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Short communication

Wells–Dawson tungsten heteropolyacid-catalyzed reactions of benzylic alcohols, influence of the structure of the substrate

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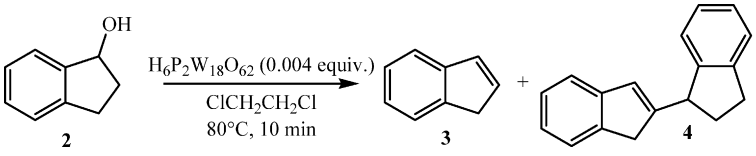
Abstract

Heterolytic cleavage of the C–OH bond of various benzylic alcohols has been catalyzed with $H_6P_2W_{18}O_{62}$. Alkenes or symmetric ethers are produced, depending on the structure of the substrate.

Keywords: Heteropolyacid; Catalysis; Benzylic alcohols; Dehydratation; Ethers; Disproportionation

Heteropolyacids (HPAs) have various catalytic applications [1] that could answer to some economic and environmental constraints. Recently, the Iranian team has investigated the characteristics of the Wells–Dawson tungsten heteropolyacid $H_6P_2W_{18}O_{62}$ (**1**) and supported forms of this HPA [2] while, over the last 20 years, the French team was involved in metal-catalyzed reactions of alcohols [3,4]. This urged us to study the **1**-catalyzed reactions of various benzylic alcohols; the results are here reported.

Heating at 80 °C a mixture of **1** (0.004 equiv.) and 1-indanol (**2**) in 1,2-dichloroethane for 10 min led to the complete conversion of the substrate to afford 1*H*-indene (**3**, 3%) and 2-(2,3-dihydro-1*H*-inden-3-yl)-1*H*-indene (**4**, 51%) [5,6] (Eq. (1)).



2 3 4 (1)

The formation of **3** and **4** is due to the acidic character of **1**. This leads to the heterolytic cleavage of the C–OH bond (Scheme 1) and the resulting species ($\mathbf{A}_1$) affords **3** via the loss of water. An other reactive pathway is the reaction of $\mathbf{A}_1$ with **3** leading to the dimeric compound [7]. In fact, the formation of **3** and **4** from **2** using Keggin-type HPAs has been already reported [6].

A similar reaction was obtained from an acyclic secondary benzylic alcohol such as 1-phenylethanol (**5**) which affords traces of styrene (**6**) and 53% of (*E*)-1,3-diphenylbut-1-ene (**7**). This last compound has been previously prepared by reaction of styrene with triflic acid [8].

In agreement with the above results and the mechanism proposed in Scheme 1, subjecting an 1:2 mixture of 1-indanol and styrene to the experimental conditions led to **4**, **7** and 2,3-dihydro-1-styryl-1*H*-indene (**8**) (Eq. (3)). The structure of **8** was established from the analysis of its mass and ^{1}H NMR spectra (see Section 1). A probable mechanism for the formation of **8** is

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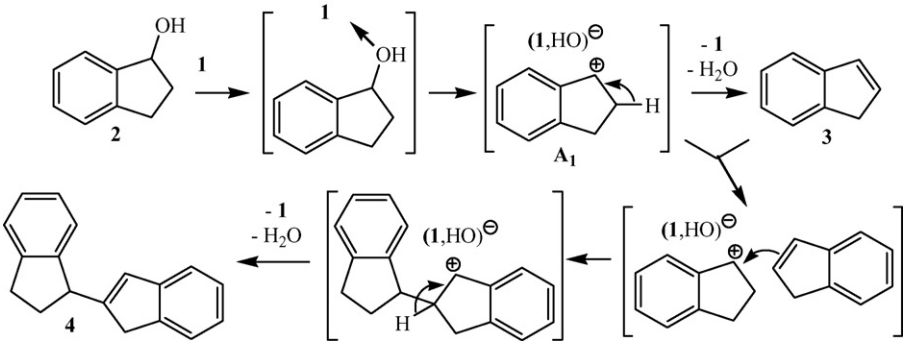
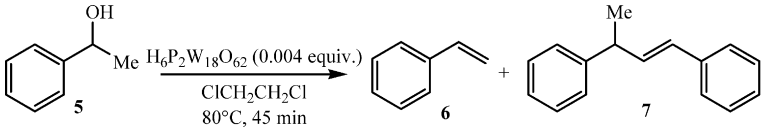
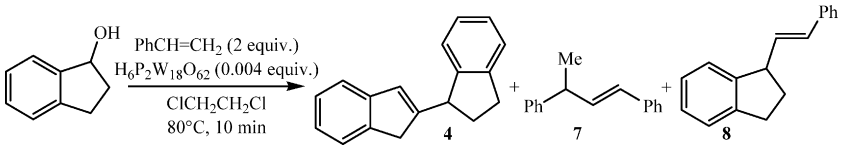


Scheme 1.

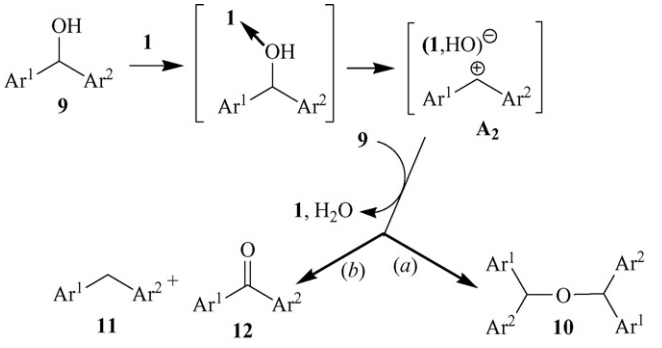
the reaction of $\mathbf{A}_1$ (Scheme 1) with **6** [7].



(2)

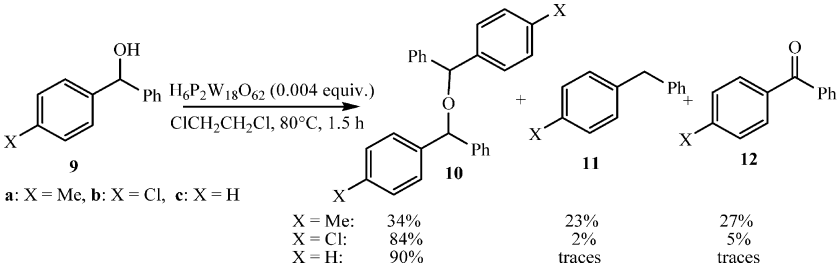


(3)

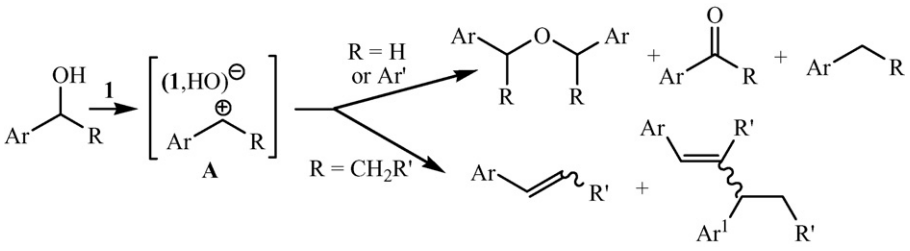


Scheme 2.

Secondary benzylic alcohols that cannot afford alkenes by dehydratation were then used as the substrates. Phenyl(*p*-tolyl)methanol (**9a**) led to a mixture of di-(phenyl(*p*-tolyl)methyl) oxide (**10a**, 34%) [9,10], phenyl(*p*-tolyl)methane (**11a**, 23%) and phenyl(*p*-tolyl)methanone (**12a**, 27%) (Eq. (4)). Switching from **9a** to either (4-chlorophenyl)(phenyl)methanol (**9b**) or diphenylmethanol (**9c**) as the substrate increased strongly the yield of the corresponding symmetric ether [9–12] to the detriment of the amount of the disproportionation products. Such compounds from **9a–c** have been already obtained using various acidic catalysts [9–13]. The formation of the symmetric ethers and the disproportionation products would occur via the reaction of the substrate with ionic species $\mathbf{A}_2$ produced from the interaction of the hydroxy group of **9** with **1** (Scheme 2) [4b,10,11].



(4)



Scheme 3.

A symmetric ether and disproportionation products were also produced from a primary benzylic alcohol, 1-naphthalenemethanol leading in 40 min to a complex mixture from which di-(α-naphthylmethyl) oxide, 1-naphthaldehyde and 1-methylnaphthalene were identified by GC/MS. The ether was subsequently isolated in 17% yield. We previously obtained this compound from 1-naphthalenemethanol using $PdCl_2(MeCN)_2$ as the catalyst [4b].

From the above results, it appears that the interaction of benzylic alcohols with $H_6P_2W_{18}O_{62}$ led to the cleavage of the C–OH bond to produce ionic species, and that the evolution of these latter towards the final products depends on the structure of the starting compound as resumed in Scheme 3. It seems of interest to point out that this evolution depends also on the nature of the acid catalyst. Indeed, di-(1-indanyl) oxide was obtained with 67% selectivity from **2** using $FeCl_3$ [4a] as the catalyst, and di-(1-phenylethyl) oxide was obtained with 94% and 86% selectivity from **5** using $AlPW_{12}O_{40}$ [13] and $PdCl_2(MeCN)_2$ [4b], respectively, as the catalysts, while these ethers were not isolated under the present conditions. We suspect that the synergistic effect of different active sites of **1** could mediate the cleavage of the C–OH bond of **2** and **5** and the almost concomitant abstraction of the proton leading to **3** and **6**, respectively.

1. General procedure

To **1** (18.3 mg, 0.004 mmol, previously dried at 120 °C overnight [2]) in $ClCH_2CH_2Cl$ (5 mL) was added a solution of the alcohol (1 mmol) in $ClCH_2CH_2Cl$ (5 mL). The mixture was stirred at 80 °C under an argon atmosphere for the time indicated in the text. After cooling to room temperature, the solvent was evaporated under vacuum and the residue was subjected to chromatography. The isolated compounds, except 2,3-dihydro-1-styryl-1*H*-indene, have been already prepared [4b,5,6,10–13].

2,3-Dihydro-1-styryl-1*H*-indene (**8**). ^{1}H NMR ($CDCl_3$, δ ppm): 1.93 (m, 1H, $ArCH_2CHH$), 2.40 (m, 1H, $ArCH_2CHH$), 2.94 (m, 1H, $ArCH_2$), 3.92 (q, J = 8.2 Hz, 1H, $ArCHCH_2$), 6.24 (dd, J = 8.5 and 15.7 Hz, 1H, PhCHCH), 6.53 (d, J = 15.7 Hz, 1H, PhCHCH), 7.17–7.40 (9H, aromatiques). MS, m/z = 221 (M + 1).

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