

Heterogeneous Catalysis in Carbonyl Regeneration from 1,3-Dithiolanes and 1,3-Dithianes by Zirconium Sulfophenyl Phosphonate

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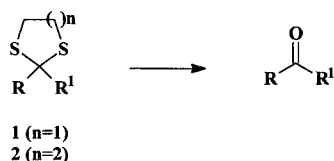
Received 26 March 1997

Abstract: Layered zirconium sulfophenyl phosphonate was found to be an efficient heterogeneous catalyst for mild hydrolysis of 1,2 dithiolanes and 1,3 dithianes to their corresponding carbonyl compounds.

Recently, we reported that layered zirconium sulfophenyl phosphate is an excellent heterogeneous catalyst for mild hydrolysis of nitrogen-containing derivatives to their corresponding carbonyl compounds.¹ The catalyst is obtained by leaving zirconium (IV) fluorocomplexes to decompose in a solution containing *m*-sulfophenylphosphonic and methanephosphonic acids in a proper ratio. As the complexing agent is slowly removed (i.e. as HF) the zirconium phosphonate of formula $\alpha\text{-Zr}(\text{O}_3\text{PCH}_3)_{1.2}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{0.8}$ is formed as a microcrystalline powder.¹ A measure of the acid strength of the solid has been obtained from the color change of Hammet indicators.² The solid gave a yellow coloration with benzalacetophenone ($\text{pK}_a = -5.6$), but was colourless with anthraquinone ($\text{pK}_a = -8.2$), and its acid strength (H_0) should lie between -5.6 and -8.2 ,³ it is similar to that of hydrogen montmorillonite but higher than that of amberlyst 15.⁴

The strongly acidic catalyst compares favourably with the most common styrene-divinylbenzene sulfonic resins, does not show marked swelling phenomena in the presence of apolar or slightly polar solvent and possesses a good thermal resistance.

Dithioacetals as the nitrogen containing derivative, are used as masked carbonyls, and several methods for the regeneration of carbonyl compounds have been proposed,⁵ but none of them is of general applicability. It was thus of interest to test the catalytic activity of zirconium sulfophenyl phosphonate in the hydrolysis of 1,3-dithiolanes **1** and 1,3-dithianes **2**.



The reactions were carried out heating a mixture of dithioacetals and catalyst (molar ratio 4:1) at 60°C in the presence of glyoxylic acid monohydrate as exchange reagent.⁶ The reaction takes from 30 min. to 4 h (see Table) and after a simple work-up affords the carbonyl compound in high yield. It is important to note that cyclic dithioacetals of enolizable aldehydes (i.e. hexanal dithioacetals) in the reaction condition give a complex mixture of unseparable products. The method described is a new entry into the dedithioacetalization process even for cyclic trimethylene dithioacetals, which are more resistant to the action of a variety of reagents⁷. The use of zirconium sulfophenyl phosphonate is equally effective or better than any reagent yet reported. The important features of this methodology are: (a) solvent is not required, (b) mild reaction conditions, (c) simple work-up.

Acknowledgment. The authors wish to thank CNR and MURST, Italy, for financial support.

Table

Reagent ^{a,b}	Product	n	Time (h)	Yield (%) ^{c,d}
		1	2.5	90
		2	0.5	95
		1	1	95
		2	1	95
		1	3.5	95
		2	0.5	95
		1	2	75
		2	0.5	77
		1	1.5	79
		2	1.5	81
		1	1	91
		2	0.5	95
		1	0.5	89
		2	0.5	92

^a All reactions were carried out at 60°C; ^b All carbonyl derivatives were prepared by known literature procedures⁸; ^c Yields of pure isolated product; ^d The regenerated carbonyl compound was checked by comparison (IR, ¹H-NMR) with an authentic sample

References and Notes

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- (3) Measurement of the acid strength: 0.5 g of zirconium sulfophenyl phosphonate, previously dried at 160°C for 12 hrs, were dispersed in 3 ml of benzene in a test tube. 0.2 mg of the chosen Hammet indicator were added to the dispersion held under stirring. The colour changes were evaluated after 30 min.
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- (6) General Procedure: To a stirred mixture of dithioacetal (5 mmol) and zirconium sulfophenyl phosphonate (1.25 mmol) at 60°C was added glyoxylic acid monohydrate (50 mmol) and the progress of the reaction monitored by tlc. Stirring was continued for the appropriate time (see tables). The reaction mixture was diluted with acetone (10 ml) filtered and concentrated under vacuum. The crude reaction mixture was dissolved in dichloromethane (15 ml), washed with saturated sodium bicarbonate solution, dried over sodium sulfate and concentrated under vacuum. The residue was purified by flash chromatography on SiO₂ (eluent CH₂Cl₂), affording the carbonyl compound.
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