Reactions of oxiranes and carbonyl compounds catalyzed by ammonium decatungstocerate(IV)

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Various types of oxiranes react with acetone in the presence of catalytic amounts of ammonium decatungstocerate(IV) icosahydrate, $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$, to give the corresponding 1,3-dioxolanes in excellent yields.

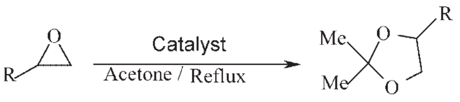
KEY WORDS: catalyst; oxirane; 1,3-dioxolane; cerium polyoxometalate; epoxide.

1. Introduction

Acetals are among the most popular protecting group for carbonyl compounds [1]. In addition, they are useful intermediates, particularly in carbohydrate [2] and steroid [3] chemistry and are very well suited for GC, GLC and mass spectral analysis of diols [4]. In the pharmaceutical [5], phytopharmaceutical, fragrance [6] and lacquer [7] industries, acetals are used both as intermediates and as end products. The formation of these compounds starting from oxiranes and carbonyl compounds can occur by hydrolysis of the oxiranes to the appropriate diol, followed by acetalization, and direct condensation of the oxirane with a carbonyl compound. Direct conversion of an oxirane to 1,3-dioxolane instead of adding water to form a diol with subsequent elimination in the presence of acetone has been studied with a few reagents. Among these reagents, anhydrous copper sulfate has been used for the preparation of 1,3-dioxolanes, but in most cases the yields of the products are low and the reaction times are relatively longer [4]. The use of zeolite [8], KSF clay [9], HBF_4 [10], $TiO(TFA)_2$, $TiCl_3(OTf)$ [11], $RuCl_3$ [12], bismuth (III) salts [13], iron (III) trifluoroacetate [14] and some Lewis acids have been reported for this transformation. Most of the Lewis acids failed to give the desired products. Anhydrous zinc [15] and magnesium halides [16] have been reported to give rearranged products. The same reaction with both $FeCl_3$ [17] and Me_3SiCl [18] gave the corresponding halohydrins, while $SnCl_4$ and $TiCl_4$ [19] produced little or no product. Among Lewis acids, $BF_3 \cdot OEt_2$ has been successfully used for the conversion of only ethylene and propylene oxides to their corresponding 1,3-dioxolanes in the presence of different carbonyl compounds [19].

Polyoxometalates comprise a class of d^0 metal complexes of the group VB and VIB elements (excluding chromium) and exhibit both diverse and tunable domains of sizes, shapes, charge densities, acidities and reversible redox potentials [20]. The catalytic function of polyoxometalate compounds has attracted much attention, and they are used in solution as well as in the solid state as acids and oxidation catalysts [21]. Heteropolyanions are widely used as model systems for fundamental research and at the same time they have become increasingly important for applied catalysis. In the last two decades, the broad utility of heteropolyanions acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic substrates [22].

Recently, we have reported that $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ can be used as an effective catalyst for the conversion of oxiranes to thiiranes [23]. According to reports on the catalytic acetalization by heteropolyacids [21,22,24] and in the course of our studies on polyoxometalates catalysis, we now report an efficient method for the conversion of oxiranes to their 1,3-dioxolanes with acetone in the presence of ammonium decatungstocerate (IV) icosahydrate ($(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$) as very efficient, reusable and heterogeneous catalyst (scheme 1).



Scheme 1.

2. Experimental

Products were characterized by the comparison of their spectral and physical data with those of known samples. Infrared spectra were recorded on a Philips PU

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9716 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ solvent on a Bruker AW 80 (80 MHz) spectrometer using TMS as an internal standard. All the analyses were performed on a Shimadzu GC-16A instrument with a flame-ionization detector using silicon D.C.-200 or carbowax 20-M columns. The catalyst was characterized by FT-IR, FT-IR Bruker Vector spectrophotometer, magnetic susceptibility, Sherwood Scientific, thermal gravimetric analysis, Mettler TG-50 and elemental analysis, Heraeus D-6450 instruments. The chemical purities of all epoxides were checked by gas chromatography and confirmed to be higher than 98%.

2.1. Preparation of the catalyst

Ammonium decatungstocerate icosahydrate was prepared according to Peacock's procedure [25]. $Na_2WO_4 \cdot 2H_2O$ (25 g, 75 mmol) was dissolved in 100 mL of ion-exchange water, the pH of which was adjusted to 7.2 by the addition of acetic acid. After heating at 90 °C with stirring, an aqueous solution containing $(NH_4)_2Ce(SO_4)_2 \cdot 2H_2O$ (4.75 g, 7.5 mmol) and a 1 equiv H_2SO_4 solution were added to make CeW_{10} form in the solution. This solution was obtained after filtration and used as catalyst. The structure of the catalyst was confirmed by IR, UV–vis, magnetic susceptibility, thermal gravimetric analysis (TGA) and elemental analysis.

2.2. Typical procedure

To a solution of oxiranes (1 mmol) in acetone (3 mL), $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ (0.04 mmol) was added. The reaction mixture was stirred under reflux conditions for the appropriate time according to table 2. The progress of the reaction was followed by TLC or GLC. After completion of the reaction, the suspension was filtered and washed with ether. Evaporation of the solvent followed by chromatography on a short column of silica gel gave the pure product, yields 77–95% (table 2).

2.3. Catalytic reactions of cyclohexene oxide with different polyoxometalates

A mixture of cyclohexene oxide (1 mmol) and polyoxometalate complex (0.04 mmol) in acetone (3 mL) was stirred at room temperature. The progress of the reaction was monitored by GLC. After completion of the reaction, the suspension was filtered and washed with ether. The eluate was concentrated under reduced pressure and chromatographed on a silica-gel column to give a pure product (table 1).

Table 1
1,3-dioxonation of cyclohexane oxide with acetone using catalytic amounts of various polyoxometalates under reflux[a]

Run	Catalyst	Conversion (%)[b]
1	No catalyst	5[c]
2	$(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$	95
3	$(NH_4)_8[CeMo_{12}O_{42}] \cdot 8H_2O$	28
4	$H_4SiW_{12}O_{40} \cdot 6H_2O$	22
5	$K_5PMnW_9Mo_2O_{39} \cdot 3H_2O$	20
6	$Na_3PW_{12}O_{40} \cdot 12H_2O$	18
7	α-$K_7PW_9Mo_2O_{39} \cdot 19H_2O$	11
8	$K_4PEeW_9Mo_2O_{39} \cdot 3H_2O$	11
9	β-$Na_8HPW_9O_{34} \cdot 24H_2O$	9

[a] All reaction carried out in 150 min.
[b] GC yields based on starting cyclohexane oxide.
[c] After 24 h.

2.4. Physical and spectral data

Compound **2a:** $n_D^{20} = 1.4465$ (lit.[20] $n_D^{20} = 1.448$); $^1HNMR(CDCl_3)\delta$: 4.34–4.05 (2H, m), 2.58–2.07 (4H, m), 1.35 (6H, s), 1.24–1.00 (4H, m); IR (neat): 2980, 2930, 2870, 1440, 1355, 1260, 1180, 1080, 960, 885, 835, 780 cm^{-1}.

Compound **2b:** $n_D^{20} = 1.5270$ (lit.[21] $n_D^{20} = 1.5273$); $^1HNMR(CDCl_3)\delta$: (5H, s), 5.00 (1H, dd, $J = 8$ Hz), 4.23 (1H, dd, $J = 7$ Hz), 3.62 (1H, dd, $J = 6$ Hz), 1.48 (3H, s), 1.40 (3H, s); IR (neat): 3036, 2990, 2870, 1600, 1495, 1450, 1365, 1230, 1150, 1055, 945, 850, 755, 700 cm^{-1}.

Compound **2c:** $n_D^{20} = 1.2495$; $^1HNMR(CDCl_3)\delta$: 4.20–3.31 (3H, m), 1.72–1.13 (16H, m), 0.82 (3H, *t*, $J = 7$ Hz); IR (neat): 2970, 2915, 2860, 1460, 1375, 1250, 1160, 1050, 950, 850, 730 cm^{-1}.

Compound **2d:** mp 63 °C (lit.[22] mp 64–65 °C); $^1HNMR(CDCl_3)\delta$: 7.47–6.72 (5H, m), 4.65–3.64 (5H, m), 1.42 (3H, s), 1.30 (3H, s); IR (KBr): 3070, 2990, 2920, 1600, 1585, 1490, 1445, 1344, 1240, 1210, 1170, 1035, 910, 810, 747 cm^{-1}.

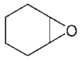
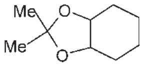
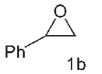
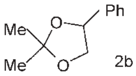
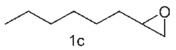
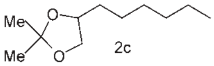
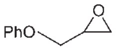
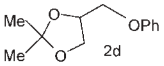
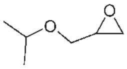
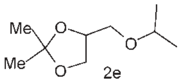
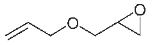
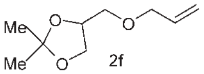
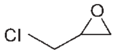
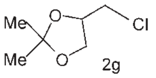
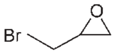
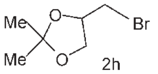
Compound **2e:** $n_D^{20} = 1.4170$ (lit.[23] $n_D^{20} = 1.4168$); $^1HNMR(CDCl_3)\delta$: 4.37–3.30 (6H, m), 1.37 (3H, s), 1.27 (3H, s), 1.15 (6H, d, $J = 6$ Hz); IR (neat): 2970, 2930, 2870, 1460, 1380, 1365, 1260, 1125, 1070, 1030, 920, 850, 735 cm^{-1}.

Compound **2f:** $n_D^{20} = 1.4318$ (lit.[24] $n_D^{20} = 1.4320$); $^1HNMR(CDCl_3)\delta$: 5.95–4.70 (3H, m), 4.35–3.32 (7H, m), 1.33 (3H, s), 1.25 (3H, s); IR (neat): 3050, 3000, 2920, 2850, 1455, 1360, 1320, 1250, 1090, 920, 840, 755 cm^{-1}.

Compound **2g:** $n_D^{15} = 1.4359$ (lit.[25] $n_D^{15} = 1.4357$); $^1HNMR(CDCl_3)\delta$: 4.34–3.12 (5H, m), 1.32 (3H, s), 1.21 (3H, s); IR (neat): 2960, 2900, 2860, 1450, 1375, 1250, 1165, 1080, 1025, 935, 870, 740 cm^{-1}.

Compound **2h:** $n_D^{20} = 1.4383$ (lit.[25] $n_D^{20} = 1.4386$); $^1HNMR(CDCl_3)\delta$: 4.21–3.01 (5H, m), 1.32 (3H, s), 1.23 (3H, s); IR (neat): 2960, 2900, 2862, 1450, 1375, 1250, 1165, 1080, 1025, 935, 872, 743 cm^{-1}.

Table 2
Conversion of oxiranes to 1,3-dioxolanes catalyzed by $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$

Run	Substrate	Product[a]	Time (min)	Yield (%)[b]
1	 1a	 2a	150	93
2	 1b	 2b	90	95
3	 1c	 2c	270	80
4	 1d	 2d	240	77
5	 1e	 2e	240	79
6	 1f	 2f	240	83
7	 1g	 2g	270	87
8	 1h	 2h	300	78

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

Catalyst: $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$; IR (KBr): 3550–3200, 1720, 1490, 950, 829, 768 cm^{-1}; magnetic susceptibility: diamagnetic; TGA: 20 H_2O; elemental analysis: calcd. N, 3.66; Ce, 4.58; W, 60.01; H_2O, 11.78; found: N, 3.54; Ce, 4.49; W, 60.33; H_2O, 12.04.

3. Results and discussion

At first, we examined the 1,3-dioxonation of cyclohexane oxide with acetone using catalytic amounts of various polyoxometalate complexes (0.04 M) at reflux and the corresponding 1,3-dioxolane was obtained in 9–93% after 150 min. It is important to note that the reaction did not proceed in the absence of the catalyst at the same time, and after 24 h only 5% conversion was observed. Among the catalysts tested, $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ was found to be highly active for the reaction (table 1).

Reactions of different aliphatic and cyclic oxiranes, including those with electron-withdrawing substituents were performed in refluxing acetone and in the presence of only 0.04 M equivalent of $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$. The possibility of reaction with other carbonyl compounds such as cyclohexanone and cyclooctanone were investigated, but low conversions were obtained under the same experimental conditions. Table 2 summarizes the results obtained for conversion of different oxiranes to their corresponding 1,3-dioxolanes.

Environmental and economical consideration prompts an urgent need to redesign commercially important processes. In this context, heterogeneous catalysts play a dramatic role [26]. The use of heterogeneous catalysts in different areas of the organic synthesis has now reached significant levels, not only for the possibility to perform environmentally benign synthesis, but also for the good yields frequently, accompanied by excellent selectivities that can be achieved. In fact, the advantages of these catalysts are (i) the easy workup (separation of the catalyst simply by filtration); (ii) the high level of purity of the products; (iii) and the possibility of recycling catalysts, as well as avoiding the use of noxious substances. In this case, we have found that $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ could be reused at different times without loss of the activity, simply by filtering the catalyst, washing with acetone, drying and immediately reusing. After each reaction, the concentration of the catalyst (tungsten) in solution was determined and it was very low (table 3); therefore, this compound can be used as a stable and recyclable catalyst.

In comparison with the results reported for some other reagents, such as, $BF_3 \cdot OEt_2$ [19], $RuCl_3$ [12], $TiO(TFA)_2$ and $TiCl_3(OTf)$ [11], the use of

Table 3
The results $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ catalyst recovery in the 1,3-dioxonation of cyclohexane oxide with acetone under reflux

Run	Conversion (%)[a]	W leaching (%)[b]	Time (min)
1	95	0	150
2	95	0	150
3	95	0	150
4	95	0	150
5	95	0	150
6	93	<1%	150
7	90	1.2%	150
8	86	1.6%	150

[a] All reactions carried out in 150 min.

[b] Reaction solutions assayed for leached tungsten using atomic adsorption spectrometer and based on initial tungsten concentration.

$(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ is more suitable. The use of $BF_3 \cdot OEt_2$ has been only for ethylene and propylene oxides and there is no reaction for oxiranes with electron-releasing substituents; $RuCl_3$ and $TiO(TFA)_2$ suffer from long reaction times (up to 5 h) and the need for large amounts of catalysts (up to 0.3 molar ratio); but in the case of $TiCl_3(OTf)$, the results obtained with the proposed catalyst show longer reaction times and lower yields. Therefore, we have introduced $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ as a nonhygroscopic, non-toxic, available, stable, reusable and heterogeneous catalyst for the reactions of oxiranes with acetone. In addition, the advantages such as mildness, ease of preparation, simple filtration at the end of reaction, cheapness of the catalyst and high yields give a new synthetic application for $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ in organic synthesis. Even though the reaction mechanism is interesting, at present it is obscure to us, and we have not been able to assign any reasonable mechanism for them in our studies.

4. Conclusion

In conclusion, we have demonstrated that $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ is a convenient, stable, reusable and heterogeneous catalyst, worthy to be mentioned for 1,3-dioxonation of oxiranes. Work on other reactions promoted by $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ and related compounds are currently underway in our laboratory.

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