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# $AlPO_4$ Supported Zinc Borohydride as a Novel Reagent for the Hydration of Aromatic Alkenes and Alkynes

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# $AlPO_4$ SUPPORTED ZINC BOROHYDRIDE AS A NOVEL REAGENT FOR THE HYDRATION OF AROMATIC ALKENES AND ALKYNES

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**Abstract**: Hydration of aromatic alkenes (styrene, α-methylstyrene and E-stilbene) and alkynes (phenyl and diphenylacetylene) has been achieved by the reaction of the corresponding alkenes or alkynes on zinc borohydride combined with $AlPO_4$ in DME. Except in the case of α-methylstyrene, $Zn(BH_4)_2/AlPO_4$ provides a more efficient and selective catalytic system than the combination with $SiO_2$ or $Al_2O_3$.

Zinc borohydride alone or supported on $SiO_2$ has received considerable attention in last years as an efficient catalytic system for the reduction of several organic compounds (aldehydes, ketones and conjugated aldehydes over conjugated ketones,[1] carboxylic esters to alcohols,[2] conjugated nitroalkenes,[3] regio- and stereo-selective reductive cleavage of epoxides[4]) and in the regioselective hydration of alkenes[5] and alkynes.[5b]

On the other hand, aluminum orthophosphates are efficient supports for metals (Ni, Ni-Cu, Pt, Pd and Rh) and thus, the metal-$AlPO_4$ supported catalysts find application in the liquid-phase catalytic hydrogenation of single alkenes[6] and cycloalkenes[7] and in the regioselective hydrogenation of the

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olefinic double bond of functionalized alkenes [$CH_2$=CH-R (R: H, $CH_2OH$, CHO, COMe, $CO_2H$, $CO_2R_1$, OCOMe, $CH_2OCOMe$, OEt, $CH_2NH_2$, and $CONH_2$)[8] and *p*-X-$C_6H_4$-CH=CH-R' (E-isomers; X= H, Me, MeO and Cl; R': H, $CH_2OH$, CHO, $COR_1$, $CO_2H$ and $CO_2Me$)[9]. Moreover, Ni and Ni-Cu/$AlPO_4$ supported catalysts show a high degree of selectivity towards allyl alcohols in the hydrogenation of propargyl alcohols[10]. Furthermore, Ni/$AlPO_4$ are also active catalysts in the gas-phase non-oxidative[11] and oxidative[12] dehydrogenation of alkylbenzenes.

$AlPO_4$ have also been used in the field of selective synthetic chemistry which involves acid- and base-catalyzed reactions: retroaldolisation of diacetone alcohol,[13] the solvent free tetrahydropyranilation of alcohols and phenols,[14] the synthesis of 1,3-dioxolanes[15] and the Diels-Alder reaction of cyclopentadiene with chiral acrylates.[16].

In a previous communication,[17] we showed the applicability of $AlPO_4$ as a new support for zinc borohydride in the reductive cleavage of epoxides. In the present communication we wish to report the hydration of aromatic alkenes (styrene, α-methylstyrene and E-stilbene) and alkynes (phenyl and diphenylacetylene) with $Zn(BH_4)_2$ supported on $AlPO_4$. Hydration of alkenes and alkynes to alcohols is one of the most useful reactions in organic synthesis. On silica gel supported zinc borohydride, the hydration of unactivated alkenes and alkynes[5] produces less-substituted alcohols according to an anti-Markovnikov process.The results with $AlPO_4$ are also compared to those obtained with commercial $SiO_2$ or $Al_2O_3$ supports. Yields are not optimized and, in most cases, the results obtained after 1 h are used for evaluation.

As shown in Table 1, alkenes underwent regioselective anti-Markovnikov hydration to give the corresponding less-substituted alcohols in high yields.

**Alkene hydration:** ***(Scheme 1).***

$$\mathrm{PhR^1C{=}CHR^2} \xrightarrow[\text{DME, rt}]{\mathrm{Zn(BH_4)_2/catalyst}} \begin{array}{ll} \mathrm{PhR^1HC\text{-}CH(OH)R^2} & \textbf{a} \\ \mathrm{PhR^1(OH)C\text{-}CH_2R^2} & \textbf{b} \end{array}$$

**1**: $R^1 = R^2 = H$
**2**: $R^1 = Me, R^2 = H$
**3**: $R^1 = H, R^2 = Ph$, E-isomer (**a**=**b**)
**Catalyst**: $AlPO_4$, $SiO_2$, $Al_2O_3$

The regioselectivity, in general, is very high and the reactions are fast. Moreover, no side products other than regioisomeric alcohols were observed in styrene. For more substituted alkenes, side products are often observed. These include 2,5-diphenyl-1-hexene and acetophenone in α-methylstyrene hydration on $Zn(BH_4)_2/SiO_2$ and $Zn(BH_4)_2/Al_2O_3$ catalysts, and benzyl alcohol and 2-phenylacetophenone in E-stilbene hydration on $Zn(BH_4)_2/AlPO_4$ and $Zn(BH_4)_2/SiO_2$ catalysts. An important observation regarding these reactions is that $SiO_2$, $Al_2O_3$ or zinc borohydride alone failed to promote any alkene hydration.

As shown in Table 1, the combination of $Zn(BH_4)_2$ with $AlPO_4$ provide a very efficient catalytic system for the hydration of styrene and E-stilbene leading to higher alkene conversions than with $SiO_2$. However, in both cases the hydration selectivities remained almost unchanged. Furthermore, the combination of $Al_2O_3$ with $Zn(BH_4)_2$ leads, in all cases, to worse results than with $AlPO_4$ or $SiO_2$.

On the other hand, in the hydration of α-methylstyrene on $Zn(BH_4)_2/AlPO_4$ catalysts, the reaction products obtained are not those corresponding to the hydration reaction (see Scheme 2 and Table 2).

Table 1: Hydration of alkenes and alkynes with $AlPO_4$ supported Zinc Borohydride *(see Schemes 1 and 2)*

| | Substrate | Time (h) | Catalyst | Yield (%) | Product Selectivities (%) | |
|---|---|---|---|---|---|---|
| | | | | | **a** | **b** |
| **1** | $Ph\text{-}CH{=}CH_2$ | 1 | $AlPO_4$-773 | 100 | 61.9 | 37.1 |
| | | 1 | $AlPO_4$-1073 | 100 | 63.5 | 36.0 |
| | | 1 | $SiO_2$-773 | 93 | 64.3 | 34.5 |
| | | 1 | $SiO_2$-1073 | 45 | 62.4 | 35.6 |
| | | 1 | $Al_2O_3$-773 | 19 | 63.6 | 32.8 |
| **2** | $PhC(CH_3){=}CH_2$ | 1.5 | $AlPO_4$ (See Scheme 2 and Table 2) | | | |
| | | 1.5 | $SiO_2$-773 | 96 | 89.7 | 1.0 |
| | | 1.5 | $Al_2O_3$-773 | 10 | 83.0 | 5.0 |
| **3** | $PhHC{=}CHPh$ (E-isomer) | 24 | $AlPO_4$-773 | 86 | 87.1 | - |
| | | 24 | $SiO_2$-773 | 33 | 95.8 | - |
| **4** | $PhC{\equiv}CH$ | 1 | $AlPO_4$-773 | 90 | 17.6 | 61.2 |
| | | 1 | $AlPO_4$1073 | 80 | 21.1 | 61.9 |
| | | 1 | $SiO_2$-773 | 74 | 13.1 | 65.7 |
| | | 1 | $SiO_2$-1073 | 49 | 14.9 | 56.5 |
| | | 1 | $Al_2O_3$-773 | 47 | 11.9 | 54.9 |
| **5** | $PhC{\equiv}CPh$ | 1 | $AlPO_4$-773 | 92 | 57.8 | - |
| | | 1 | $SiO_2$-773 | 42 | 42.9 | - |

**Scheme 2**

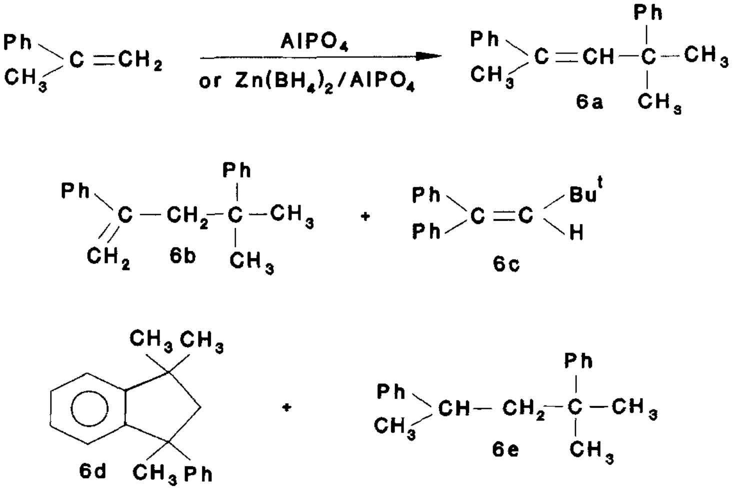
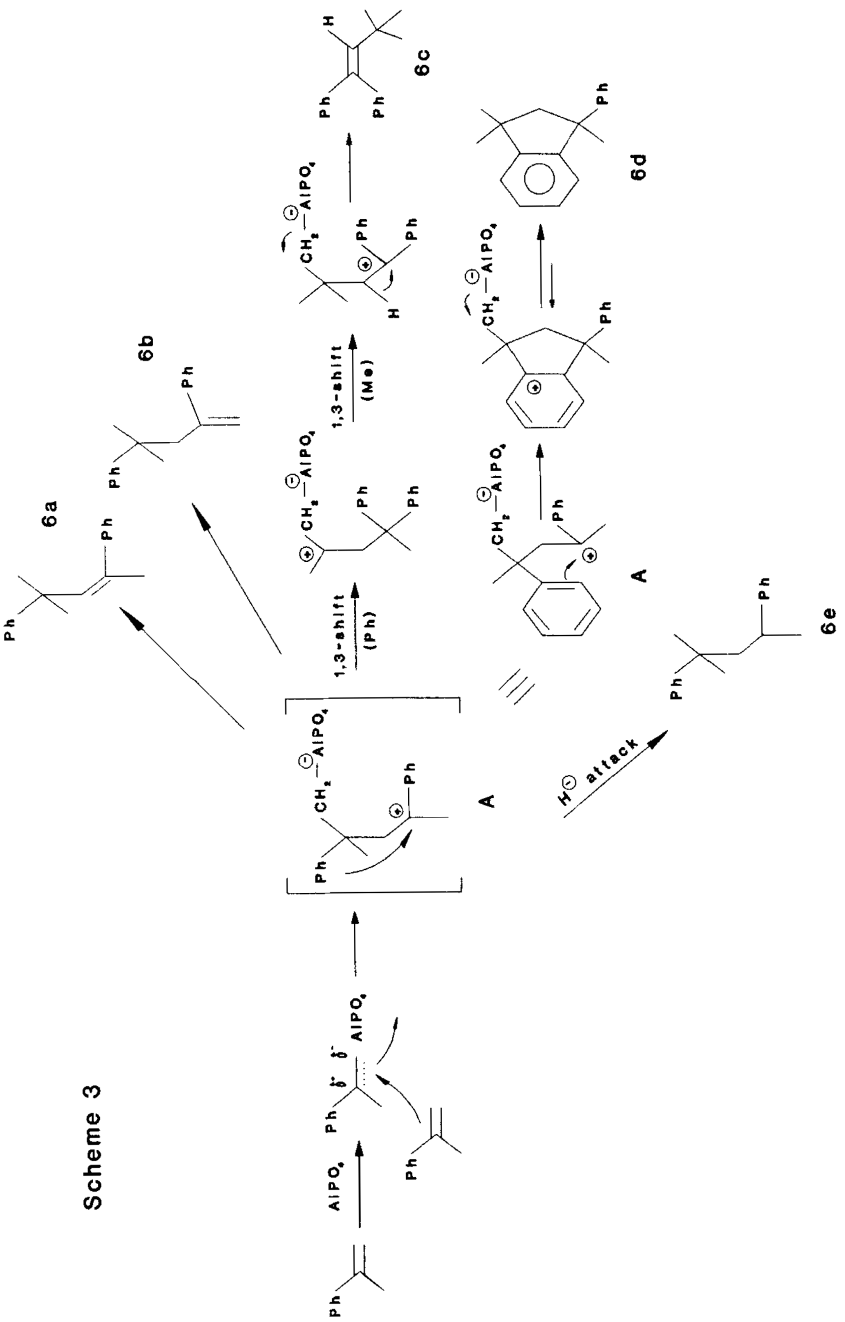


Table 2 Reaction of α-methylstyrene with zinc borohydride supported on $AlPO_4$ and with $AlPO_4$ *(see Scheme 3)*

| Time (h) | Catalyst | Yield (%) | Product Selectivities (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | **6a** | **6b** | **6c** | **6d** | **6e** |
| 1.5 | $Zn(BH_4)_2/AlPO_4$-773 | 100 | 55.8 | 34.9 | 8.0 | 0.8 | 0.5 |
| 1,5 | $Zn(BH_4)_2/AlPO_4$-1073 | 100 | 64.5 | 25.9 | 8.6 | 0.5 | 0.5 |
| 1,5 | $AlPO_4$-773 | 99.5 | 62.4 | 36.4 | 0.3 | 0.3 | - |
| 1,5 | $AlPO_4$-1073 | 99.1 | 78.5 | 20.2 | 0.1 | 0.2 | - |


AlPO₄
Ph
δ⁺ δ⁻
AlPO₄
CH₂—AlPO₄
A
1,3-shift (Ph)
1,3-shift (Me)
H⁻ attack
6a
6b
6c
6d
6e
Ph
H

Scheme 3

Besides, α-methylstyrene on $AlPO_4$ alone produced almost the same result that on $Zn(BH_4)_2/AlPO_4$. So, the reaction products obtained are those corresponding to the reaction of α-methylstyrene on surface acid sites of $AlPO_4$ catalyst. Moreover, styrene and E-stilbene on $AlPO_4$ alone failed to promote any reaction.

A possible reaction pathway for α-methylstyrene/$AlPO_4$ reaction is shown in Scheme 3.

In the hydration of **4** a mixture of 1- (**4b**) and 2-phenylethanol (**4a**) is obtained, the more substituted alcohol (**4b**) being the major product formed in all cases. Also, as in the hydration of alkenes, the combination of zinc borohydride with $AlPO_4$ provides a more efficient catalytic system than the combination with $SiO_2$ or $Al_2O_3$, although reaction selectivities always remained almost unchanged. Moreover, side products are observed. These include styrene (major), benzyl alcohol, phenylacetaldehyde and acetophenone.

The difference in performance between $AlPO_4$ and $SiO_2$ is greater in case of **5** than in **4**. Thus, $Zn(BH_4)_2/AlPO_4$ show higher conversion of **5** and greater selectivity to 1,2-diphenylethanol. Besides, side products on $Zn(BH_4)_2/SiO_2$ are obtained in higher yields than on $Zn(BH_4)_2/AlPO_4$. These side products include predominantly, benzyl alcohol (major), Z- and E-stilbene and stilbene oxides. Moreover, $AlPO_4$, $SiO_2$, $Al_2O_3$ or $Zn(BH_4)_2$ alone failed to promote any alkyne hydration. Furthermore, $AlPO_4$ alone do not promote any alkyne conversion.

Thus, the combination of zinc borohydride and $AlPO_4$ provides an efficient catalytic system for the hydration of alkenes (producing predominantly less-substituted alcohols) and alkynes (generating predominantly more-substituted alcohols). Except in the case of α-methylstyrene, the combination of $Zn(BH_4)_2$ with $AlPO_4$ provides a more

**Alkyne hydration *(Scheme 4).***

$$\mathrm{PhC{\equiv}CR^3} \xrightarrow[\text{DME, rt}]{\mathrm{Zn(BH_4)_2/catalyst}} \begin{array}{ll} \mathrm{PhH_2C\text{-}CH(OH)R^3} & \mathbf{a} \\ \mathrm{Ph(OH)HC\text{-}CH_2R^3} & \mathbf{b} \end{array}$$

**4**: $R^3$ = H
**5**: $R^3$ = Ph (**a**=**b**)
**Catalyst**: $AlPO_4$, $SiO_2$, $Al_2O_3$

efficient and selective catalytic system than the combination with $SiO_2$ or $Al_2O_3$. Moreover, α-methylstyrene is converted in $AlPO_4$ alone yielding the same products that on $Zn(BH_4)_2/AlPO_4$ catalyst. A possible reaction pathway for α-methylstyrene/$AlPO_4$ reaction with participation of surface acid sites on $AlPO_4$ was included.

## EXPERIMENTAL

All alkenes and alkynes were commercial quality chemicals purchased from Aldrich and were purified prior to use and the purity was verified by GC. Zinc borohydride in dry DME was prepared from $ZnCl_2$ and $NaBH_4$ according to the reported procedure.[18] All reaction products were characterized and identified by GLC and mass spectrometry. GLC analysis were performed with a column (2 m, 3.2 mm i.d.) packed with 10% DEGS on Chromosorb G AW-DMCS or with a capillary Supelcowax-10 (30 m, 0.2 mm i.d.) column. GLC-MS characterization was carried out by HRMS (VG Auto-Spec) in the Mass Spectrometry Service of Cordoba University.

**Catalysts.** Three catalysts were used. A synthetic $AlPO_4$, obtained by precipitation with aqueous ammonia from aqueous solutions of $AlCl_3.6H_2O$ and $H_3PO_4$ (85 wt%).[19] The solid thus obtained was washed with isopropyl alcohol, dried at 393 K for 24 h and then calcined at 773 K ($AlPO_4$-773; surface area 235 $m^2g^{-1}$) or 1073 K ($AlPO_4$-1073; surface area 225 $m^2g^{-1}$) for 3 h. 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 $m^2g^{-1}$).

**General procedure for hydration.** The alkene or alkyne (1 mmol) was uniformly adsorbed on catalyst (1 g) under stirring for 5 min. A solution of $Zn(BH_4)_2$ (1.5 mmol) in DME (3 mL) was then added to the catalyst impregnated with alkene or alkyne, at rt., and the mixture was stirred for a specified period of time (Table 1). The reaction mixture was then decomposed by careful dropwise addition of water and filtered. The filtrate was extracted with ether and the extract was dried over anhydr. sodium sulphate and solvent evaporated to leave the product. The products were characterized and identified by GC-MS.

**Reaction of α-methylstyrene without $Zn(BH_4)_2$ but in presence of $AlPO_4$ catalyst.** α-Methylstyrene (1 mmol) was adsorbed on $AlPO_4$ catalyst (1 g) under stirring for 5 min. Dry DME (3 mL) was then added to the catalyst impregnated with α-methylstyrene at room temperature and the mixture was stirred for 1.5 h. The reaction mixture was then filtered and the solvent was evaporated lo leave the products (Table 2). These were characterized and identified by GC-MS.

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