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Juan M. Campelo [a] , Rupak Chakraborty [a] & Jose M. Marinas [a]

[a] Department of Organic Chemistry , University of Cordoba , Avda. S. Alberto Magno, Córdoba, E-14004, Spain

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REDUCTIVE CLEAVAGE OF EPOXIDES WITH ZINC BOROHYDRIDE SUPPORTED ON $AlPO_4$

Juan M. Campelo,* Rupak Chakraborty and Jose M. Marinas

Department of Organic Chemistry, University of Cordoba
Avda. S. Alberto Magno, E-14004 Córdoba, Spain

Abstract: Reductive cleavage of styrene oxide and epichlorohydrin to alcohols have been achieved using zinc borohydride supported on $AlPO_4$. In the styrene oxide reductive cleavage, $Zn(BH_4)_2$ supported on $AlPO_4$ is a better catalyst than $Zn(BH_4)_2/SiO_2$ previously described.

The reductive cleavage of epoxides to alcohols is one of the most useful reactions in organic syntheses.[1,2] In general, more substituted alcohols are easily obtained by reduction of epoxides with nucleophilic hydride transferring reagents, whereas access to less substituted alcohols by reverse opening is not so simple.[3] Recently, has been described a simple methodology for the reductive cleavage of unsymmetrical epoxides to the less substituted alcohols using zinc borohydride supported on silica gel.[4] In the absence of silica gel the epoxides remained almost unaffected, although after a prolonged period, a mixture of products resulted.

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* To whom correspondence should be addressed.

The use of inorganic solids such as silica, alumina or zeolites provide opportunities for catalysis and control of organic reactions. Thus, the supported reagent technique has attracted considerable interest among synthetic chemists in recent years.[5,6] Besides, yields are often higher and work-up procedures easier than for the corresponding homogeneous reactions, it may be use to improve isomer selectivity. In this sense, the surface acid character of $AlPO_4$ catalysts enable them to be used for a number of organocationic reactions in gas phase[8] or in the field of selective synthetic chemistry which involves acid- and base-catalyzed reactions.[8-12] Thus, we have previously reported their use as catalysts in the retroaldolisation of diacetone alcohol, the solvent free tetrahydropyranilation of alcohols and phenols,[9] the synthesis of 1,3-dioxolanes[10,11] and in the Diels-Alder reaction of cyclopentadiene with chiral acrylates.[12] They have also been used as metal supports in the liquid-phase hydrogenation of the double bond of alkenes bearing a variety of organic functions.[13-15]

Thus, in the present communication we wish to report the reductive cleavage of epoxides (styrene oxide and epichlorohydrin) with zinc borohydride supported on $AlPO_4$. The results with $AlPO_4$ are also compared to those obtained using silica gel or alumina as supports. All results are summarized in Table. Yields are not optimized and the results obtained after 24 h are used for evaluation.

Several effects are evident from the results in Table. First of all it is clear that the reductive cleavage of epoxides occurred with all catalysts.

Moreover, as shown in Table, the styrene oxide underwent cleavage of the C-O bond to the more substituted carbon atom to give the less

Table: Reductive cleavage of styrene oxide with zinc borohydride supported on $AlPO_4$, SiO_2 and Al_2O_3

Epoxide	Catalyst	Conversion[a] (%)	Products[b] (Selectivities, %)		
			(1)	**(2)**	**(3)**
Styrene Oxide	$AlPO_4$-773	84	95.4	0.3	4.2
	$AlPO_4$-1073	75	97.3	-	2.7
	SiO_2-773	83	92.2	2.5	5.3
	SiO_2-1073	52	89.8	3.6	6.6
	Al_2O_3-773	54	84.3	13.6	2.1
	Al_2O_3-1073	38	81.4	16.6	2.0
			(4)	**(5)**	**(6)**
Epichlorohydrin	$AlPO_4$-773	84	62.8	34.9	2.2
	$AlPO_4$-1073	75	69.3	29.3	1.4
	SiO_2-773	97	54.1	44.9	1.0
	SiO_2-1073	91	71.9	26.9	1.7
	Al_2O_3-773	57	77.1	21.1	1.7
	Al_2O_3-1073	57	74.3	22.8	2.8

[a] Determined by GLC analysis

[b] Characterized and identified by GLC-MS (high resolution)

substituted alcohol (2-phenylethanol, **1**) in excellent yields. 1-Phenylethanol **(2)** and styrene **(3)** were also found.

Moreover, in the reductive cleavage of epichlorohydrin the main reaction product, in all cases, is the more substituted alcohol (1-chloro-2-propanol, **4**), although the reaction is less selective. Other reactions products were: $ClCH_2CH(OH)CH_2Cl$ **(5)** and $[ClCH_2(CH_2)_3]_2O$ **(6)**.

Furthermore, $AlPO_4$ is very efficient as support for zinc borohydride leading to higher styrene oxide conversion and greater selectivities to 2-phenylethanol than SiO_2. However, in the epichlorohydrin reaction, the $AlPO_4$ is somewhat less efficient than SiO_2 although selectivities to 1-chloro-2-propanol are almost the same. Finally, Al_2O_3 is a worse support than SiO_2 or $AlPO_4$.

On the other hand, in the absence of zinc borohydride, the $AlPO_4$-773 support converted completely styrene oxide to phenylacetaldehyde, (±)-1-phenyl-1,2-ethanediol and benzaldehyde with reaction selectivities of 82, 10 and 8% respectively. In the same conditions the SiO_2-773 support afforded only 9% conversion, yielding exclusively, phenylacetaldehyde and benzaldehyde with selectivities of 85 and 15% respectively.

The excellent yields with $AlPO_4$ demonstrate its utility as an effective support for zinc borohydride in the reductive cleavage of epoxides. Besides, the results indicate that a hydroxylated support is required for zinc borohydride, since the use of the same support, but calcined at higher temperatures (greater dehydroxylation of the support surface) lead to slightly worse results. Moreover, in the absence of hydride, the acid character of the $AlPO_4$ surface is responsible for the isomerization of styrene oxide to phenylacetaldehyde.

Finally, the present results prompt us to the utilization of zinc borohydride supported on $AlPO_4$ in other selective transformations and thus, the hydration of alkenes and alkynes is in progress and will be reported in due course.

EXPERIMENTAL

Styrene oxide and epichlorohydrin were commercial quality chemicals purchased from Aldrich and were purified prior to use. Zinc borohydride in dry 1,2-dimethoxyethane (DME) was prepared from $ZnCl_2$ and $NaBH_4$ according to the reported procedure.[16] Tetrahydrofuran (THF) used in the reaction was dried over Ph_2CO-K under nitrogen immediately before use. All reaction products were characterized and identified by GLC and Mass spectrometry. GLC analysis were run on a HP-5890 II GC with FID using a 10% DEGS/Chromosorb G AW-DMCS 80/100 (3 mm i.d., 2 m) column. GLC-MS characterization was carried out in the Mass Spectrometry Service of Cordoba University (VG Auto-Spec).

Catalysts

Three catalysts were used: a synthetic $AlPO_4$, obtained by precipitation from aluminum chloride and H_3PO_4 (85 wt%), using aqueous ammonia,[7] dried at 393 K (24 h) and calcined at 773 K ($AlPO_4$-773; surface area 235 m^2g^{-1}) or 1073 K ($AlPO_4$-1073; surface area 225 m^2g^{-1}). A commercial silica gel (230-400 mesh, Kieselgel 60) from Merck calcined at 773 K (SiO_2-773; surface area 392 m^2g^{-1}) or 1073 K (SiO_2-1073; surface area 289 m^2g^{-1}). A commercial γ-alumina from Merck calcined at 773 K (Al_2O_3-773; surface area 100 m^2g^{-1}) or 1073 K (Al_2O_3-1073; surface area 82 m^2g^{-1}).

Preparation of catalyst supported zinc borohydride

A solution of $Zn(BH_4)_2$ (3 mmol) in DME (4 ml) was added on catalyst surface (1 g) taken in a 50 ml round bottom flask. It was then stirred at room temperature for 30 min. Solvent was then evaporated under reduced pressure at room temperature to give the supported reagent, which was then used for the reductive cleavage of epoxides (1 mmol).

General procedure for reductive cleavage of epoxides

The epoxide (1 mmol) was stirred with $Zn(BH_4)_2$ supported on catalyst surface in dry THF (10 ml) at room temperature for 24 h. The reaction mixture was then decomposed with careful dropwise addition of water and filtered. The filtrate was extracted with ether and the extract was dried with anhydrous Na_2SO_4 and solvent evaporated to leave the pure product. The products were characterized and identified by GLC and Mass spectrometry (Table).

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