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Oppenauer's oxidation by paraformaldehyde of piperonyl alcohol to heliotropine

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A B S T R A C T

3,4-Methylenedioxybenzaldehyde [1-3-benzodioxole-5-carboxaldehyde or heliotropine (HEL)] is widely used in fragrance and pharmaceutical preparations. The synthesis of HEL by Oppenauer's oxidation of the corresponding 3,4-methylenedioxybenzyl alcohol [piperonyl alcohol (PA)] has been investigated using both homogeneous and heterogeneous catalysts. Commercial paraformaldehyde (PFA) was used as hydrogen acceptor and the oxidation proceeded with high activity and selectivity, operating in liquid phase at 383 K, with toluene as solvent and a molar ratio PFA/PA = 2.5. In all cases, a critical step was the removal of the possible water coming from the reactants. Homogeneous Al *iso*-propoxide catalyst gave rise to a very fast and selective reaction, although presenting relevant economic and environmental drawbacks. Among the heterogeneous catalysts, best initial results were obtained using commercial zirconia-type catalysts, with high yield values regardless of catalyst amount and reagent concentration. However, these catalysts cannot be regenerated. Calcined Mg/Al commercial hydrotalcites not only showed good catalytic results (with only lower reaction rates lower than zirconia-type ones), but also an almost complete recovery of the initial activity after calcinations at 823 K.

1. Introduction

3,4-Methylenedioxybenzaldehyde, also known as 1-3-benzodioxole-5-carboxaldehyde, piperonal or heliotropine (HEL), is the basis for the heliotrope-type perfumes and is widely used for the cosmetic preparations, being also applied as intermediate for agrochemical and pharmaceutical products [1,2] (Fig. 1). Moreover, it is also a controlled substance being the precursor of the hallucinogen 3,4-methylenedioxy-*N*-methylamphetamine (MDMA or ecstasy) [3]. Currently, HEL is mainly produced by the isomerization of safrole [4–7], isolated from the essential oil of *Ocotea Cymbarum* and *Pretiosa* trees [8], and following oxidation (chemical, electrochemical or by ozone) [9–13]. This source is getting less available and consequently more expensive, because it contributes to the exhaustion of these perennial forests, pushing the demand of industrial alternatives of synthetic HEL, that may be considered attractive for a price of natural safrole higher than 6 US$/kg ca. It is noteworthy that the market of HEL remains almost stable, since the decrease of the availability of natural safrole is almost fully compensated by the direct synthesis of Heliofresh® [14], other trade name of the fragrance Helional®.

Industrial processes for preparing HEL can be shared into two groups: the first starting from 1,2-methylenedioxybenzene and the second from 3,4-dihydroxybenzaldehyde [15–18]; furthermore, a promising alternative is the production of HEL by oxidation of the corresponding 3,4-methylendioxybenzyl alcohol [or piperonyl alcohol (PA)] [19,20]. However, it is noteworthy that the oxidation with air presents relevant safety drawbacks, since operates with air in the presence of organic solvents at reflux temperature, thus an interesting alternative may be the Oppenauer's oxidation that can be performed under safe and mild reaction conditions, using either both homogeneous or heterogeneous catalysts [21–25], generally obtaining high selectivity values, without the risk of oxidizing other functional groups. Corma et al. reported that the reaction proceeds via a six-member intermediate, in which both reactants are coordinated to the active site [26]. Carbonyl compounds with high oxidation potential, as aromatic and aliphatic aldehydes or ketones (acetaldehyde, acrolein, acetophenone, benzaldehyde, *p*-benzoquinone, benzophenone, cyclohexanone, etc.) have been used as oxidants. Although acetone has a low oxidation potential, it is commonly applied, because considering its low price it can be used in large excess to shift the equilibrium towards the wished direction [27].

Aim of this paper was to shed light on a new economic and safe industrial alternative to produce HEL by Oppenauer's oxidation of PA with different heterogeneous commercial catalysts using a

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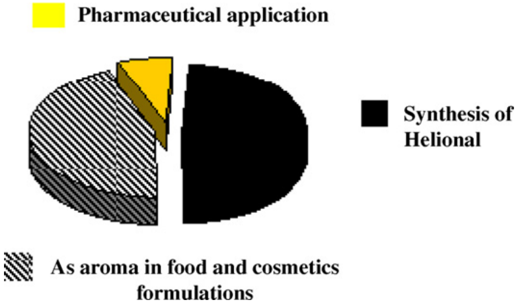

Fig. 1. Distribution of the world market of heliotropine.

commercial paraformaldehyde (PFA), a cheap and widely accessible reactant [28]. As sake of comparison, the results obtained with homogeneous Al *iso*-propoxide catalyst have been also reported. Al *iso*-propoxide and *ter*-butoxide are commonly used as the homogeneous catalysts because of their easy preparation and good solubility in organic solvents.

2. Experimental

3,4-Methylendioxybenzyl alcohol (piperonyl alcohol or PA), 3,4-methylendioxy benzaldehyde (heliotropine or HEL), toluene and Al *iso*-propoxide were purchased from Aldrich Chemicals ($\geq$98 wt.%) and used without further purification. Commercial PAF was employed without any further purification. The heterogeneous commercial zirconia-type catalysts [ZHSA and HWA-ZHSA (Millennium) and XZO 632/03 MELChemicals)] were used without any pretreatment, while the Mg/Al commercial hydrotalcites [Pural MG 50, Pural MG 61, Pural MG 70 and HT C388 (Sasol), Hycite 713, Sorbacid 911 and Sorbacid 696 (Süd-Chemie)] were used after calcination at 723 K for 8 h. Commercial zeolites (Süd-Chemie and Zeolyst) were also investigated, as such or after ion exchange with different cations (Na, Cs, Ti or Zr). B.E.T. surface area values were determined by physical adsorption of N_2 at 77 K using a Micromeritics AUTOCHEM 2910, pre-treating the samples under vacuum at 373 K for 10 min to eliminate the adsorbed water. X-ray diffraction (XRD) analyses were carried out with a Philips PW 1050/81 diffractometer (40 kV, 25 mA), equipped with a PW 1710 unit, and a Cu Kα radiation (λ = 0.154118 nm). A 2θ range from 10° to 80° was investigated at a scanning rate of 0.10°/s. The catalytic tests were performed in a three-necks 250-mL flask (equipped with a stirring, a thermometer and a refrigerator connected to a Dean-Stark column) introducing at first 5.0 g of PA (0.033 mol), 100.0 g of toluene and a catalyst amount between 10 and 50 wt.% (referred to PA); then the reaction mixture was heated at 383 K under stirring and about 2.5 g of PAF were slowly added (PFA/PA molar ratio = 2.5). The solution was maintained for the reaction time at the above temperature under stirring; finally, it was cooled, the catalyst filtered off and the solution distilled under vacuum (303 K and 131.6 Pa) to obtain a crude reaction product, that was analysed using a Carlo Erba 4300 gas chromatograph, equipped with FID and a wide-bore OV1 column (length 30 m, i.d. 0.53 mm, film width 0.5 μm). The products were tentatively identified by GC–MS with a Hewlett-Packard GCD 1800 system equipped with a HP5 column (length 25 m, i.d. 0.25 mm, film width 1.5 μm); the identifications were subsequently confirmed by comparison of the experimental GC–MS patterns with those obtained for pure reference compounds.

3. Results and discussion

According to the literature [21,22], as sake of comparison a preliminary test was performed using Al *iso*-propoxide as homogeneous catalyst, that showed a very high activity reaching already after 15 min almost complete PA conversion (98.1% in comparison to 99.9% after 120 min), with a constant selectivity of about 99.0% in HEL (Fig. 2). However, Al *iso*-propoxide presents relevant drawbacks, first of all the requirement to eliminate carefully H_2O and CH_3OH from the reaction solution, because the first deactivates the catalyst forming aluminium hydroxide, while methanol forms non-active complex [29]. Furthermore, this catalyst cannot be reused, because at the end of the reaction the solution has to be added with an aqueous 1 M NaOH solution to form sodium aluminate, separating the aqueous from the organic phase. Thus, to apply industrially it is necessary to consider the tedious and expensive treatment of waste water to eliminate the aluminium presence.

Thus the possibility to use heterogeneous catalysts was investigated to overcome the drawbacks related to the use of homogeneous catalysts. Literature reports of many examples of different heterogeneous catalysts applied in Oppenauer's oxidation of organic substrates [23,30–36]. However, it must be noted that usually a high amount of catalyst was employed (same weight of the organic substrate), with very few examples of oxidation of benzylic alcohols, no one at our knowledge using PFA as hydrogen acceptor. At first, we tested different zeolites as such or exchanged with different cations, observing always very poor results (yield values in HEL lower than 4%), with the almost complete oligomerization of PA to heavy products before the addition of PFA. On the contrary, very interesting results were observed using zirconia-type catalysts and commercial Mg/Al hydrotalcites calcined at 723 K for 8 h (Table 1). However, Mg/Al mixed oxides required a longer reaction time (6 h) to obtain comparable results and their activity was more affected by the composition of the starting hydrotalcites; in fact, best results were obtained starting from hydrotalcite with a Mg/Al molar ratio of about 2. On the contrary, the catalytic activity of zirconia-type catalysts was less influenced by composition and preparation method, similar results being obtained with catalysts supplied by different manufacturing industries.

Also the zirconia-type catalysts and the Mg/Al mixed oxides obtained by calcinations of commercial hydrotalcites were very sensitive to the presence of water formed by the progressive depolimerization of PFA, that bound on the active sites; in fact, with both catalysts the conversion almost halved without water removal, while the selectivity was less affected (Fig. 3). On the contrary no effect was observed due to the presence of small

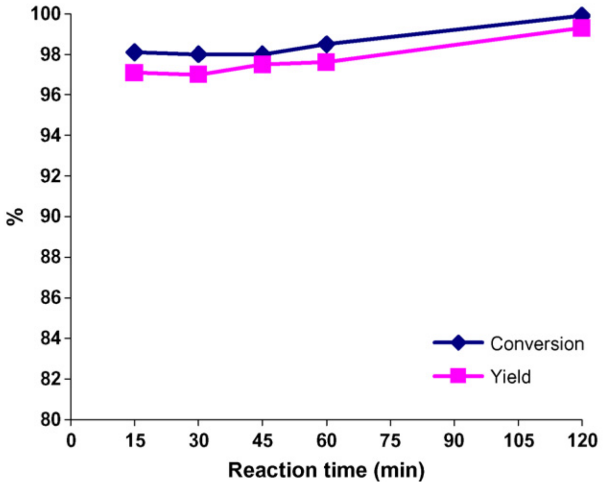

Fig. 2. Oppenauer's oxidation of piperonyl alcohol by a commercial paraformaldehyde using Al *iso*-propoxide as homogeneous catalyst [Cat = 10 wt.%].

Table 1
Oppenauer's oxidation of piperonyl alcohol by a commercial paraformaldehyde using zirconia-type catalysts or commercial hydrotalcites calcined at 723 K for 8 h [Cat = 25 wt.%].

Catalyst	Mg/Al molar ratio	Reaction time (h)	Conversion (%)	Yield (%)
ZHSA	–	2	97.0	87.0
HWA-ZHSA	–	2	96.9	89.6
XZO 632/03	–	2	97.4	88.4
HT C388	2.3	6	88.5	56.6
Pural MG 61	2.0	6	99.2	92.2
Pural MG 50	1.0	6	86.9	58.9
Pural MG70	3.0	6	94.8	72.2
Sorbacid 696	2.0	6	98.8	91.2
Sorbacid 911	2.1	6	95.9	79.5
Hycite 713	2.5	6	98.6	87.3

Table 2
Oppenauer's oxidation of piperonyl alcohol by a commercial formaldehyde using zirconia-type catalysts as a function of the catalyst amount.

Catalyst	Amount (wt.%)	Reaction time (h)	Conversion (%)	Yield (%)
ZHSA	50	2	97.0	87.0
HWA-ZHSA	50	2	96.9	89.6
XZO 632/03	50	2	97.4	88.4
XZO 632/03	25	2	95.6	87.3
XZO 632/03	10	6	96.4	85.9

Table 3
Role of time-on-steam and regeneration by calcination in the Oppenauer's oxidation of piperonyl alcohol by a commercial paraformaldehyde using a zirconia-type catalyst [Cat = 25 wt.%].

Catalyst	Catalytic cycle	Reaction time (h)	Conversion (%)	Yield (%)
XZO 632/03	I	4	98.0	91.1
	II	8	97.6	90.7
	III	8	98.8	93.1
	IV	10	97.6	87.6
	V	12	97.8	88.3
	Regenerated	8	0.0	0.0

amounts of methanol, unlike that previously reported for homogeneous Al *iso*-propoxide catalyst, simplifying the scale-up of the reaction.

Almost no connection was observed in the range investigated between the catalytic activity of the zirconia-type catalysts and the catalyst amount, with only an increase of the reaction time for the lowest value (Table 2). Also the increase of the initial PA concentration in the toluene solution gave rise only to an increase of the reaction time, without any effect on the selectivity due to the by-product formation by PA oligomerization. These latter tests have been performed considering that the different industrial processes to produce PA may be economically optimized for different final concentration of the alcohol. After each cycle, the zirconia-type catalysts were simply washed by toluene and reused, maintaining a high activity for more than 40 h of time-on-stream (Table 3); however, trying to regenerate the catalysts by calcinations at 823 K for 6 h, to burn the traces of heavy by-products adsorbed on the surface, a complete loss of catalytic activity was surprisingly observed.

To try to understand this unusual behaviour, we checked the catalytic activity of a zirconia-type catalyst calcined for 3 h at increasing temperature. Fig. 4 shows that the selectivity values start to decrease above 673 K, while the conversion ones remain almost constant up to 773 K, decreasing dramatically above this temperature. This trend cannot be simply correlated to the surface area values, that decrease almost linearly with the calcination temperature (with a trend similar to that observed for the selectivity), but rather with the structural change between amorphous zirconia-type hydroxide and tetragonal structure that occurs at 773 K [37], evidencing a key role of surface hydroxyl groups in the reaction, probably stabilizing the six-member intermediate [26]. It is noteworthy that the sample calcined at 823 K showed a residual catalytic activity, unlike that previously reported for that regenerated at the same temperature (Table 3). This difference may be attributed both to a longer calcination time

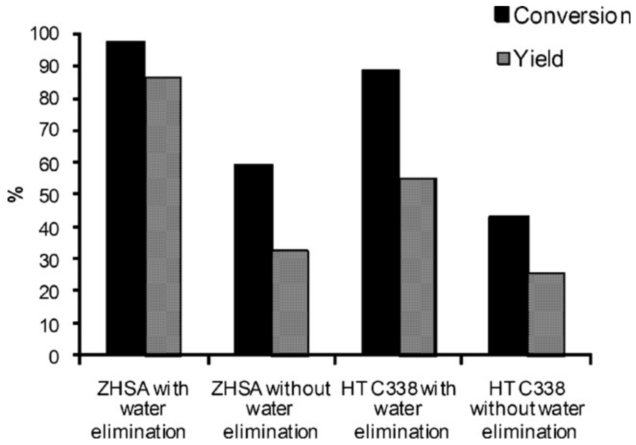

Fig. 3. Oppenauer's oxidation of piperonyl alcohol by a commercial paraformaldehyde using a zirconia-type catalyst or a Mg/Al (molar ratio = 2.3) hydrotalcite calcined at 723 K for 8 h [Cat = 25 wt.%, reaction time = 2 h for zirconia-type catalysts and 6 h for Mg/Al mixed oxides].

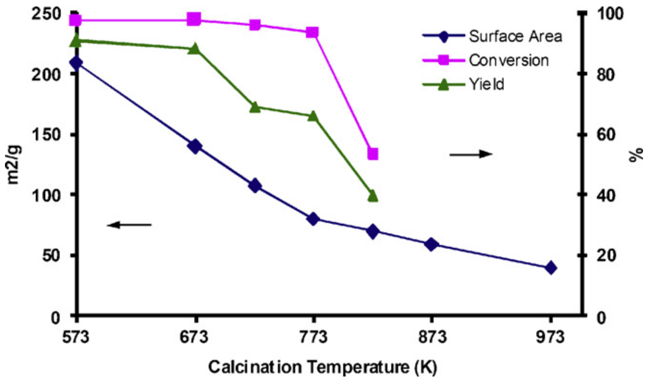

Fig. 4. Surface area and catalytic activity in the Oppenauer's oxidation of piperonyl alcohol by a commercial paraformaldehyde as function of the calcination temperature using the XZO 632/03 zirconia-type catalyst [Cat = 25 wt.%, reaction time 2 h].

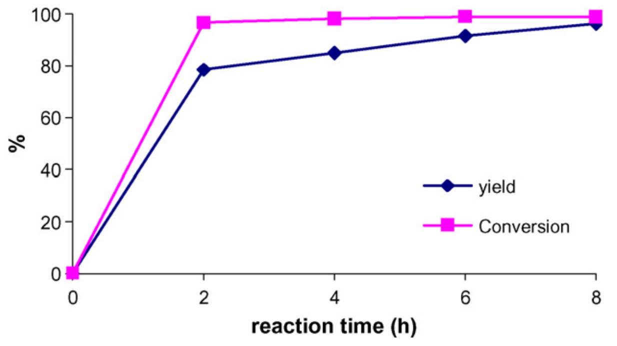

Fig. 5. Oppenauer's oxidation of piperonyl alcohol by a commercial formaldehyde using the commercial Mg/Al hydrotalcite Sorbacid 696 calcined at 723 K for 8 h [Cat = 25 wt.%].

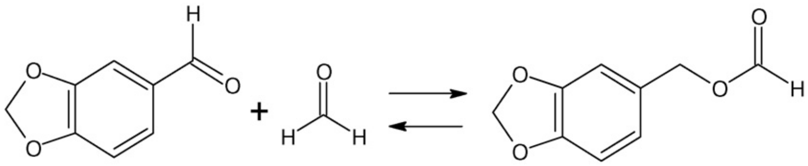

Fig. 6. Mixed Tishchenko's reaction between heliotropine and paraformaldehyde.

(6 instead of 3 h) and to possible hot spots related to the combustion of the heavy by-products.

Considering the impossibility to regenerate the deactivated zirconia-type catalysts by calcination, the catalytic activity of rock-salt-type Mg/Al mixed oxides [38–40] obtained by calcination of commercial hydrotalcites was investigated more deeply. Fig. 5 shows that already after 2 h a high conversion value was achieved, although 8 h were required to obtain a very high selectivity in heliotropin (>97.0%). Thus Mg/Al mixed oxides showed final catalytic activities similar to those of zirconia-type catalysts, although requiring longer reaction times. This behaviour may be justified on the basis of the different reaction products identified, assuming that initially piperonyl formate, deriving from a mixed Tishchenko's reaction between one molecule of HEL formed and one of PFA, was preferentially formed (Fig. 6). However, this is an equilibrium reaction and increasing the reaction time the PFA excess was decomposed moving the equilibrium towards the formation of free HEL.

Also the Mg/Al mixed oxides after each cycle were simply washed with toluene and reused, maintaining a high activity for about 20 h of time-on-stream, i.e., for lower times than the zirconia-type catalysts previously discussed. However, unlike these latter, they can be completely regenerated by calcination at 823 K for 6 h, recovering the conversion values of the fresh catalysts, with only a slight decrease of selectivity (Fig. 7). Thus, notwithstanding their lower catalytic performances, Mg/Al mixed oxides obtained by controlled calcinations of commercial hydrotalcites appear very interesting catalysts for industrial applications, considering their low cost, wide availability, easy and almost complete regeneration.

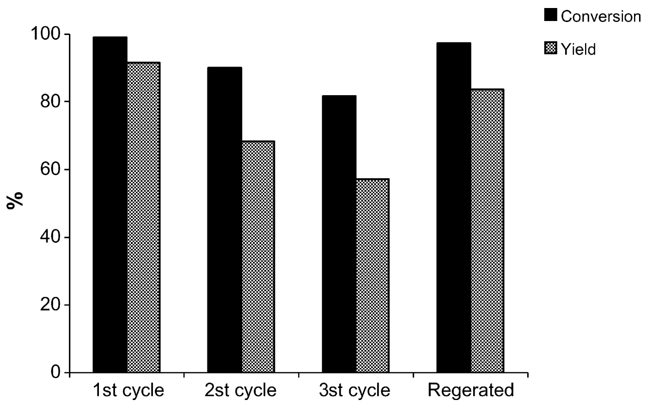

Fig. 7. Role of time-on-steam and regeneration by calcination in the Oppenauer's oxidation of piperonyl alcohol by a commercial paraformaldehyde using the calcined commercial Mg/Al hydrotalcite Sorbacid 696 [Cat = 25 wt.%, reaction time 6 h].

Table 4

Oppenauer's oxidation of some substituted benzyl alcohols by a commercial formaldehyde using the Mg/Al Sorbacid 696 commercial hydrotalcite calcined at 723 K for 8 h. [Cat = 25 wt.%, reaction time = 6 h].

Substrate	Conversion (%)	Yield (%)
3,4-Dimethoxybenzyl alcohol	92.2	76.1
3-Methoxybenzyl alcohol	71.3	68.5
4-Methoxybenzyl alcohol	80.9	70.3
3-Methylbenzyl alcohol	88.1	66.4
Benzyl alcohol	76.6	60.4
4-Chlorobenzyl alcohol	40.0	14.1

Finally, the possibility of a wider application of PFA as hydrogen acceptor in the Oppenauer's oxidation of aromatic substrates was checked feeding some benzyl alcohols containing different electron-donating or withdrawing groups on the aromatic ring (Table 4). It must be noted that the reaction may be applied to benzylic alcohol containing electron-donating groups (methoxy or methyl), while the conversion and the yield in the corresponding aldehyde dramatically decrease in presence of an electron-withdrawing groups, as chlorine. It is noteworthy that the activation effect occurs either for inductive (methyl group) or mesomeric effect (methoxy group). On the other hand, feeding the 4-chlorobenzyl alcohol the main by-product resulted the corresponding 4-cholorobenzoic acid [yield 18.9% in comparison to 14.1% of the 4-chlorobenzaldehyde (Table 4)], suggesting that the presence of a electron-withdrawing group as chlorine affected negatively the oxidation of the alcohol (by inductive effect), but favoured the following oxidation of the aldehyde to the carboxyilic acid by mesomeric effect. This latter may be justified considering that the carbonyl group may delocalise the negative charge deriving from the chlorine present in four position.

4. Conclusions

The Oppenauer's oxidation of PA to HEL using PFA commercially available hydrogen acceptor represents an interesting example of economic and environmentally friendly industrial process, able to by-pass the safety drawbacks of the PA oxidation by air. By this way, it is possible to obtain very high yield values in HEL (>90%), operating in mild and safe conditions using both homogeneous and heterogeneous catalysts. It was found that Al *iso*-propoxide was the most suitable catalyst, allowing to achieve high selectivity values in HEL and almost complete conversion after only 15 min. However, this catalyst presented many relevant economic and environmental drawbacks as deactivation by both H_2O and CH_3OH, the impossibility to be reused and the tedious and expensive treatment of waste water.

While zeolites, as such or exchanged with different cations, gave rise always to very poor results (yield values in HEL lower than 4%), with the almost complete oligomerization of PA to heavy products, very interesting results were observed using zirconia-type catalysts and calcined commercial Mg/Al hydrotalcites, although requiring longer reaction times than the previous homogeneous catalyst. Zirconia-type catalysts resulted the most active heterogeneous catalysts, requiring only 2 h to reach yield values in HEL higher than 90% and maintaining high catalytic performances for more than 40 h of time-on-steam. However, these catalysts cannot be reused because during the regeneration by calcination at 823 K the surface hydroxyl groups were removed irreversibly and the solid texture moved from amorphous to tetragonal one.

Mg/Al mixed oxides obtained by controlled calcination of commercial hydrotalcites showed final catalytic activities similar to those of zirconia-type catalysts, although requiring longer reaction times, because initially piperonyl formate, deriving from a mixed Tishchenko's reaction between one molecule of HEL formed and one of PFA, was preferentially formed. The Mg/Al mixed oxides maintained a high activity only for about 20 h of time-on-stream, i.e., for lower times than the zirconia-type catalysts, However, unlike these latter, they can be completely regenerated by calcination at 823 K for 6 h, recovering the conversion values of the fresh catalysts, with only a slight decrease of selectivity. Thus, notwithstanding their lower catalytic performances, Mg/Al mixed oxides obtained by controlled calcinations of commercial hydrotalcites appear very interesting catalysts for industrial applications, considering their low cost, wide availability, easy and almost complete regeneration. Finally, it is noteworthy that the described process may be applied to a wide number of substituted benzylic alcohol containing electron-donating groups, in which the activation effect may occur either for inductive (methyl group) or mesomeric effect (methoxy group). On the contrary, the presence of electron-withdrawing groups, as chlorine, decreases the yield in the corresponding aldehyde, favouring its further oxidation to the acid.

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