

## MODIFIED WACKER TBHP OXIDATION OF 1-DODECENE

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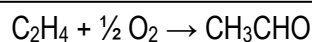
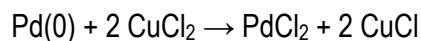
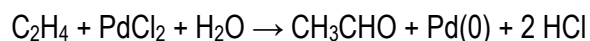
## Abstract

A higher 1-olefin (1-dodecene) was oxidized to 2-dodecanone and other ketones in a modified Wacker system featured by omitting the use of copper chloride and employing tert-butylhydroperoxide (TBHP) as oxidant. Acetonitrile was the solvent of choice due to its higher selectivity towards 2-dodecanone, the reaction occurring mostly in the interface. A maximum in conversion and selectivity was measured for a ratio  $[\text{CH}_3\text{CN}] / [1\text{-dodecene}] = 10$ . The temperature abatement enhances the 2-dodecanone selectivity (61% at 40°C) because of the lower extent of the competing isomerization reactions. An optimum in 2-dodecanone selectivity was found for a  $[\text{TBHP}] / [1\text{-dodecene}]$  ratio = 7. The use of  $\text{H}_2\text{O}_2$  as oxidant led towards slower oxidation rates than TBHP. Other palladium salts ( $\text{PdSO}_4$  and  $\text{Pd}(\text{CH}_3\text{COO})_2$ ) and several R-CN solvents (propionitrile, benzonitrile, isobutyronitrile) yielded lower performances than palladium chloride and acetonitrile, respectively. On the contrary,  $\beta$ -cyclodextrin, a phase transfer catalyst, improved the selectivity towards 2-dodecanone.

Keywords: palladium chloride, Wacker oxidation, tert-butylhydroperoxide, 2-dodecanone, acetonitrile

## Introduction

The oxidation of ethene towards acetaldehyde using the catalytic system PdCl<sub>2</sub> / CuCl<sub>2</sub> and oxygen as final oxidant constitutes the well-known Wacker –Smidt process which has been widely used at a commercial scale since 1959 [1]. The system comprises the following twofold catalytic scheme, wherein copper chloride acts as reactivating cocatalyst of the palladium salt, being itself finally reoxidized by aerobic oxygen:



Wacker oxidation can be extended to higher 1-olefins, giving rise chiefly to 2 methylketones as well as to a mixture of internal ketones due to the occurrence, prior to oxidation, of competing double bond isomerization reactions. These are rather useful feedstocks which might be applied for the preparation of polar waxes, cetane index improvers, varnishes, printer inks, etc. In this regard, oxidation chemistry based on palladium salts offers unique possibilities in reaction medium with complex makeups (e.g. 1-olefins from waste polyethylene thermal cracking) [2]. The presence of different heteroatoms (N, S) appears not to affect meaningfully the oxidation course which makes it a rather supple catalytic system [3].

However, conventional Wacker oxidation shows some drawbacks. Firstly, the kinetics of the oxidation of higher 1-olefins is slow due to their low solubility in water which decreases

steadily with growing chain length [4,5]. Secondly, the use of copper chloride as cocatalyst brings about the formation of unwanted chlorine containing compounds along with the ketones, especially when working with higher 1-olefins [6]. Finally, palladium salts tend to deactivate by aggregating into clusters which lead towards the precipitation of palladium black. To avoid this, hydrogen chloride is usually added giving rise to highly corrosive reaction systems [7].

Many modified Wacker based oxidation processes may be found in literature that try to overcome the aforementioned bounds. In order to facilitate catalyst recovery and also avoid loss of palladium by aggregation, copper chloride containing Wacker systems with palladium species were heterogenised over montmorillonite [8], zeolite Y [9], pore glass [10] and cyano-functionalized polyimide beads [11,12]. In this respect, a Pd nanocluster (cationic Pd<sub>2060</sub>) was immobilised on TiO<sub>2</sub> and used in the oxidation of higher 1-olefins (C<sub>6</sub> - C<sub>12</sub>) [13]. Another different alternative consists of employing other redox pairs instead of the Cu(II) / Cu(I) one. Typical examples includes p-benzoquinone/hydroquinone [14], Fe(III)/Fe(II) [15], and several heteropolyacids [6,7,16]. In addition, some of these systems have also been heterogenized on several supports, e.g. H<sub>3+n</sub>PVMo<sub>12-n</sub>O<sub>40</sub> on silica [7] or Pd(OAc)<sub>2</sub> / NPMoV on activated carbon [16]. However, many of them lack of fast kinetic rates and the yields towards methyl ketones vary widely depending on the chosen system.

On the other hand, different solvents have been also tested to increase the miscibility of the higher 1-olefins, the best results being attained with dimethylformamide [5] and acetonitrile [2], respectively, with yields in the range 60 – 80%. Surfactants (sodium lauryl sulphate) [17], ionic liquids ([bmim][BF<sub>4</sub>]) [18-20] and inverse phase transfer catalysts (calixarenes, β-calixarenes) [21,22] have been reported to exhibit better performances in regards to their

respective Wacker systems. Specially remarkable are the results of Mitsudome et al. [23] which succeeded in the oxidation of higher 1-olefins (around 85% yields) with molecular oxygen using palladium chloride and N,N-dimethylacetamide as solvent, without the need for copper chloride.

In this work, the oxidation of a standard 1-olefin (1-dodecene), selected as a model of higher 1-olefins ( $C_{10} - C_{18}$ ), was tested in a modified Wacker system consisting of tert-butylhydroperoxide (TBHP) as oxidant and acetonitrile as solvent. Neither hydrogen chloride nor copper chloride was present avoiding all their related risks. TBHP was included in its makeup regarding additionally its remarkable performance in several Wacker systems [24,25], e.g. the ligand-modulated palladium catalyzed Wacker oxidation of styrenes [25]. The usage of peroxides also seems to accelerate the kinetics, according to the results of Melgo et al. [26]. Consequently, this work reports the modified Wacker TBHP oxidation ( $PdCl_2$  /TBHP/  $CH_3CN$ ) of the higher olefin 1-dodecene, a difficult substrate to be oxidized in conventional Wacker systems, investigating the influence wielded by several reaction variables.

## Experimental Section

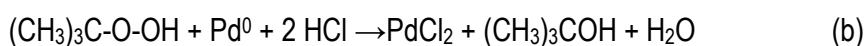
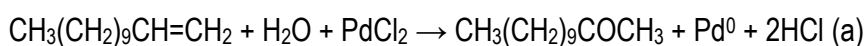
**Chemicals.** The chemicals used in the present research were the following: 1-dodecene (95 wt. %, Aldrich), tert-butyl hydroperoxide (TBHP, 70 wt. % aqueous solution, Aldrich), anhydrous tert-butyl hydroperoxide (TBHP, Fluka, 5.5 M in decane), acetonitrile (99.5 wt. % Scharlau) and palladium (II) chloride (99 wt. %, Fluka). Additionally, other used chemicals were hydrogen peroxide (30 wt. % Scharlau), palladium sulphate (Aldrich), palladium (II) acetate (Aldrich),  $\beta$ -cyclodextrin ( $C_{42}H_{70}O_{35} \cdot xH_2O$ , Aldrich), propionitrile (Aldrich, 99 wt.%), isobutyronitrile (Aldrich, 99.6 wt.%) and benzonitrile (Aldrich, 99%).

**Experimental installation and oxidation reactions.** The catalytic experiments were carried out in a stirred glass batch reactor equipped with a reflux column and a propeller stirrer. The reactor was placed inside a thermostatic bath, the temperature being kept constant with a temperature controller within  $\pm 1^\circ\text{C}$ . In a typical experiment, 5.0 g of the substrate 1-dodecene, 21.6 g of TBHP and 0.1 g of palladium (II) chloride were loaded into the reactor along with 11.6 g of acetonitrile. The mixture was left under stirring (300 rpm) at the corresponding reaction temperature (ranging from 40 to 80°C) during the reaction time (0 – 18 h). Once the reaction is finished, tetrahydrofuran (179.0 g) was added to the reaction mixture in order to homogenize the biphasic medium for the subsequent analysis of the obtained products.

**Analysis of the reaction products.** The reaction samples were analysed in a Varian 3900 GC equipped with a CP8907 methylsilicone column of 15 m length x 0.25  $\mu\text{m}$  width and provided with a flame ionization detector (FID). Prior to the analyses, tetralin was added as internal standard to the reaction mixture previously dissolved in tetrahydrofuran. The identification of the different compounds was performed by comparison with the retention times of reference commercial standards (2-dodecanone, 1-2 epoxydodecane, dodecanal, dodecanoic acid). Subsequently, both the 1-dodecene conversion and the selectivity towards the obtained products were determined. The conversion was defined as  $(\text{mol of reacted 1-dodecene})/(\text{mol of starting 1-dodecene}) \cdot 100$ . Selectivities were evaluated in regards to the three product groups: 2-dodecanone ( $S_{2\text{-dodecanone}}$ ), other ketones ( $S_{\text{other ketones}}$ ) and dodecene isomers ( $S_{\text{C}_{12} \text{ isomers}}$ ).

## Results and discussion

**Pathways in the modified Wacker TBHP oxidation.** Wacker oxidation using TBHP may proceed according to different mechanisms. Initially, our reaction system contains water from the TBHP reagent (70 wt. % aqueous solution) which can act as oxygen source for the olefin according to the following scheme of reactions:



The addition of water proceeds according to the conventional hydroxypalladation mechanism of the Wacker – Schmitt oxidation [1] with TBHP leading subsequently to the reoxidation of the palladium. On the other hand, TBHP is capable of directly ketonizing the olefin through a peroxypalladation step, similar to those depicted by Mimoun et al [24] and Cornel et al [25]. Hence, the scheme of reactions shown in Figure 1 may be envisaged. Step 1 of the mechanism consists of the complexation of the reacting olefin to the palladium (II) complex. Subsequently, the complex may proceed through step 2 giving rise to the appearance of a  $\pi$ -allylpalladium species which drives to the formation of the different dodecene isomers (step 3). Step 4 means the incorporation of the tert-butyl hydroperoxide within the palladium complex of the dodecene isomers forming a five-membered pseudocyclic peroxypalladium complex, similar to those reported to lead to the ketonization of terminal olefins by rhodium peroxo complexes [24]. This is followed by a 1,2-hydride shift and the release of both tert-butanol and the desired product (other ketone) (Step 5). Step 6 is similar to step 4 but this time, the peroxypalladium complex is

formed with 1-dodecene instead of the dodecene isomers, releasing the desired product 2-dodecanone (step 7).

The feasibility of the direct oxidation of the olefin by TBHP in our reaction medium was tested by using anhydrous tert-butyl hydroperoxide as reagent. The obtained results are shown in Table 1, being compared to those attained with 70 wt. % aqueous TBHP. Anhydrous TBHP clearly oxidizes the reagent 1-dodecene. The conversion is even higher than that with aqueous TBHP (88 vs 75%). The usage of anhydrous TBHP led to a slightly lower amount of total oxidized compounds (2-dodecanone + other ketones) and a higher one of 1-dodecene isomers. In this regard, Cornel [25] observed in their isotopic experiments of styrene oxidation with TBHP that the majority of the incorporated oxygen comes from the TBHP instead of water.

**Reactions in the modified Wacker system.** Figure 2 illustrates the evolution with the time obtained in the modified Wacker oxidation of 1-dodecene using either acetonitrile or isopropanol at 80°C as solvents. The solvent plays a key role since it works as mixing medium increasing the solubility of the olefin species [5] and, it alters the electronic properties of the catalyzing palladium complex [23]. Acetonitrile was chosen as solvent because it showed the best performance according to the results of a previous work [2]. In addition, acetonitrile makes up a biphasic reaction medium while isopropanol gives rise to a monophasic one. Blank experiments without olefin indicated that neither solvent was oxidized under our reaction conditions. Figure 2 points out that the conversion climbs quickly to 80-90% over both solvents just after 0.5 h of reaction, with scarce modifications along the time. The main differences are appreciated in the selectivity results. Acetonitrile promotes less isomerization ( $S_{C_{12}}$  isomers) and provides more 2-dodecanone than isopropanol. The isomerization reaction proceeds rather fast leading towards a 53% of



isomerization over acetonitrile and a huge 72% over isopropanol after 0.5 h. Consequently, the amount of 2-dodecanone ( $S_{2\text{-dodecanone}}$ ) rises to 30% after 0.5 h with acetonitrile whereas with isopropanol is just 10%. The selectivity towards other ketones ( $S_{\text{other ketones}}$ ) is similar with both solvents at 0.5 h of reaction (17%). Neither the aldehyde nor any epoxide were detected in our reaction medium. The kinetics indicates that the 1-dodecene isomers are oxidized along the time, and to much higher extent over isopropanol. Thereby, the isomers selectivity dropped from 72% to 36% in isopropanol after 6 h while for acetonitrile fell from 53 to 35%. In addition, the total sum of ketones after 6 h is practically identical with both solvents (64%), although the selectivity towards 2-dodecanone is higher with acetonitrile (41%). The reported results suggest the following scheme of reactions:



Isomerization is a fast reaction (pathway 1) which competes with the slower oxidation of 1-dodecene (pathway 2). However, it is also a reversible reaction that may be reverted towards the starting 1-dodecene as the latter is consumed in the oxidation reaction. This is appreciated clearly when acetonitrile is used as solvent, since the amount of 2-dodecanone increases continuously as a result of the dodecene isomers reacting back to 1-dodecene. In contrast, when using isopropanol, not only the reversion of the isomers equilibrium appears to occur but also the direct oxidation of some dodecene isomers takes place (pathway 3), since both the selectivity towards 2-dodecanone and especially to other ketones enhances along the time. Note that the

formation of other ketones is rather remarkable regarding that they are more difficult to be oxidized than the terminal 1-olefins.

The reason of the higher share of 2-dodecanone when acetonitrile is used as solvent could be related to the biphasic nature of the system. However, other similar biphasic systems with H<sub>2</sub>O as solvent and TBHP as oxidant led towards less than 10% selectivity to 2-dodecanone. Therefore, the occurrence of a specific interaction of the solvents with the palladium chloride complex is likely to happen. Due to the remarkable selectivity with acetonitrile towards 2-dodecanone, this was the solvent of choice for the subsequent study.

**Influence of the main reaction variables.** The presence of a biphasic medium poses the question of the possible influence of the drop size in the emulsion over the obtained conversions and selectivities. In order to check this point, several experiments were carried out varying the stirring speed in the range 100 – 500 rpm for 0.5 h at 40°C. Figure 3 illustrates the obtained results in terms of conversion and selectivity. The conversion increases steadily with the stirring speed reaching 43% at 500 rpm. In contrast, the selectivity data indicate the existence of a turning point placed at higher speeds (400 – 500 rpm). Thus, the selectivity towards 2-dodecanone remains steady at 40% and diminishes to 33% at 500 rpm. Likewise, the selectivity towards dodecene isomers keeps the same trend and decreases to 42% at 500 rpm. Finally, the selectivity towards other ketones gives rise to roughly 11% within 100 – 400 rpm and rises to 23% at 500 rpm. The enhancement in conversion may be ascribed to both the parallel abatement of the drop size as well as the growing mass transfer coefficients with increasing stirring speed. This is in keeping with the reaction taking place in the interface, since the likely charged nature of the palladium species make them remain in the aqueous phase. Another explanations would be that

the isomerization reactions may take place to a larger extent at high stirring speeds ( $N = 400 - 500$  rpm) and the suggestion of a different concentration of the species within the reaction zone alongside the drop beyond a critical droplet size.

Figure 4 shows the effect of the  $[\text{CH}_3\text{CN}]/[1\text{-dodecene}]$  molar ratio within the 0 -15 range in the modified Wacker oxidation at  $80^\circ\text{C}$  for 2 h. Seemingly, the existence of an optimum appears to occur in both selectivity and conversion. Thus, the conversion varies within 65 – 88%, with the maximum placed at the molar ratio of 10. Likewise, the selectivity towards 2-dodecanone as well as to other ketones also exhibit a maximum corresponding to the same molar ratio of 10. Thus, the selectivity towards 2-dodecanone rose to 34% while the corresponding one to other ketones reached 23%. These results confirm the key role played by the solvent. In addition, they point out that the solvent may not only favour the Wacker oxidation but also be detrimental if an excess is added. This fact may be explained considering that an excess of acetonitrile dilute the reactants and it is likely to displace them from the oxidation sites once a given level of concentration is surpassed.

Figure 5 illustrates the effect of temperature in the Wacker oxidation of 1-dodecene with TBHP. The conversion increases with the temperature reaching 86% at  $80^\circ\text{C}$  after 0.5 h of reaction while at  $40^\circ\text{C}$  it is distinctly lower (34%). Longer reaction times ( $> 1$  h) at 60 and  $80^\circ\text{C}$  do not change meaningfully the conversion which remains around 84 - 88%, respectively. In contrast, the conversion rises progressively at  $40^\circ\text{C}$  up to reaching 76% after 3 h of reaction without any visible plateau being achieved. The selectivities towards the different products are markedly affected by the temperature. The highest selectivity towards 2-dodecanone is attained at  $40^\circ\text{C}$  and decreases steadily with growing temperatures. Hence, a remarkable 61% of 2-

dodecanone is attained at 40°C after 3 h of reaction. This amount dropped to 44 and 39% at 60 and 80°C respectively. The selectivities towards other ketones follows the opposite trend as their highest values are reached at 80°C (~ 20%) while at 40 and 60°C the obtained values are rather similar (around 11%). Unlike the selectivities towards 2-dodecanone, the selectivities towards other ketones only vary slightly with the time. The selectivities to 1-dodecene isomers indicates that the highest amount of isomers are formed at the beginning of the reaction (0.5 h) for the three temperatures, the highest share being measured at 80°C (53%). Likewise, the lowest isomer amounts are measured at 40°C. The three graphs follows the same decreasing trend for the isomers with the time, so at 40°C the amount of isomers dropped to 26%. The increase of selectivity to 2-dodecanone when decreasing the temperature could be explained by the lower extent of isomerization reactions which favours the existence of higher amounts of the reagent 1-dodecene for the Wacker oxidation. On the other hand, higher temperatures (80°C) are required for the further oxidation of internal dodecene isomers towards other ketones, which is in agreement with the bigger difficulty for the oxidation of these compounds with regards to 1-dodecene [27].

H<sub>2</sub>O<sub>2</sub> (30 wt.%) was also tested as oxidant for the modified Wacker oxidation of 1-dodecene at 40°C with acetonitrile as solvent. The results obtained after 2 h of reaction are summarized in Table 2. The conversion obtained with H<sub>2</sub>O<sub>2</sub> was just 40%, rather lower than that of TBHP (71%). In addition, the selectivity towards 2-dodecanone and other ketones was also higher with TBHP, leading towards 56 and 11%, respectively. Note that the selectivity towards other ketones with H<sub>2</sub>O<sub>2</sub> was very low (2%) which is indicative of the inferior ability of this reagent to oxidize the internal isomers. In addition, it is known that TBHP may form complexes [24] with palladium salts such as [CF<sub>3</sub>CO<sub>2</sub>PdOO-t-Bu]<sub>4</sub> with oxidizing properties. Consequently, TBHP

shows a deeper oxidizing performance than  $\text{H}_2\text{O}_2$ . In addition, it should be mentioned that oxygen was also used as oxidant, but in this case, only traces of oxygenated compounds were detected.

Figure 6 illustrates the influence of the TBHP / 1-dodecene molar ratio upon the selectivities in the modified Wacker oxidation of 1-dodecene at  $80^\circ\text{C}$  for 2 h using acetonitrile as solvent. The obtained conversions for all the reported molar ratios were in the range 82 – 88%. The selectivities towards 1-dodecene isomers and 2-dodecanone follows opposite trends. Hence, the selectivity towards dodecene isomers dropped from 94% for 1/1 molar ratio to 45% for 6/1, remaining roughly at this value from 6/1 to 8/1 molar ratio. The selectivity towards 2-dodecanone increased from a negligible 1% (1/1) to a remarkable 44% (7/1). In contrast, the selectivity towards other ketones reached a maximum (23%) for a molar ratio of 6/1. Therefore, the highest selectivity towards 2-dodecanone was attained for a [TBHP] / [1-dodecene] molar ratio of 7/1 - 8/1. The amount of isomers is minimized to ~ 40% while the corresponding one of 2-dodecanone is maximized to 44%. This may be ascribed to the higher trend of TBHP for being incorporated into the coordination sphere of palladium with its growing concentration, which reduces the extent of the isomerization reactions.

Other different palladium salts ( $\text{PdSO}_4$  and  $\text{Pd}(\text{CH}_3\text{COO})_2$ ) were also tested as catalysts in the modified Wacker oxidation of 1-dodecene at  $40^\circ\text{C}$  with acetonitrile as solvent. Figure 7 shows the obtained results, being compared with those of  $\text{PdCl}_2$ . The reported conversion with  $\text{PdSO}_4$  and  $\text{Pd}(\text{CH}_3\text{COO})_2$  were rather low (11 – 15%) in regards to  $\text{PdCl}_2$  (75%). In addition, these low conversions were not accompanied by high selectivities towards 2-dodecanone. Thus, the highest selectivity to 2-dodecanone was achieved over  $\text{PdCl}_2$  (57%), followed by  $\text{Pd}(\text{CH}_3\text{COO})_2$  (47%).  $\text{PdSO}_4$  gives rise mainly to dodecene isomers (49%) and to other ketones

(35%). Then, the nature of the counterion present in the palladium salt affects heavily on the modified Wacker oxidation performance.

Owing to the good results obtained with acetonitrile in terms of 2-dodecanone selectivity, another solvents containing cyano groups (R-CN= propionitrile, isobutyronitrile, benzonitrile) were tested in the modified Wacker oxidation of 1-dodecene at 80°C for 2 h. Figure 8 exhibits the obtained results including those of acetonitrile for comparison. All the R-CN solvents give rise to conversions around 82%, slightly lower than that of acetonitrile (88%). The selectivity data point out that the best R-CN solvent for the preparation of oxygenated products is acetonitrile. Propionitrile, isobutyronitrile and benzonitrile mostly promotes isomerization, ranging the selectivity values from 60% (propionitrile) to 70% (isobutyronitrile). The best of the three additional solvents was propionitrile which contains an aliphatic chain of three carbons. The selectivities towards 2-dodecanone and other ketones amount to 24 and 15%, respectively, although clearly below the reported values for acetonitrile (34 and 23%). Isobutyronitrile, which incorporates a methyl branching in the aliphatic chain, is the worst of the solvents while benzonitrile, with a phenyl substituent, presents an intermediate performance within the series. It is interesting to note that the reported selectivity performance correlates rather well with the respective dielectric constant: acetonitrile (37.5 at 70°F) > propionitrile (27.7) > benzonitrile (26.0) > isobutyronitrile (20.8). Then, the presence of the different organic substituents linked to the cyano group must modify the miscibility of the involved phases. In addition, the different nature of the organic substituents alters the electronic and steric properties of the cyano group which coordinates with the palladium chloride catalyst. An example of this interaction was the usage of polyimide bead carrying cyano groups for anchoring the palladium (II) which allowed to create an heterogeneous catalyst [11].

$\beta$ -cyclodextrins have been used as phase transfer catalysts in the Wacker oxidation of 1-olefins. They form inclusion complexes with the higher 1-olefin, transferring them from the organic towards the aqueous phase. Thus, increased yields of methyl ketones were achieved so an optimum in size and shape of the 1-olefin was found for 1-dodecene [4].  $\beta$ -cyclodextrins were also tested in the present research at 80°C, the results being shown in Table 3. The conversion was around 90% after both 2 and 6 h of reaction when  $\beta$ -cyclodextrins were present in the reaction medium. The selectivity towards 2-dodecanone showed a slight increase after 2 h of reaction in regards to those without  $\beta$ -cyclodextrins. In contrast, after 6 h, the selectivity towards 2-dodecanone rose to 57% with  $\beta$ -cyclodextrins, instead of the 43% without them. Thus, a positive effect of the  $\beta$ -cyclodextrin appears to be detected, especially at longer reaction times, when the amounts of reacting 1-dodecene are markedly lower.

## Conclusions

The modified Wacker oxidation system herein reported allows to carry out the oxidation of the higher 1-olefin dodecene by means of a peroxypalladium complex as well as through the hydroxypalladation mechanism of the conventional Wacker oxidation. The use of acetonitrile as solvent enhances the 2-dodecanone selectivity with regards to isopropanol, by making a biphasic reaction system and more likely, by interacting with the palladium catalyst. Additionally, an optimum in the [acetonitrile] / [1-dodecene] molar ratio of 10 was found. Reaction temperature plays a key role as the selectivity towards 2-dodecanone increased at lower temperatures (61% at 40°C after 3 h) due to the lower extent of the competing isomerization reaction.

On the other hand, H<sub>2</sub>O<sub>2</sub> exhibited less oxidizing capacity than TBHP due to the higher amounts of isomers obtained. Additionally, the existence of an optimum in the [TBHP] / [1-dodecene] molar ratio was observed, placed at 7/1-8/1, corresponding to 2-dodecanone selectivity of 44% at 80°C. This was ascribed to the larger trend of TBHP to incorporate inside the coordination sphere of palladium with its growing concentration. PdCl<sub>2</sub> showed the best performance both in terms of activity and selectivity in regards to the other tested palladium salts (PdSO<sub>4</sub>, Pd(CH<sub>3</sub>COO)<sub>2</sub>). Other cyano containing solvents (propionitrile, isobutyronitrile, benzonitrile) exhibited worse performance than acetonitrile. Finally, β-cyclodextrins, a phase transfer catalyst, led to an increase of the selectivity towards 2-dodecanone (57%) at 80°C after 6 h of reaction.

## References

- [1]. G. O. Spessard, G. L. Miessler, *Organometallic Chemistry*; Prentice Hall; New Jersey; 1997.
- [2]. J. A. Botas, M. Bravo, J. M. Escola, P. García, *J. Mater. Cycles Waste Manag.* 8 (2006) 122 - 125.
- [3] A. C. Frisch, M. Beller, *Angew. Chem. Int. Ed.* 44 (2005) 674 - 688.
- [4] E. Monflier, A. Mortreaux, in: B. Cornils, W. A. Herrman, W. A. (Eds.) *Aqueous Phase Organometallic Catalysis: Concepts and Applications*, Wiley-VCH, Weinham, 1998, pp. 514.
- [5] J. Tsuji, *Synthesis* 1984, 369 - 384.
- [6] A. Lambert, E. G. Derouane, I. V. Kozhevnikov, *J. Catal.* 211 (2002) 445 - 450.
- [7] A. W. Stobbe-Kreemers, R. B. Dielis, M. Makkee, J. J. F. Scholten, *J. Catal.* 154 (1995) 175 - 186.



- [8] T. Mitsudome, T. Umetani, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Tetrahedron Lett.*, 47 (2006) 1425 - 1428.
- [9] P. H. Espeel, M. C. Thielen, P. A. Jacobs, *J. Chem. Soc., Chem. Commun.* 10 (1991) 669 - 671.
- [10] J. P. Arhancet, M. E. Davis, B. E. Hanson, *Catal. Lett.* 11 (1991) 129 - 136.
- [11] J. H. Ahn, D. C. Sherrington, *Macromolecules*, 29 (1996) 4164 - 4165.
- [12] H. G. Tang, D. C. Sherrington, *J. Catal.* 142 (1993) 540 - 551.
- [13] K. M. Choi, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Lett.* 32(2) (2003) 180 - 181.
- [14] K. I. Matveev, N. B. Shitova, E. G. Zhizhina, *Kinet. Catal.* 17 (1976) 893 - 902.
- [15] N. B. Shitova, L. I. Kuznetsova, K. I. Matveev, *Kinet. Catal.* 15 (1974) 72 - 75.
- [16] A. Kishi, T. Higashino, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* 41 (2000) 99 - 102.
- [17] C. Lapinte, H. Riviere, *Tetrahedron Lett.* (1977) 3817 - 3820.
- [18] A. Ansari, S. Joyasawal, M. K. Gupta, J. S. Yadav, R. Gree, *Tetrahedron Lett.* 46 (2005) 7507 - 7510.
- [19] A. L. Maksimov, A. A. Shakarov, T. Y. Filippova, A. Y. Zhuchkova, E. A. Karakhanov, *Ind. Eng. Chem. Res.* 44 (2005) 8644 - 8653.
- [20] V. V. Namboodiri, R. S. Varma, E. Sahle-Demessie, U. R. Pillai, *Green Chem.* 4 (2002) 170 - 173.
- [21] E. Karakhanov, T. Buchneva, A. Maximov, M. Zavertyaeva, *J. Mol. Catal. A* 184 (2002) 11 - 17.
- [22] E. Monflier, E. Blouet, Y. Barboux, A. Mortreux, *Angew. Chem. Int. Ed.* 33 (1994) 2100 - 2102.
- [23] T. Mitsudome, T. Umetani, N. Nosaka, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Angew. Chem. Int. Ed.* 45 (2006) 481 - 485.

- [24] H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, R. Weiss, R. J. Am. Chem. Soc. 102(3) (1980) 1047 - 1054.
- [25] C. N. Cornell, M. S. Sigman, J. Am. Chem. Soc. 127 (2005) 2796 - 2797.
- [26] M. S. Melgo, A. Lindner, U. Schuchardt, Appl. Catal. A, 273(1-2) (2004) 217 - 221.
- [27] C. N. Cornell, M. S. Sigman, Org. Lett. 8(18) (2006) 4117 – 4120.

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**Table 1.** Wacker oxidation of 1-dodecene using anhydrous (anTBHP) and aqueous TBHP (aqTBHP)

<b>Oxidant</b>	<b>Conversion</b>	<b>S<sub>2</sub>-dodecanone</b>	<b>S<sub>other ketones</sub></b>	<b>S<sub>C12 isomers</sub></b>
anTBHP	88	35	42	23
aqTBHP	75	56	25	19

T = 40°C; N = 300 rpm; t = 2 h; [C<sub>12</sub>H<sub>24</sub>] / [PdCl<sub>2</sub>] = 50, [CH<sub>3</sub>CN] / [C<sub>12</sub>H<sub>24</sub>] = 10, [TBHP] / [C<sub>12</sub>H<sub>24</sub>] =

6

**Table 2.** Modified Wacker oxidation of 1-dodecene with aqueous TBHP and H<sub>2</sub>O<sub>2</sub>.

<b>Oxidant</b>	<b>Time (h)</b>	<b>Conversion</b>	<b>S<sub>2</sub>-dodecanone</b>	<b>S<sub>other ketones</sub></b>	<b>S<sub>C12 isomers</sub></b>
TBHP	2	71	56	11	33
H <sub>2</sub> O <sub>2</sub>	2	40	41	2	57

T = 40°C, N = 300 rpm, [C<sub>12</sub>H<sub>24</sub>] / [PdCl<sub>2</sub>] = 50, [CH<sub>3</sub>CN] / [C<sub>12</sub>H<sub>24</sub>] = 10, [Oxidant] / [C<sub>12</sub>H<sub>24</sub>] = 6

**Table 3.** Modified Wacker oxidation of 1-dodecene with and without  $\beta$ -cyclodextrins.

$\beta$ -cyclodextrin	Time (h)	Conversion	S <sub>2</sub> -dodecanone	S <sub>other ketones</sub>	S <sub>C12 isomers</sub>
Yes	2	87	40	20	40
No	2	89	34	23	43
Yes	6	89	57	21	22
No	6	89	43	23	34

T = 80°C; N = 300 rpm, [C<sub>12</sub>H<sub>24</sub>] / [PdCl<sub>2</sub>] = 50, [CH<sub>3</sub>CN] / [C<sub>12</sub>H<sub>24</sub>] = 10, [TBHP] / [C<sub>12</sub>H<sub>24</sub>] = 6, [C<sub>12</sub>H<sub>24</sub>] / [ $\beta$ -ciclodextrin] = 40

## FIGURE CAPTIONS

**Figure 1.** Scheme of the main reaction pathway occurring in the modified Wacker oxidation of 1-dodecene with TBHP.

**Figure 2.** Evolution of 1-dodecene conversion and selectivity in the Wacker oxidation using acetonitrile (A) and isopropanol (B) as solvent ( $T = 80^{\circ}\text{C}$ ,  $N = 300$  rpm,  $[\text{C}_{12}\text{H}_{24}] / [\text{PdCl}_2] = 50$ ,  $[\text{solvent}] / [\text{C}_{12}\text{H}_{24}] = 10$ ,  $[\text{TBHP}] / [\text{C}_{12}\text{H}_{24}] = 6$ ).

**Figure 3.** Influence of the stirring rate ( $N$ ) in the conversion and selectivity obtained in the Wacker oxidation of 1-dodecene using acetonitrile as solvent ( $T = 40^{\circ}\text{C}$ ,  $t = 0.5$  h,  $[\text{C}_{12}\text{H}_{24}] / [\text{PdCl}_2] = 50$ ,  $[\text{TBHP}] / [\text{C}_{12}\text{H}_{24}] = 6$ ,  $[\text{CH}_3\text{CN}] / [\text{C}_{12}\text{H}_{24}] = 10$ ).

**Figure 4.** Influence of the  $[\text{CH}_3\text{CN}] / [1\text{-dodecene}]$  molar ratio in the conversion and selectivity obtained in the modified Wacker TBHP oxidation of 1-dodecene ( $N = 300$  rpm,  $T = 80^{\circ}\text{C}$ ,  $t = 2$  h,  $[\text{C}_{12}\text{H}_{24}] / [\text{PdCl}_2] = 50$ ,  $[\text{TBHP}] / [\text{C}_{12}\text{H}_{24}] = 6$ ).

**Figure 5.** Effect of the temperature in the conversion and selectivity achieved in the Wacker oxidation of 1-dodecene ( $N = 300$  rpm,  $[\text{C}_{12}\text{H}_{24}] / [\text{PdCl}_2] = 50$ ,  $[\text{TBHP}] / [\text{C}_{12}\text{H}_{24}] = 6$ ,  $[\text{CH}_3\text{CN}] / [\text{C}_{12}\text{H}_{24}] = 10$ ).

**Figure 6.** Influence of the  $[\text{TBHP}]/[1\text{-dodecene}]$  molar ratio in the selectivity of the modified Wacker oxidation of 1-dodecene. ( $T = 80^{\circ}\text{C}$ ,  $t = 2$  h,  $N = 300$  rpm,  $[\text{C}_{12}\text{H}_{24}] / [\text{PdCl}_2] = 50$ ,  $[\text{CH}_3\text{CN}] / [\text{C}_{12}\text{H}_{24}] = 10$ ).

**Figure 7.** .Effect of the palladium salt in the modified Wacker oxidation of 1-dodecene. ( $T = 40^{\circ}\text{C}$ ,  $t = 2$  h,  $N = 300$  rpm,  $[\text{C}_{12}\text{H}_{24}] / [\text{PdCl}_2] = 50$ ,  $[\text{TBHP}] / [\text{C}_{12}\text{H}_{24}] = 6$   $[\text{CH}_3\text{CN}] / [\text{C}_{12}\text{H}_{24}] = 10$ )

**Figure 8.** Effect of the R-CN solvent in the modified Wacker oxidation of 1-dodecene. ( $T = 80^{\circ}\text{C}$ ,  $t = 2$  h,  $N = 300$  rpm,  $[\text{C}_{12}\text{H}_{24}] / [\text{PdCl}_2] = 50$ ,  $[\text{TBHP}] / [\text{C}_{12}\text{H}_{24}] = 6$   $[\text{R-CN}] / [\text{C}_{12}\text{H}_{24}] = 10$ )

FIGURE 1

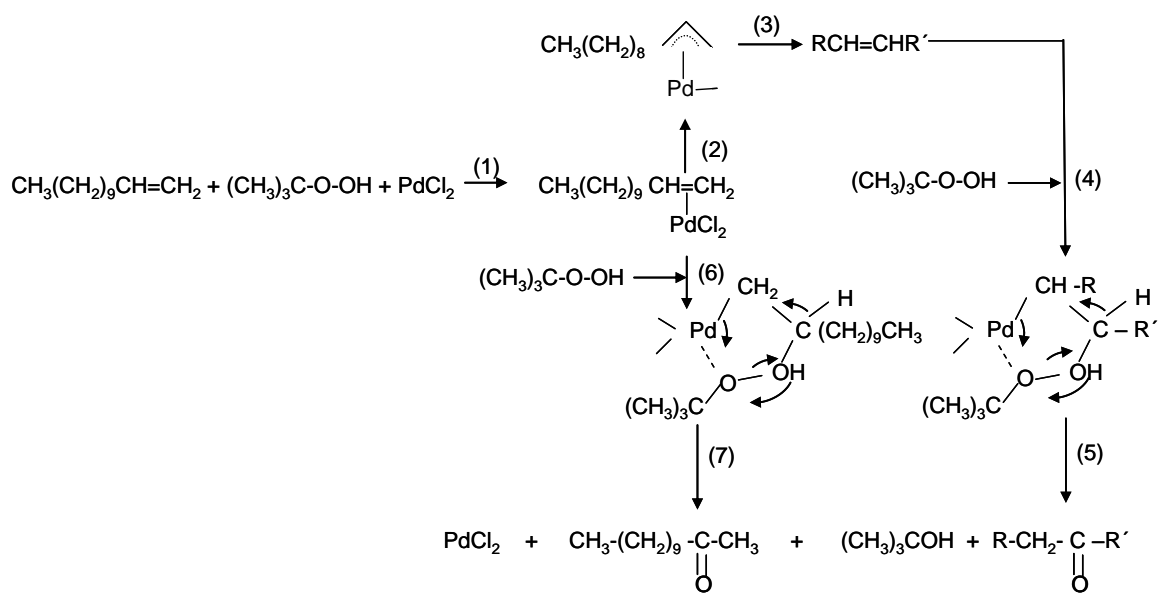


FIGURE 2

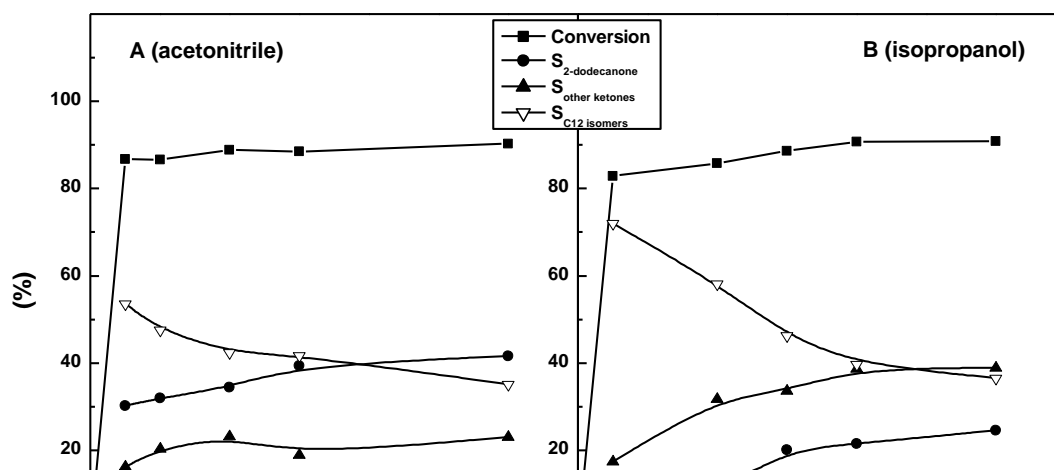




FIGURE 3

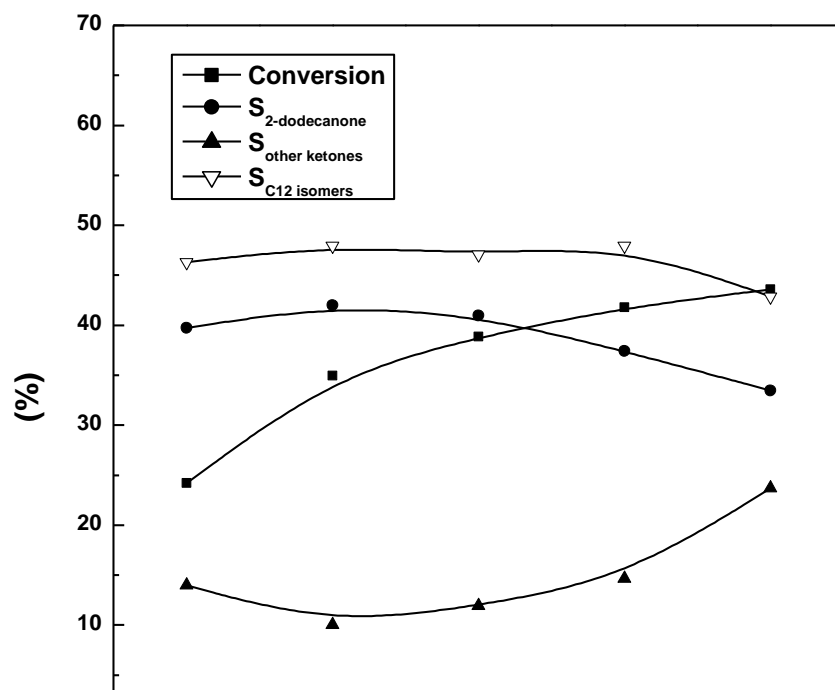


FIGURE 4

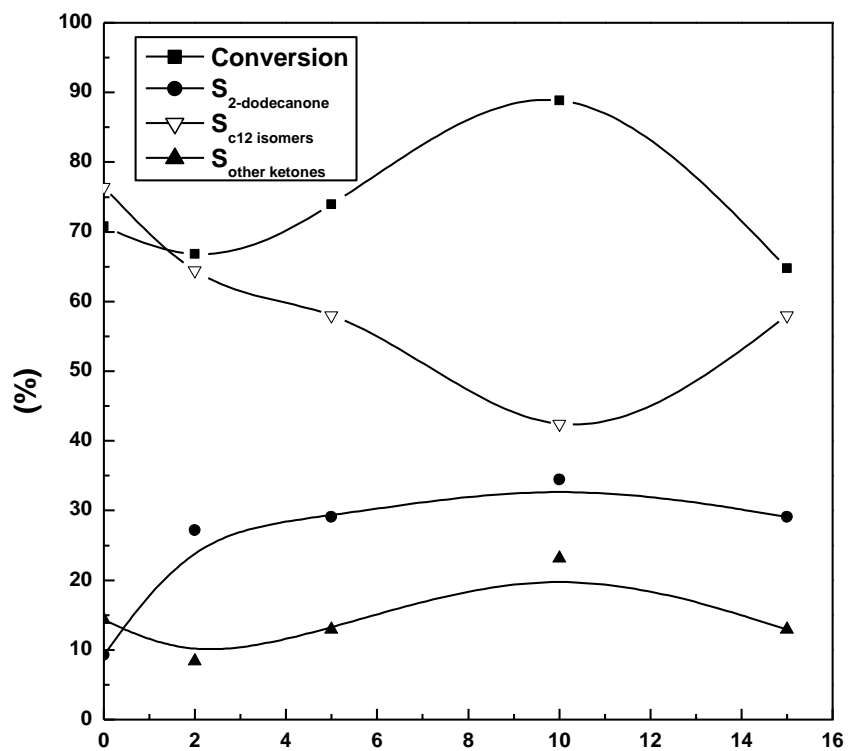


FIGURE 5

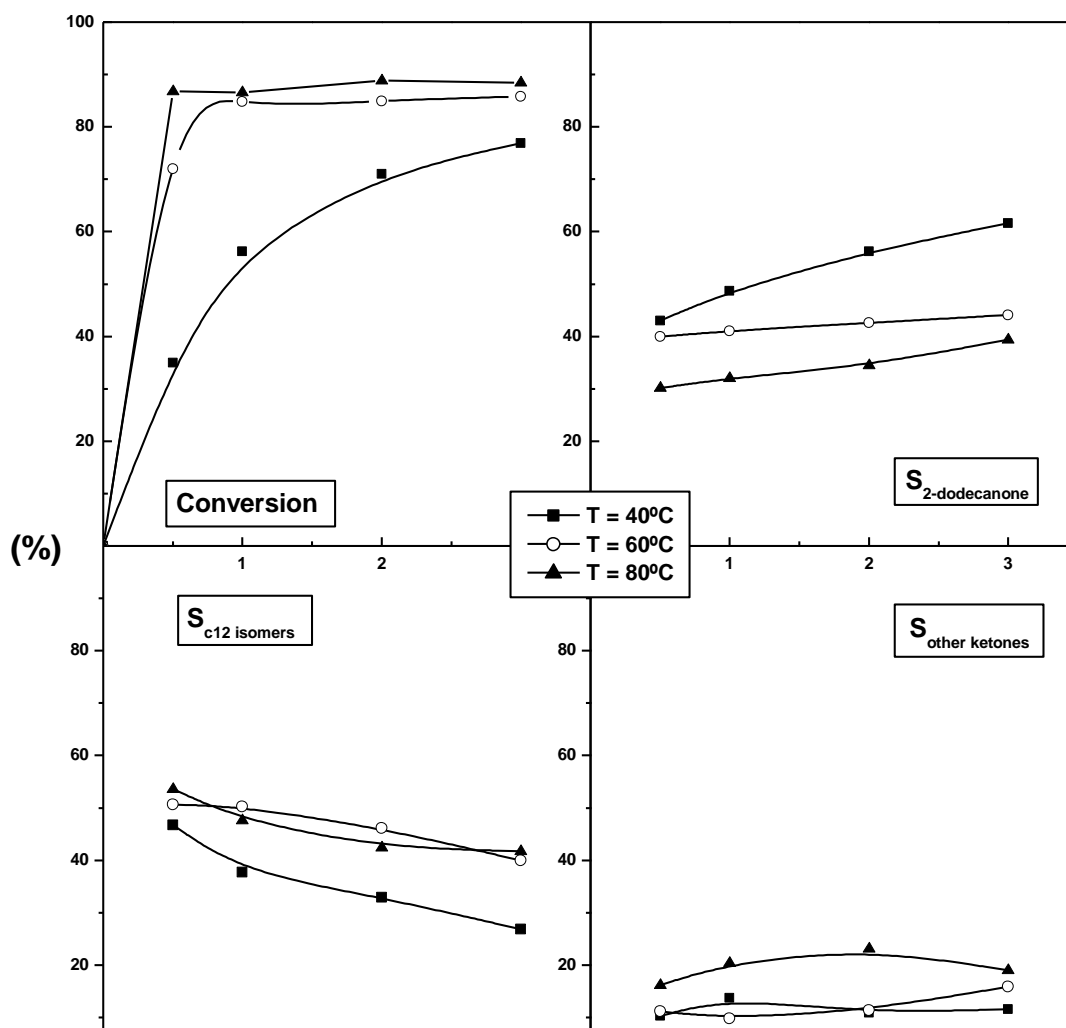


FIGURE 6

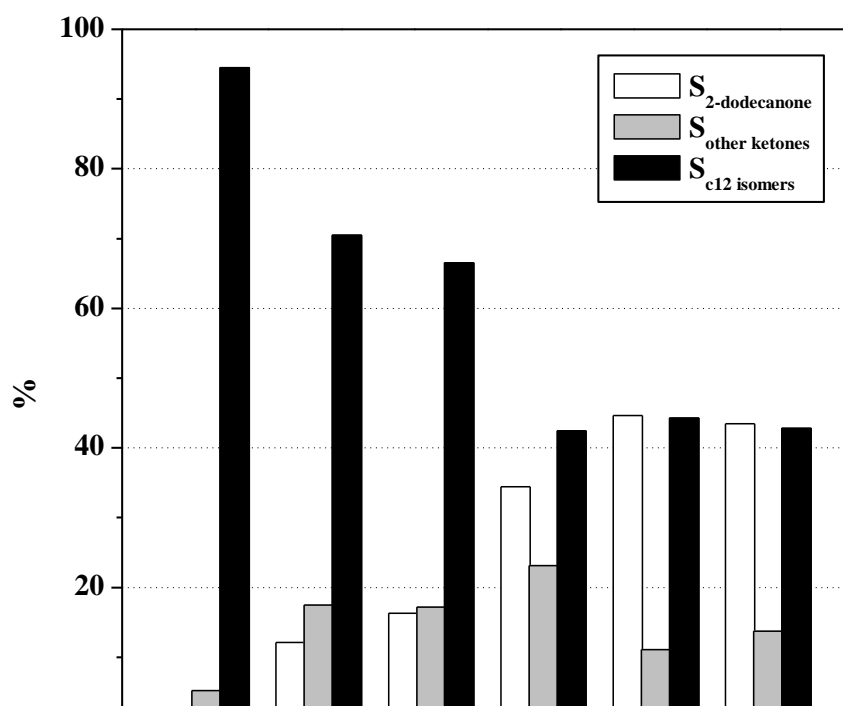


FIGURE 7

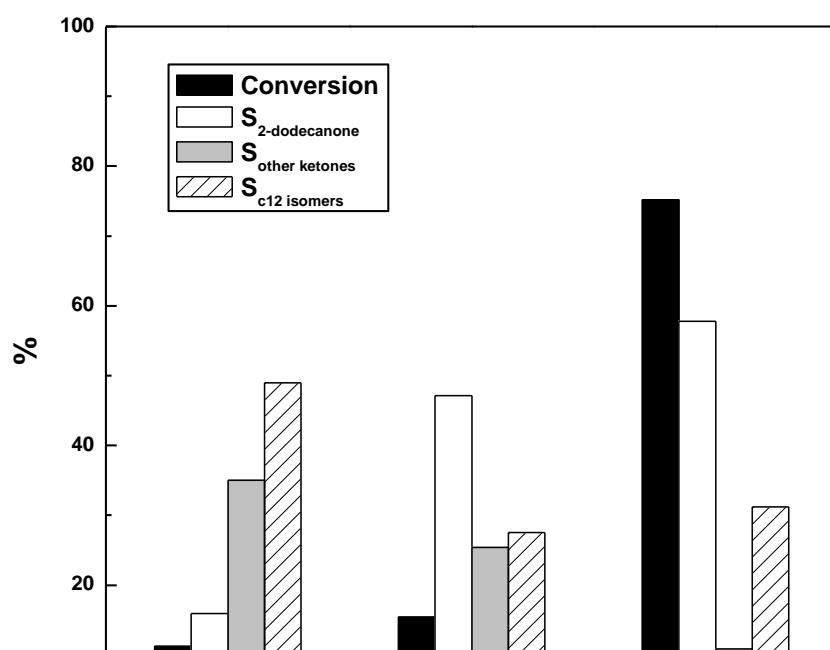


FIGURE 8

