

Hydrogenation versus isomerization in α,β -unsaturated alcohols reactions over Pd/TiO₂ catalysts

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Abstract

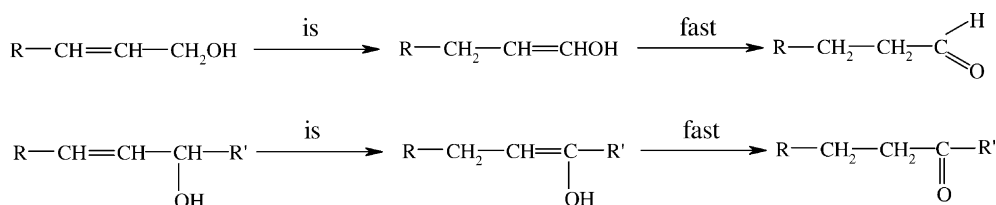
Liquid phase hydrogenation and isomerization of some α,β -unsaturated primary and secondary alcohols have been investigated in tetrahydrofuran over a 2.5% TiO₂ supported palladium catalyst at 303 K and 0.01 MPa partial hydrogen pressure. The double bond isomerization reaction of these substrates leads also to formation of the corresponding saturated aldehydes or ketones. Catalytic activity and selectivity were found to depend strongly on the steric and electronic effects of the substituents on the double bond of the alcohol. The less crowded is the olefinic bond of the unsaturated alcohol, the higher is the activity. Formation of two σ -alkyl palladium bonded intermediates was postulated to explain the different selectivity towards hydrogenated and isomerized products observed for α,β -unsaturated alcohols used. 2-Propen-1-ol exhibited the highest activity and selectivity for double bond migration leading to propanal up to 80% yield.

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Keywords: α,β -Unsaturated alcohols; Hydrogenation; Double bond isomerization; TiO₂ supported palladium catalyst; σ -Alkyl intermediates

1. Introduction

The catalytic hydrogenation of alkenes to the saturated analogous is frequently accompanied by double bond migration and/or *cis-trans* isomerization [1–3]. In particular, in the case of α,β -unsaturated alcohols, the double bond isomerization reaction can afford the corresponding saturated aldehydes or ketones through the following sequence:



The extent of formation of these products depends on the catalyst used as well as the reaction conditions. Therefore, an important challenge is to obtain the carbonyl derivative with high selectivity. It is also well known that supported palladium catalysts are both the most active and selective

for hydrogenation and isomerization reactions of alkenes [4–6]. In previous papers we have presented the results on the liquid phase hydrogenation of an α,β -unsaturated diol, *cis*-2-butene-1,4-diol, over supported palladium catalysts. It was observed that, under the experimental conditions adopted, the *cis*-2-butene-1,4-diol is hydrogenated to butane-1,4-diol through a complex reaction network, involving also double bond and *cis-trans* isomerization and

hydrogenolysis reactions [7,8]. The study of the effect of some parameters, such as the nature of the support and the solvent and the partial hydrogen pressure, highlighted that high yield to double bond migration products can be obtained using TiO₂ as material support, aprotic solvents (tetrahydrofuran, ethyl acetate) and low partial hydrogen pressure.

In this work a systematic study on the catalytic hydrogenation and isomerization of a series of α,β -unsaturated

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alcohols, such as 2-propen-1-ol (A2), (*E*)-2-buten-1-ol (tB2), 3-buten-2-ol (B3), (*E*)-2-penten-1-ol (tP2), (*Z*)-2-penten-1-ol (cP2), (*E*)-3-penten-2-ol (tP3), (*E*)-2-hexen-1-ol (tH2), carried out at low partial hydrogen pressure and over a Pd/TiO₂ catalyst, is reported in order to verify the possibility of a new synthetic route to carbonyl derivatives. The influence of the organic substrate structure on the activity and products distribution was also investigated.

2. Experimental

2.1. Materials

The compounds studied, 2-propen-1-ol (A2), (*E*)-2-buten-1-ol (tB2), 3-buten-2-ol (B3), (*E*)-2-penten-1-ol (tP2), (*Z*)-2-penten-1-ol (cP2), (*E*)-3-penten-2-ol (tP3), (*E*)-2-hexen-1-ol (tH2), were commercial products, purchased from Aldrich. Distilled tetrahydrofuran (Fluka, 99.8% analytical grade) and ultra high purity hydrogen (multigas > 99.9%) were used.

The support used for the catalyst preparation was a commercial TiO₂ (anatase phase) of low surface area (SA = 8.6 m²/g), supplied by Fluka. Palladium catalyst (2.5%) was prepared by incipient wetness impregnation of the support with an acidic aqueous solution of PdCl₂ in HCl 0.1 M. After impregnation, the catalyst was dried at 393 K for 2 h and reduced at 423 K for 1 h under flowing hydrogen.

2.2. Reaction procedure

The hydrogenation of α,β -unsaturated alcohols was carried out in liquid phase at 0.01 MPa partial hydrogen pressure and 303 K, using tetrahydrofuran as solvent in a five-necked flask of 100 ml, equipped with a reflux condenser and a thermocouple. Nitrogen was used to balance the total reaction pressure at 0.1 MPa. The reaction temperature was maintained at the constant value (± 0.5 °C) by circulation of silicone oil in an external jacket connected with a thermostat. The catalyst was added to the solvent used (25 ml) and reduced in situ at 323 K for 1 h under H₂ flow. After

cooling at the desired reaction temperature, 15 ml of a 0.6 M solution of the α,β -unsaturated alcohol in tetrahydrofuran, containing an internal standard, was added through one arm of the flask. The reaction mixture was stirred with a stirrer head having a permanent magnetic coupling at a stirring rate of 500 rpm. The progress of the reaction was followed by analyzing a sufficient number of samples withdrawn from the reaction mixture. Products analysis was performed with a gas chromatograph (HP model 5890) equipped with a flame ionization detector. The products separation was obtained using a wide-bore capillary column (CP Wax 52 CB, 30 m, i.d. = 0.53 mm). Quantitative analyses were carried out by calculating the area of the chromatographic peaks with an electronic integrator (HP model 3395).

3. Results and discussion

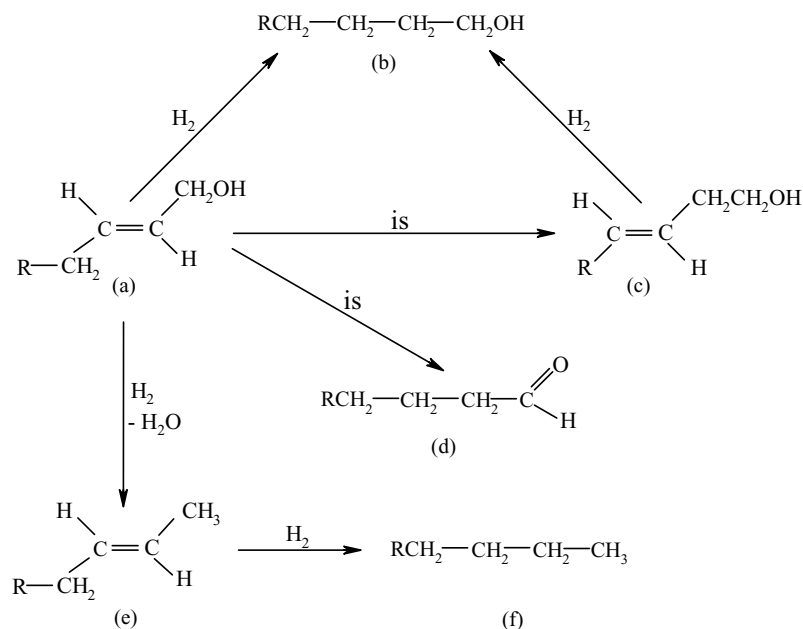
Reactions of α,β -unsaturated alcohols were carried out over titania supported palladium, at 303 K and 0.01 MPa partial hydrogen pressure, using tetrahydrofuran as solvent, in order to favor the isomerization versus the hydrogenation process [8,9]. All experimental results concerning the activity and the products distribution are reported in Table 1. Under the experimental conditions used, the reaction proceeds according to Scheme 1. Hydrogenation of the starting compound (supposed to be a *trans*-derivative) gives the fully hydrogenated product (b). On the other hand double bond isomerization from 2 to 1 position affords the aldehyde (d), through a vinyl alcohol intermediate, whereas the analogous isomerization from 2 to 3 double bond position leads to formation of the *trans*-olefin derivative (c). This gives (b) as final hydrogenation product. Furthermore, hydrogenolysis of the starting material gives (e) that can be further hydrogenated to the compound (f). An analogous scheme can be formulated for olefinic secondary alcohols. In this case ketones are formed as isomerization final products instead of aldehydes. Subsequent hydrogenation of the carbonyl group of aldehydes or ketones does not occur on palladium catalysts in mild conditions. Furthermore, no isomerization takes place in absence of hydrogen or using only the Lewis acid

Table 1

Hydrogenation and isomerization of α,β -unsaturated alcohols over a 2.5% Pd/TiO₂ catalyst at 303 K and 0.01 MPa partial hydrogen pressure, using tetrahydrofuran as solvent

Substrate code	V_i (mol _{sub} g _{Pd} ⁻¹ S ⁻¹) × 10 ⁴	Final yield (%)		
		Hydrogenated ^a product	Aldehyde or ketone	Hydrogenolysis product
A2	1.54	18.0	82.0	0
tB2	1.40	25.6	58.9	15.5
cP2	4.19	41.5	42.1	16.3
tP2	1.29	39.4	26.9	33.7
tH2	0.52	33.3	29.7	37.0
B3	2.60	22.2	62.7	15.1
tP3	0.94	40.4	43.6	16.0

^a Yield of hydrogenation products of (a) and (c) derivatives (Scheme 1).



support. Then hydrogen is necessary for isomerization reactions to proceed on palladium catalysts.

A typical products composition–time plot showing the course of the reaction at 303 K and 0.01 MPa hydrogen pressure for the α,β -unsaturated alcohol, (*E*)-2-penten-1-ol, is reported in Fig. 1. Besides final products (pentanal, 1-pentanol and pentane), (*E*)-3-penten-1-ol, (*Z*)-3-penten-1-ol and (*E*)-4-penten-1-ol are the main intermediates detected. They are formed by double bond isomerization from 2 to 3 and from 3 to 4 position, respectively. It should also be noted that double bond migration leads to both geometric isomers of the olefinic alcohol, but the thermodynamically more stable *trans*-isomer is predominantly formed. Subsequent intermediates hydrogenation affords the saturated alcohol, 1-pentanol.

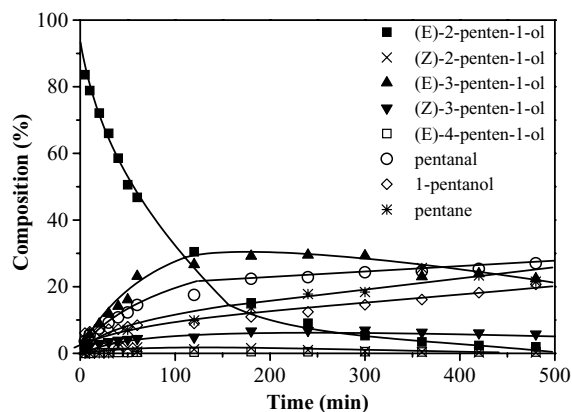


Fig. 1. Composition–time profile relative to the hydrogenation and isomerization reaction of (*E*)-2-penten-1-ol in tetrahydrofuran over a 2.5% Pd/TiO₂ catalyst, at 303 K and 0.01 MPa partial H₂ pressure.

3.1. Hydrogenation and isomerization of α,β -unsaturated primary alcohols

Fig. 2 shows the activities comparison concerning different α,β -unsaturated primary alcohols over the 2.5% Pd/TiO₂ used at 303 K and 0.01 MPa partial hydrogen pressure. It appears that the activity decreases as the chain length of the organic substrate increases. The highest activity observed, when A2 is used as substrate, is about three times bigger than that obtained with tH2. The results are in agreement with literature data and can be explained taking into account the Lebedev's rule (the more substituted is the olefinic bond, the slower is the process of hydrogen addition) [10]. Therefore, the steric effect of C sp² substituents is the most important factor affecting the reactivity of the substrate.

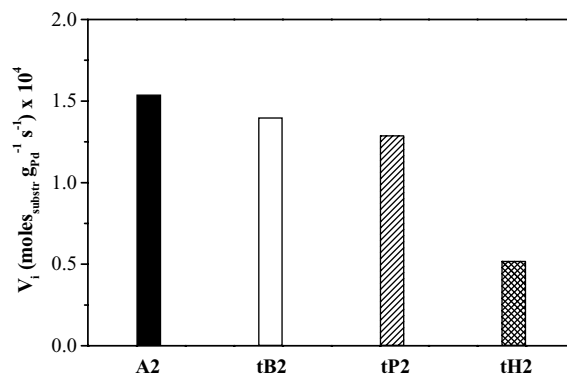


Fig. 2. Activities comparison in the reaction of α,β -unsaturated primary alcohols with hydrogen in the presence of a 2.5% Pd/TiO₂ catalyst at 303 K and 0.01 MPa partial H₂ pressure. A2: 2-propen-1-ol; tB2: (*E*)-2-buten-1-ol; tP2: (*E*)-2-penten-1-ol; tH2: (*E*)-2-hexen-1-ol.

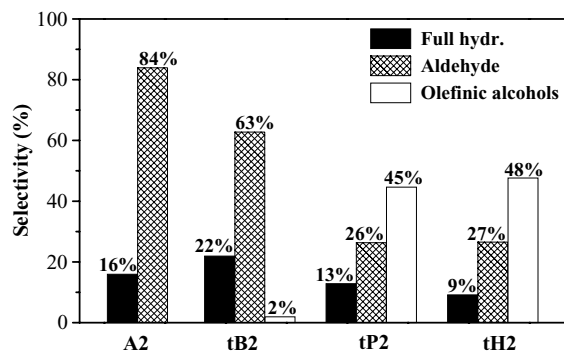


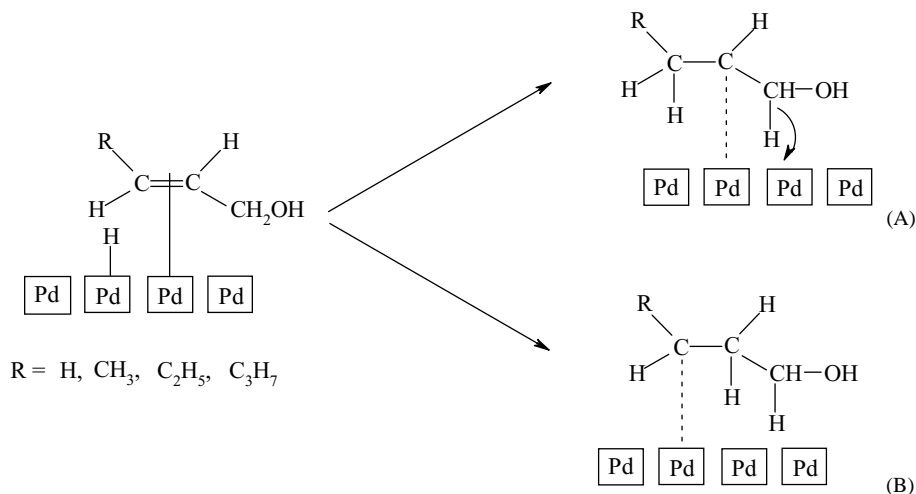
Fig. 3. Selectivity comparison, at 80% conversion, towards hydrogenation products, aldehydes and double bond isomerization deriving olefinic alcohols, in the reaction of α,β -unsaturated primary alcohols with hydrogen over a 2.5% Pd/TiO₂ catalyst, at 303 K and 0.01 MPa partial H₂ pressure.

Fig. 3 displays the selectivity towards hydrogenation and isomerization products at 80% conversion of the organic substrate. The results indicate that the selectivity towards the saturated aldehydes depends on the substrate structure and it decreases on increasing the chain length of the unsaturated alcohol. Conversely, the opposite double bond migration increases. The best yield to aldehyde, so far obtained, is $\sim 80\%$ when propanal is formed from 2-propen-1-ol. Furthermore, on this substrate, no hydrogenolysis reaction was detected. Moreover, an increase of hydrogenolysis products was observed on other long chain alcohols (Table 1). In a recent paper concerning a detailed kinetic study on the hydrogenation and isomerization of *cis*-2-butene-1,4-diol, we have shown that formation of hydrogenation and isomerization products can be explained on the basis of an unique σ -alkyl palladium bonded intermediate [8]. Since no reaction occurs in absence of hydrogen, when α,β -unsaturated alcohols are isomerized, formation of a surface palladium hydride species is a fundamental requirement. Therefore the different selectivity towards the corresponding saturated al-

cohols, aldehydes and other unsaturated compounds deriving from a double bond migration process can be explained on the basis of two σ -alkyl palladium bonded intermediates, formed by an interaction between a chemisorbed unsaturated alcohol and a Pd–H (Scheme 2). The proposed formation of two intermediates stems from a hydrogen addition to the 3 carbon atom (intermediate A) and the 2 one (intermediate B) of the associatively adsorbed olefinic substrate. Accordingly, the results obtained indicate that the selectivity towards saturated aldehydes decreases as the C sp² substituents become larger and it follows the order: CH₃CH₂CH₂ \cong CH₃CH₂ < CH₃ < H. Therefore the different stability of both intermediates involved in the process depends strongly on the electronic effects of the substituents: the more important is the electron donor effect of the substituent, the most stable is the intermediate. Propyl, ethyl, methyl group stabilize the intermediate B with respect to the intermediate A. It is also worth noting that no appreciable difference of selectivity was observed between tH2 and tP2, probably because the reactivity differences, due, as previously reported, mainly to electronic effects, reduce as the bulkiness of the groups increases.

3.2. Hydrogenation and isomerization of (*Z*)-2-penten-1-ol and (*E*)-2-penten-1-ol

Table 1 and Fig. 4 display the results concerning the activity and the selectivity towards the main products observed when the geometric isomers (*Z*)-2-penten-1-ol and (*E*)-2-penten-1-ol react with hydrogen. As expected, the (*Z*) isomer is more reactive than the (*E*) analogous: its reaction rate, in fact, is about three times higher and takes into account the stronger steric hindrance of the (*E*) substrate [11]. A different products distribution was also detected. Indeed, when we use cP2, as substrate, a remarkable *cis*–*trans* isomerization reaction takes place together with a lower formation of other double bond migration alcoholic olefins. Moreover, no appreciable difference to aldehyde selectivity,



Scheme 2. σ -Alkyl intermediates involved in the hydrogenation and isomerization process of various α,β -unsaturated primary alcohols.

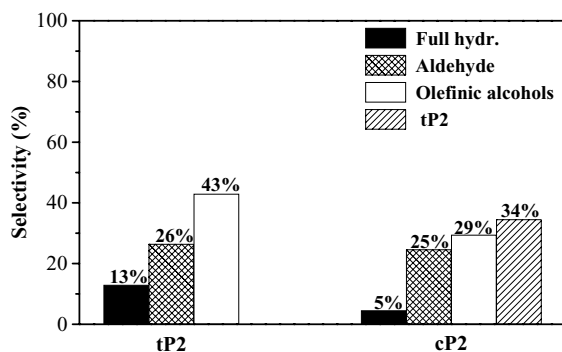


Fig. 4. Selectivity comparison, at 80% conversion, towards the main observed products in the reaction of geometric (*Z*) and (*E*)-2-pentene-1-ol isomers with hydrogen over a 2.5% Pd/TiO₂ catalyst, at 303 K and 0.01 MPa partial H₂ pressure.

pentanal, at 80% conversion of both geometric isomers is observed. As far as the hydrogenolysis product, pentane, is concerned the highest yield occurs starting from tP2. This is quite well understandable on the basis of steric reasons. Furthermore, since the reaction of cP2 and tP2 leads to the same final products, it is suggested that the same σ -alkyl intermediates are also involved (see Scheme 3). Therefore, in order to understand the different selectivity data, reported in Fig. 5, we have to consider that: (i) the (*E*) derivative is thermodynamically more stable than the (*Z*) one; (ii) at 80% conversion the selectivity to aldehyde of both cP2 and tP2 are nearly equal. This may imply that, besides the fully hydrogenated compound, the σ -alkyl intermediate C gives, as the only product, the aldehyde derivative, whereas the intermediate D affords other double bond and geometric isomerization products. As a consequence the final yield to aldehyde increases when cP2 is used as starting material.

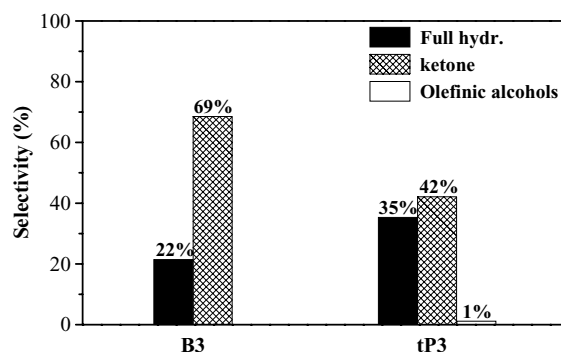
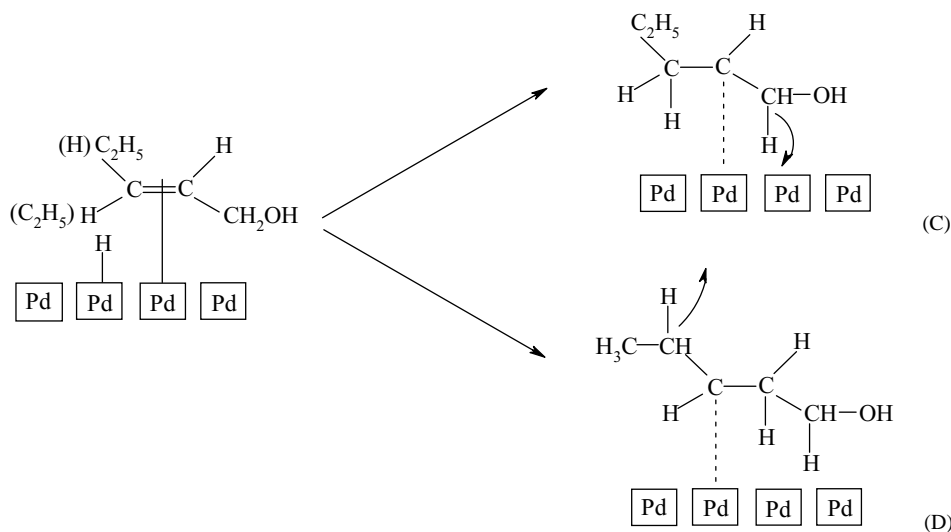


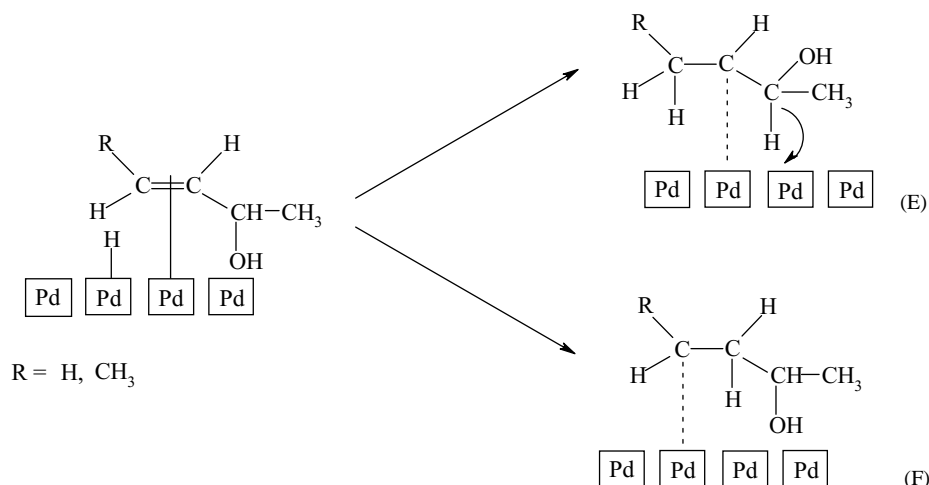
Fig. 5. Selectivity comparison, at 80% conversion, towards hydrogenation products, ketones and double bond isomerization deriving olefinic alcohols in the reaction of α,β -unsaturated secondary alcohols with hydrogen over a 2.5% Pd/TiO₂ catalyst, at 303 K and 0.01 MPa partial H₂ pressure.

3.3. Hydrogenation and isomerization of α,β -unsaturated secondary alcohols

In order to study the feasibility of saturated ketones from α,β -unsaturated secondary alcohols, 3-buten-2-ol and (*E*)-3-penten-2-ol were chosen as substrates, following their reaction with hydrogen on Pd/TiO₂ at 0.01 MPa partial hydrogen pressure and 303 K. Table 1 and Fig. 5 show both activity and selectivity distribution observed. Again, as above reported for analogous unsaturated primary alcohols, these parameters depend on the length of the chain and the mechanism involves two σ -alkyl intermediates as shown in Scheme 4. In particular the selectivity to ketones increases on changing the C sp² substituent from CH₃ to H and it is higher than that to analogous aldehydes. The best explanation for the observed results considers a greater stability of the σ -alkyl intermediate E (Scheme 4) deriving from a secondary alcohol, due to an additional CH₃ on the C bearing the OH group.



Scheme 3. σ -Alkyl intermediates involved in the hydrogenation and isomerization process of the geometric isomers, (*E*)-2-penten-1-ol and (*Z*)-2-penten-1-ol.



Scheme 4. σ -Alkyl intermediates involved in the hydrogenation and isomerization process of the α,β -unsaturated secondary alcohols, 3-buten-2-ol and (*E*)-3-penten-2-ol.

4. Conclusions

The main results of this work indicate that at 0.01 MPa partial hydrogen pressure and over a 2.5% Pd/TiO₂ catalyst double bond isomerization and hydrogenolysis products are formed in addition to hydrogenated compounds, starting from α,β -unsaturated alcohols. Aldehydes or ketones are the isomerized final products. The activity and selectivity of the reactions investigated are strongly dependent on the steric and electronic effects of the C sp² substituents. The more important is the electron donor effect of the substituent, the lower is the formation of aldehydes or ketones.

A high yield to aldehyde (~80%) was obtained starting from 2-propen-1-ol. This result and others experimentally observed make the reaction studied, at least for some unsaturated alcohols, attractive for a new catalytic route leading to carbonyl compounds.

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