 1,2-diol diacetate in high to excellent yields (Table 1).

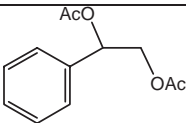
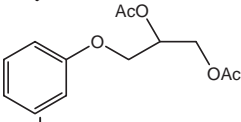
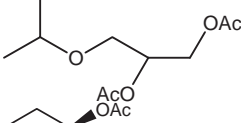
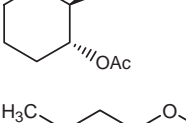
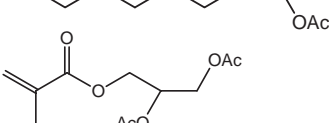
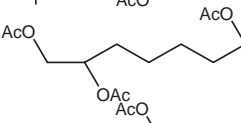
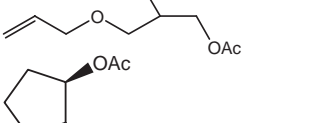
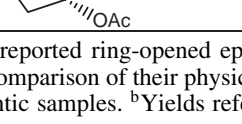
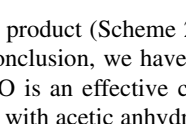
As shown in Table 1, the reaction of various epoxides such as cyclohexene and cyclopenten oxides, styrene oxide, allyl 2,3-epoxypropyl ether, 2,3-epoxypropyl isopropyl ether, and 2,3-epoxypropylphenyl ether as examples of aliphatic, alicyclic, activated and deactivated epoxides, affording the corresponding 1,2-diol diacetates in high to excellent yields and good reaction times. Moreover, the reactions are clean and chemoselective while no side products or decomposition of the products is observed. For example, with α,β -unsaturated 2,3-epoxypropyl metacrylate and allyl 2,3-epoxypropyl ether, we have only diacetylated product and any of other side products have not obtained. Thus, in comparison with some of the reported results for other catalytic systems,⁹ the use of $(\text{TBA})_4\text{PFeW}_{11}\text{O}_{39} \cdot 3\text{H}_2\text{O}$ is more suitable and give better results.

One could imagine a mechanism for this reaction in which Fe in $(\text{TBA})_4\text{PFeW}_{11}\text{O}_{39} \cdot 3\text{H}_2\text{O}$ (POM) undergoes addition to one of the carbonyl groups of acetic anhydride, the resulting intermediate reacts with epoxide and then reacts with CH_3COO^- , that is produced in this step, gives the final 1,2-diol



Scheme 1.

Table 1. Fe^{III}-substituted polyoxometalate ((TBA)₄PFeW₁₁-O₃₉·3H₂O) catalyzed ring opening of epoxides with acetic anhydride

Entry	1,2-Diol diacetate ^a	Time /h	Yield /% ^b
1		2	95
2		3	93
3		3.5	91
4		2.75	96
5		3.25	95
6		2.3	93
7		4	94
8		3.5	95
9		2.5	93

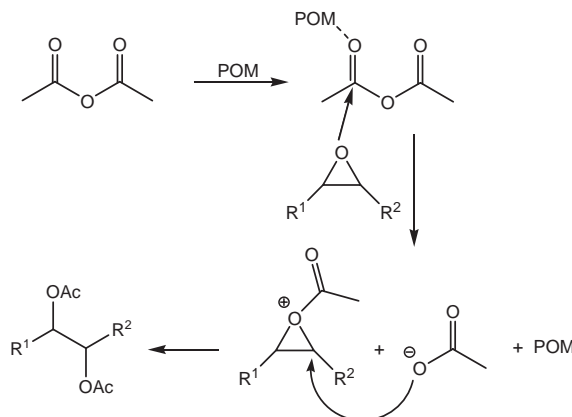
^aAll the reported ring-opened epoxide derivatives were identified by comparison of their physical and spectral data with those of authentic samples. ^bYields refer to isolated yield.

diacetate product (Scheme 2).

In conclusion, we have demonstrated that (TBA)₄PFeW₁₁-O₃₉·3H₂O is an effective catalyst for the ring opening of 1,2-epoxides with acetic anhydride. The reaction occurs with excellent regioselectivity giving the *trans*-1,2-addition products for a wide range of epoxides. This system is a novel, mild, simple, and clean method, and with advantages such as ease of preparation of catalyst, good reaction times, simplicity in operation, the low cost of reagents, and high to excellent yields, it is a valuable method for one-pot synthesis of 1,2-diol diacetates. Further investigations on the catalytic role of transition metal-substituted polyoxometalates in organic reactions are underway.

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**Scheme 2.** Proposed mechanism for the ring opening of 1,2-epoxides with acetic anhydride in the presence of Fe^{III}-substituted polyoxometalate.

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