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Efficient Route for the Synthesis of 1,3-Dioxolanes Catalyzed by Sulfated Mixed Oxides of Yttria-Zirconia

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Abstract:- A mild, simple, environmentally benign catalytic protocol for transforming epoxides (oxiranes) into their respective 1,3-dioxolanes. The different epoxides with ketones give exclusively 1,3-dioxolanes catalyzed by sulfated yttria-zirconia with moderate to good yields (A [3+2] cycloaddition approach). The GC and GC-MS analysis shown in most instances that the product obtained was exclusively 1,3-dioxolanes. The catalysts were characterized by using X-ray powder diffraction (XRD), EDAX, FTIR, Thermal methods, and n-butylamine potentiometric titration method. Simple work-up, mild process conditions, and solvent-free approach make the procedure superior to current techniques.

Keywords:- *Sulfated yttria-zirconia, 1,3-Dioxolanes, Solvent-free, green chemistry, heterogenous catalysis*

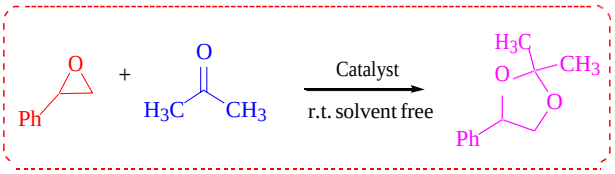
I. INTRODUCTION

Dioxolane compounds are essential intermediates in various organic processes [1-3]. Alternatively, certain compounds containing 1,3-dioxolane units have physiological and biological properties [4-7]. In the case of aldehydes and ketones in carbohydrates and steroid chemistry, the form of 1,3-Dioxolane is often used as a moiety that protects a carbonyl group. Besides this, diols converted to dioxolanes are used in various spectroscopic and chromatographic techniques [8].

Most often, dioxolanes (acetonides) were synthesized from the reaction of epoxides with compounds containing carbonyl moiety [9]. This transformation was investigated by using BF_3•OEt_2 [10], Zeolite [11], HBF_4, [12], graphene oxide [13], $[Cp^*Ir(NCMe)_3]^{2+}$ [14], MoO_3/SiO_2 [15], $Cu(OTf)_2$ [16], Chromium-pillared montmorillonite [17], Phosphomolybdic Acid [18], Iron oxide-pillared clay [19], Amberlyst-15 [20], heteropolyacids [21] and 2-methyl benzimidazole-zeolite complexes with d-block metal ions [22]. Boron trifluoride-etherate system was successfully used in the synthesis of 1,3-dioxolanes from carbonyl compounds with only epoxyethane and 2-Methyloxirane [10]. Besides, 1,3-dioxolanes can be synthesized from diols with carbonyl compound using an acid catalyst and azeotropic water extraction conditions. The process is restricted to the carbonyl compounds for both thermal and chemical stability to water under reflux conditions. However, several other catalytic protocols developed more easily and conveniently by converting epoxides to dioxolanes [23]. The substitution of "non-green" protocols with "green" protocols has industrial relevance to overcome environmental problems. Hence, a viable catalytic protocol that can address these drawbacks must be formulated.

The surface-modified systems of metal and mixed metal oxides are extensively used as solid acid catalysts for various functional group transformations. Sulfated yttria-zirconia used as an efficient catalyst for the pericyclic reaction between a conjugated diene and the dienophile [24], synthesis of β-amino carbonyl compounds [25], protecting hydroxy, thiol and amino groups with carboxylic acids [26], synthesis *N*-Boc protected amines [27] and alkoxycarbonylation of amines [28]. I herein report, the synthesis of 1,3-dioxolanes using a modified form of the yttria-zirconia system as a recyclable catalyst under neat conditions.

To strengthen an environmentally sustainable framework for different organic transformations [29-33], and the outcome obtained for ring opening of oxiranes with nucleophiles [34] encourage exploring surface-modified yttria-zirconia system for acetalization of ketones using oxiranes (Scheme 1). Recyclability of catalysts, neat reaction medium, mild reaction procedure, and environmentally friendly approach make the method more appealing and environmentally sustainable.



Scheme 1: Synthesis of 1,3-dioxolanes from epoxide with carbonyl compounds.

II. MATERIALS AND METHODS

A. *Catalyst preparation*

Sulfated yttria-zirconia catalysts with varying quantities of yttria loading (4–24 mol.%), were synthesized using co-precipitation followed by the impregnation method [24, 34].

B. *A typical procedure for the synthesis of dioxolanes*

To a mixture of 2-phenyloxirane (240 mg) and 2-propanone (116 mg), catalyst (24 mg, 10 (wt%) w.r.t. 2-phenyloxirane) was added in 10 mL round bottom flask. For the appropriate time and temperature, the reaction mass has been stirred. During workup, the catalyst was retrieved via

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filtration by adding ethyl acetate (5 mL) as a solvent and concentrated to dryness. The progress of the reaction was investigated by using TLC and GC (Thermofisher GC-1000 equipped with a capillary column (30 m × 0.32 mm ID-0.25 µm BP-10) with an FID detector and high purity nitrogen as the carrier gas.) All the products obtained and discussed in this work have been previously reported in the literature and selected compounds characterized by using of Gas chromatography-Mass spectroscopy (Shimadzu QP-2010, E.I. mode with high purity helium as carrier gas).

2,2-Dimethyl-4-phenyl-1,3-dioxolane (Table 2, entry 1);GC-MS (Electron Impact, 70 eV), m/z (%) = 178 (1 %) [M+], 163 (35 %), 148 (5 %), 133 (2 %), 120 (25 %), 103 (8 %), 91 (19 %), 77 (9 %), 72 (65 %), 65 (8 %), 52 (7 %), 48 (100 %).

2-Phenyl-1,4-dioxaspiro[4.5] decane (Table 2, entry 4); GC-MS (Electron Impact, 70 eV), m/z (%) = 218 (70 %) [M+], 189 (25%), 175 (100 %), 162 (10 %), 120 (30 %), 104 (100 %), 91 (50 %).

III. RESULTS AND DISCUSSION

Initially, we studied, the influence of various catalysts for the synthesis of 1,3-dioxolanes at an ambient temperature (Table 1). The reaction conducted without catalysts does not proceed even after a protracted 5 h reaction time for the model reaction of phenyloxirane with 2-propanone (Table 1, entry 1). The reaction of epoxides with ketones was further investigated in the presence of a catalytic amount (10 wt. %) of different catalysts and their surface-modified counterparts. No product was observed with ZrO_2 alone, whereas mixed metal oxide of ($Y_{0.16}Zr_{0.84}O_2$) gave 30 % yield and sulfated zirconia provided only 34% yield of the 1,3-dioxolanes (Table 1, entries 2-4). In the present investigation, the amount of yttrium present in the catalysts shows a significant effect on the catalytic activity. The acidity values increase from (1.23 to 4.19 mmol. g^{-1}), whichreveals good agreement with catalytic activities for a model reaction (Table 1, entries 5-10). The highest catalytic activity observed for $SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$ (Table 1, entry 8) was due to the highest total acid sites and the initial electrode potential (E_i). The measurement of total acid sites and strength was carried out using the potentiometric titration method [35].

Table 1: Study of catalytic activity for the conversion of epoxides to acetonides[a]

Entry	Catalyst	Acidity (mmol/g)[b]	E_i (mV)[c]	Yield(%)[d]
1[e]	-	-	-	-
2[e]	ZrO_2	0.80	55	-
3	$Y_{0.16}Zr_{0.84}O_2$	0.90	91	30
4	SO_4^{2-}/ZrO_2	2.07	168	34
5	$SO_4^{2-}/Y_{0.04}Zr_{0.96}O_2$	1.23	148	47
6	$SO_4^{2-}/Y_{0.08}Zr_{0.92}O_2$	1.64	195	55
7	$SO_4^{2-}/Y_{0.12}Zr_{0.88}O_2$	1.93	310	78
8	$SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$	4.19	530	95
9	$SO_4^{2-}/Y_{0.20}Zr_{0.80}O_2$	2.91	330	67
10	$SO_4^{2-}/Y_{0.24}Zr_{0.76}O_2$	2.65	248	50

[a]**Reaction conditions**: phenyloxirane (2 mmol), 2-propanone (2 mmol), solvent free, catalyst (24 mg, 10 wt%), solvent free, 2.0 h, Reaction temperature- r.t (32°C), [b]potentiometric titration method, [c]E_i- Inital electrode potential (mV), [d]Isolated yield, eReaction time- 5 h.

To generalize the methodology, it was initially established for the reaction of 2-phenyloxirane with various substrates, such as 2-propanone, 1-phenylethanone, 2-butanone, and cyclohexanone, provided 1a-4a products with 84-95% yields (Table 2, entries 1-4).

Sterically hindered 7-oxabicyclo (4.1.0) heptane was found to react sluggishly with 2-propanone and cyclohexanone were provide comparatively lower yields of 5a-6a (Table 2, entries 5-6). Similarly, the reaction of 2-(chloromethyl) oxirane with various ketones also smoothly took place with good yields of 7a-9a (Table 2, entries 7-9). The reaction between 1,2-epoxy-3-phenoxypropane with 2-propanone also smoothly took place provided 88% yield of 10a (Table 2, entry 10). We have also noted that the substituents attached to epoxide and ketones produce a negligible influence on the yield of the products (Table 2, entries 1-10).

The reusability of the catalysts is a crucial aspect that decides the applicability of the catalysts system for industries. We have also executed the recyclability study of catalysts for the reaction of phenyloxirane (20 mmol) with 2-propanone (20 mmol). The catalyst was washed with propanone after separation from the reaction mass and dried for 3 h. in an oven at elevated 120 °C temperature before the succeeding catalytic run. Under experimental conditions, sulfated yttria-zirconia was completely recoverable up to five successive cycles and there was no noticeable loss in its catalytic activity (Figure 1).

To confirm the heterogeneous nature of the catalyst and to test the stability of surface sulfate ions, a leaching experiment was carried out. The catalyst was retrieved after 1 h. reaction time via filtration by adding ethyl acetate (5 mL), and the further reaction was continued without any catalyst. There was no increase in yield even after 5 h reaction time, indicating that no leaching of catalyst was involved.

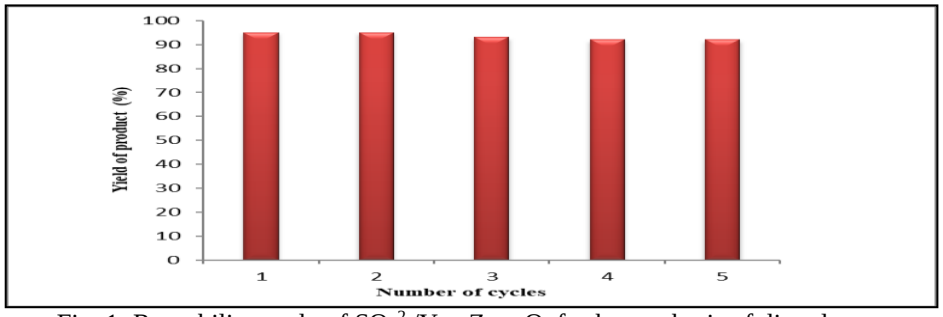
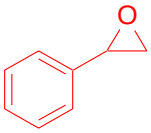
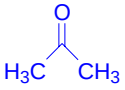
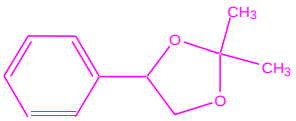
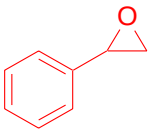
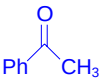
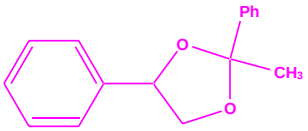
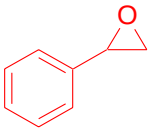
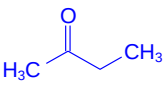
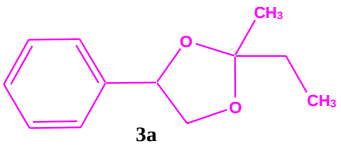
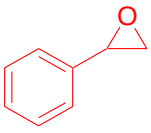
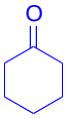
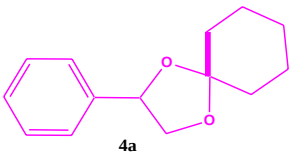
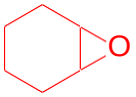
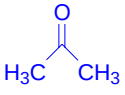
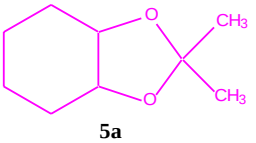
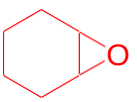
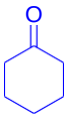
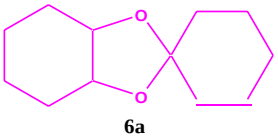


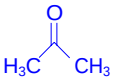
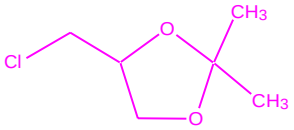
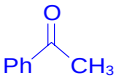
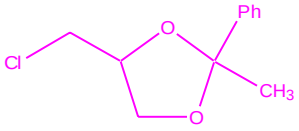
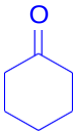
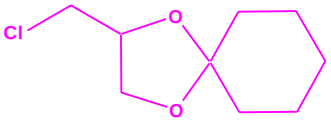
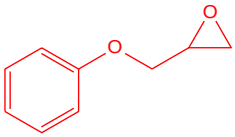
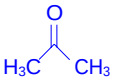
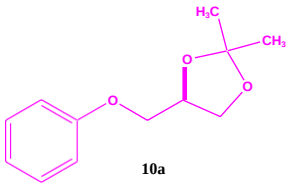
Fig. 1: Reusability study of $SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$ forthe synthesis of dioxolanes.

IV. CONCLUSIONS

Sulfated yttria-zirconia as surface modified catalysts were successfully intended for the synthesis of 1,3-dioxolanes under solvent free conditions. The catalyst shows remarkable activity tolerance when using structurally varied oxiranes and carbonyl compounds for the synthesis of acetonides. During the study, it was observed that the catalyst was retrieved simply by filtration with retention of catalytic activity for five sequential cycles.

Table 2: Sulphated yttria-zirconia catalyzed the synthesis of 1,3-dioxolanes[a]

Entry	Epoxide	Ketone	1,3-dioxolane	Yield (%)[b]	Reference
1			 **1a**	95	[13, 18]
2			 **2a**	93	[19]
3			 **3a**	84	[13]
4			 **4a**	87	[13]
5			 **5a**	88	[18]
6			 **6a**	79	[21]

7			 **7a**	89	[15]
8			 **8a**	93	[15]
9			 **9a**	84	[15]
10			 **10a**	88	[13]

[a]Reaction conditions: epoxide (3 mmol), ketone (3 mmol), $SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$:10 wt% of epoxide, temp. - r.t. (32 °C), time- 2 h, solvent free, [b]Isolated yield.

Among the several catalysts and compositions studied, $SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$ was found to be the best in terms of catalytic activity. The simple recovery process of catalyst, mild reaction conditions, recyclability of the catalysts and solvent-free approach makes the procedure preferable to the currently existing methods.

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