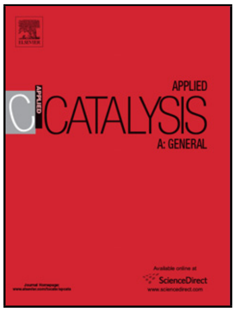

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TITLE PAGE

Optimization of process conditions for nickel-catalyzed selective aerobic *O*-debenzylation

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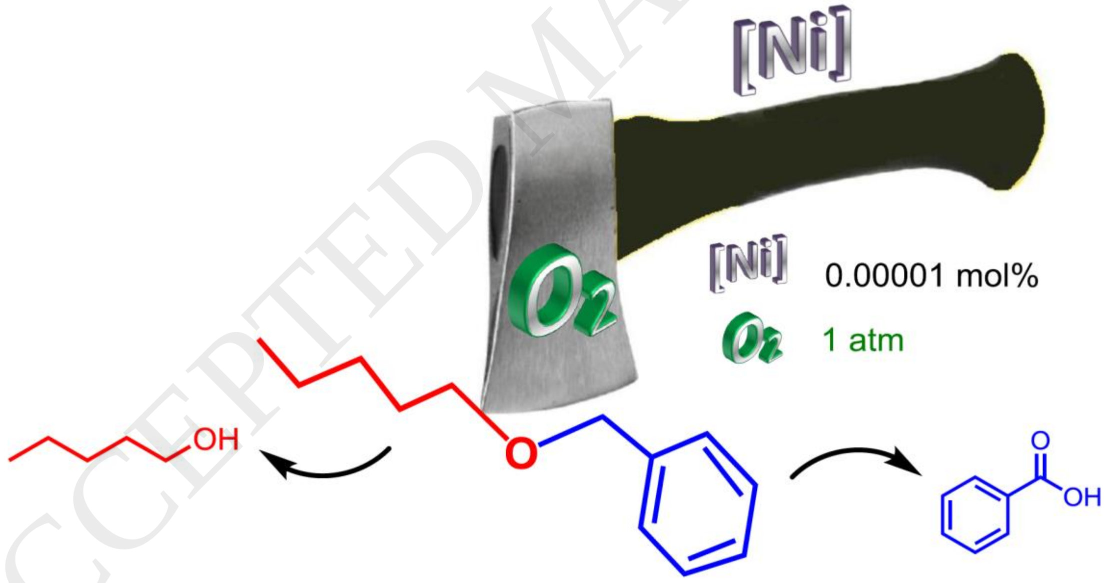
Dedicated to Professor Pablo Espinet on the occacion of his 70th birthday

Graphical abstract



Highlights

- *Debenzylation of benzyl pentyl ether using molecular oxygen is studied in the presence of nickel catalysts.*

- *1-Pentanol and benzoic acid are found to be the main products when low loadings of NiBr2 and MBTB are employed at atmospheric pressure.*
- *The debenzylation reaction takes place with complete selectivity, and it can be scaled up to 1g with the same outcome.*
- *Participation of catalytically active homogenous species and pentyl benzoate as intermediate is evidenced by several poisoning, kinetic and reactivity experiments.*

Abstract

An alternative nickel-based catalyst for the aerobic debenzylation of benzyl ethers has been devised in order to provide a complement to the well-known hydrogenolysis strategy as well as to other reductive or oxidative procedures, including vanadium-catalyzed cleavage under molecular oxygen. A systematic study of reaction conditions has led to an optimized procedure from (pentyloxy)methyl)benzene (POMB) that provides selectively target 1-pentyl alcohol (PA), releasing the benzyl group as benzoic acid (BA). The participation of homogeneous species is supported by several experiments, which also reveal the intermediacy of pentyl benzoate.

Keywords: Nickel; Nitrogen ligand; Oxidation; Benzyl ethers

Abstract

An alternative nickel-based catalyst for the aerobic debenzylation of benzyl ethers has been devised in order to provide a complement to the well-known hydrogenolysis strategy as well as to other reductive or oxidative procedures, including vanadium-catalyzed cleavage under molecular oxygen. A systematic study of reaction conditions has led to an optimized procedure from (pentyloxy)methyl)benzene (POMB) that provides selectively target 1-pentyl alcohol (PA), releasing the benzyl group as benzoic acid (BA). The participation of homogeneous species is supported by several experiments, which also reveal the intermediacy of pentyl benzoate.

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1. Introduction

Nickel-catalyzed oxidative processes have attracted much attention, due to the distinctive properties of nickel catalysts and their relative availability and low cost [1-5]. Among the oxidizing agents required (Ag_2CO_3, Ag_2O, Ag_3PO_4, DTBP, TBHP, H_2O_2 and other peroxides, etc.) [6-18] molecular oxygen stands out as a safe and convenient reagent. Indeed, nickel sources in combination of molecular oxygen have been extensively used in the Baeyer-Villiger reaction [19-23], and occasionally for the α–hydroxylation of silyl enol ethers and silyl ketene acetals [24], and for the synthesis of carbodiimides by reaction between primary amines and isocyanides [25].

More recently, the nickel-catalyzed aerobic oxidation of alcohols, methylene compounds or β–ketoesters has been reported [26-33]. Both symmetric and non-symmetric diynes have been prepared by oxidative coupling of terminal alkynes [34-35], and homocoupling of aryl Grignard reagents provided several bisaryls [36]. Reaction between alkynes and boronic acids to provide diarylalkynes under aerobic conditions was performed in the presence of $Ni_2(BDC)_2(DABCO)$/2,2'-bipyridine catalyst system [37].

Other alkynylation reactions, such as the C-2-alkynylation of 1,3-diazoles [38], the *o*-alkynylation of N-PIP benzamides [39], and the *o*-alkynylation/annulation of N-PyObenzamide derivatives to provide 3-alkylidenisoindolones [40] can be found in the literature. Hydroxycarboxylation of 1,2-dienes [41], cleavage of alkenes and alkynes [33,42], *o´*-trifluoromethylation of anilides [43], and oxidative isocyanide insertion of 2-(o-aminoaryl)benzimidazoles [44] have been also reported using the couple nickel catalyst/O_2.

There are several reports in the literature on the deprotection of benzyl ethers mediated by nickel, and all of them involving hydrogenolysis [45-49] or other reductive methods ($NiCl_2$-$NaBH_4$) [50]. Low-weight alcohols, alkanes, alkyl ethers, and xylene are the organic solvents employed, although organic/aqueous mixtures have been described [51]. Common problems associated to chemoselectivity issues and overreduction side-products have been satisfactorily overcome [45-49], but the loading of the nickel catalyst is in the range of 0.25-20 mol%, and even higher amounts of catalyst are required when Ni-Raney or $NiCl_2$-$NaBH_4$ are employed. Therefore, an efficient non-reductive deprotection protocol could constitute a useful alternative when reduction-sensitive functionalities are present in the starting benzyl ether, or catalyst amount is to be minimized.

Following our research on molecular oxygen mediated oxidative processes [33,42] that included the discovery of a method for the vanadium-catalyzed debenzylation of ethers [52], we wondered if a nickel catalyst could also promote the oxidative deprotection of *O*-benzyl ethers under aerobic conditions, thus providing an alternative metal catalyst for a known transformation. Indeed, the development of alternative metal catalysts for a number of reactions (cross couplings, hydrogenations, carbonylation and carboxylations, *inter alia*) has attracted much attention in the last years [53-58]. In this work we explore the use of nickel catalysts for the synthesis of alcohols by deprotection of *O*-benzyloxy derivatives mediated by molecular oxygen.

2. Experimental

2.1. General comments

Commercially available reagents were used throughout without purification unless otherwise stated. (Pentyloxy)methyl)benzene (POMB) was prepared from 1-pentyl alcohol (PA) and benzyl bromide. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 instrument (300 MHz for ^{1}H and 75.4 MHz for ^{13}C) at 20 ºC. Chemical shifts (δ) are given in ppm downfield from Me_4Si and are referenced as internal standard to the residual solvent (unless indicated) $CDCl_3$ (δ=7.26 for ^{1}H and δ=77.00 for ^{13}C). Coupling constants, J, are reported in hertz (Hz). Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, Merck, 230-400 mesh ASTM). Evaporation of solvents was accomplished with a Büchi rotatory evaporator. MS and HR-MS were measured using a Waters GCT mass spectrometer.

2.2. Nickel-catalyzed aerobic O-debenzylation of (pentyloxy)methyl)benzene

A round bottom flask equipped with a magnetic stirrer bar was charged with POMB (178 mg, 1 mmol), sodium acetate (8.0 mg, 0.1 mmol), nickel(II) bromide (20 μL of a 5 x 10^{-6} M solution in polyethylene glycol 400, 10^{-7} mmol), MBTB (20 μL of a 5 x 10^{-6} M solution in polyethylene glycol 400, 10^{-7}mmol) and polyethylene glycol 400 (1 mL) at room temperature. The system was purged with molecular oxygen, an oxygen-filled balloon (1-1.2 atm) was connected, and the mixture was stirred and heated at 120 ºC for 48 h. Upon completion, the mixture was cooled to room temperature and purified by flash column chromatography using hexane:ethyl acetate (1:1) as eluent to provide PA (67 mg , 76%) as a colorless oil and BA (91 mg, 75%) a white powder.

2.3. Nickel-catalyzed aerobic cleavage of pentyl benzoate

A round bottom flask equipped with a magnetic stirrer bar was charged with PB (192 mg, 1 mmol), sodium acetate (8.0 mg, 0.1 mmol), nickel(II) bromide (20 μL of a 5 x 10^{-6} M solution in polyethylene glycol 400, 10^{-7} mmol), MBTB (20 μL of a 5 x 10^{-6} M solution in polyethylene glycol 400, 10^{-7}mmol) and polyethylene glycol 400 (1 mL) at room temperature. The system was purged with molecular oxygen, an oxygen-filled balloon (1-1.2 atm) was connected, and the mixture was stirred and heated at 120 ºC for 48 h. Upon completion, the mixture was cooled to room temperature and purified by flash column chromatography using hexane:ethyl acetate (1:1) as eluent to provide PA (68 mg , 77%) as a colorless oil and BA (92 mg, 76%) a white powder.

3. Results and Discussion

In order to make our method more convenient for industrial applications, the pressure of molecular oxygen was set at 1 atm. (Pentyloxy)methyl)benzene (POMB) was chosen as model substrate, and in a preliminary set of experiments, it was heated at 120ºC in dioxane under 1 atm of O_2 in the presence of a variety of nickel sources ($NiBr_2$, $NiCl_2$, $Ni(OAc)_2$, $Ni(NO_3)_2$, $[Ph_2P(CH_2)_3PPh_2]NiCl_2$, NiO, $Ni(OH)_2$, and $NiCO_3·H_2O$). Low conversion rates (< 10%) and poor selectivity towards target PA (< 5%) were observed. However, the addition of ligands changed completely the scenario. As shown in Figure 1, a number of nitrogen and phosphorus ligands were combined with $NiBr_2$ and $Ni(OAc)_2$ as nickel sources (0.01 mol%). POMB conversion reached acceptable values (55%) only when $NiBr_2$ was tested along with methyl 3,5-*bis*((1H-1,2,4-triazol-1-yl)methyl)benzoate (MBTB). Other 1,2,4- and 1,2,3-triazol derivatives provided poor results and interestingly, although the only relatively competing ligand was methyl 3,5-*bis*((1H-pyrazol-1-yl)methyl)benzoate (MBPB), very low conversion rates were observed with pyrazole and other diazole, imidazole.

3.1. Investigating the effect of solvent and nickel source on catalyst performance

Encouraged by the results from the $NiBr_2$/MBTB system, we decided to explore different reaction media. Priority was given to water and polyol solvents due to environmental reasons, although other more conventional solvents (tetrahydrofuran, dimethylacetamide or ethanol) were also tested. We discovered that, in some cases, the results could be slightly improved (up to a 7% of POMB conversion) by adding a catalytic amount (10 mol%) of sodium acetate. This additive probably provides a slightly basic environment as well as a source of acetate ligands. In fact, sodium acetate has been employed as additive to increase catalyst performance and/or selectivity in metal-catalyzed aerobic oxidation of organic compounds [59]. Therefore in all the experiments displayed in Figure 2 NaOAc was used. To our delight, it was found that three of the four polyols assayed (glycerol, ethylene glycol (ETG) and polyethylene glycol 400 (PEG 400) promoted conversion rates higher than 80%. The latter PEG 400 was chosen for further optimization experiments on account of the difficulty for product isolation from glycerol and ETG (isolated yields of PA and BA ranged from 8 to 19% depending on the extraction or chromatography method employed).

The initial array of nickel sources were then tested along with MBTB ligand in PEG 400 as solvent. A blank experiment was also carried out, revealing the need of a nickel catalyst for the reaction. Figure 3 compares the results from the aforementioned nickel salts and complexes, showing a better performance by nickel(II) bromide. In fact, even relatively similar nickel(II) chloride or nickel(II) acetate promoted as much as half the POMB conversion. A relatively higher solubility of $NiBr_2$ in the reaction media may be behind this behavior. Although selectivity will be discussed in section 3.2, it should be pointed out that benzaldehyde and pentanal were detected as by-products from the reactions carried out in the presence of nickel sources other than nickel(II) bromide. Similar selectivity issues were encountered when dioxane was used as the solvent.

3.2. Investigating the effect of temperature, reaction time and catalyst amount on catalyst performance

With a good conversion rate at hand, we investigated the effect of temperature and reaction time not only on POMB conversion, but also on selectivity, product distribution and isolated yields. Reaction temperatures were set at 150ºC, 120ºC and 100ºC and experiments run for different reaction times. After work-up and purification, 1-pentyl alcohol (PA) and benzoic acid (BA) products were isolated and the corresponding yields shown in Figure 4. A temperature of 120ºC was found optimal for both conversion and selectivity, as at 100ºC poor POMB conversion (< 10%) was observed even for long reaction times (120h), and at 150ºC, although full conversion was observed for reaction times longer than 48h, target alcohol PA was obtained with much lower yields due to the presence of complex reaction mixtures. However, PA and BA were selectively isolated in good yields from the reactions performed at 120ºC and no other by-product was detected. A possible explanation for the difference between the almost quantitative conversion rates observed and the significantly lower yields of isolated PA and BA may lie on a complexation and/or covalent linkage to the PEG-400 matrix. As discussed later, partial oxidative degradation of PEG chains to carbonyl or carboxy ending groups may have a positive effect on the reaction outcome, but probably provoked esterification and acetalization with target PA and BA. In fact, when the reaction crude (reaction performed at 120ºC, 96h) was submitted to acidic hydrolysis conditions (HCl 0.5M, 100ºC, 5h) both PA and BA were exclusively isolated in higher yields (84 and 88% respectively). We decided to prioritize the simplicity of the process over slight improvements in the yield to avoid implementing further hydrolysis steps.

Further optimization involved study of the effect of catalyst loading in reaction yields. Temperature was then set at 120ºC, and taking 24h, 48h and 96h as the most promising reaction times, several experiments were carried out decreasing the amount of the $NiBr_2$/MBTB system. To our surprise, in comparison with other catalyst loadings assayed, a slight improvement was observed when as little as 0.00001 mol% of both ingredients was used (Figure 5). Enhanced performance at low catalyst loading has been described for several metal- and organocatalyzed reactions, such as C-C coupling of chloroarenes, ring-closing metathesis or enamine catalysis [60-62]. In view of these results, a catalyst amount of 0.00001 mol% and reaction time of 48 h were established as optimal in order to explore the scalability of the process. When 1.5 g of POMB was submitted to the optimized reaction conditions, 0.52 g of PA (70%) and 0.75 g of BA (73%) were obtained.

A further decrease of the amount of the $NiBr_2$ and/or MBTB resulted in negligible results. Neither PA nor BA were detected when blank experiments in the absence of the nickel source or the ligand were performed. With regard to catalyst recycling, several unsuccessful attempts were made to reuse the PEG-400 phase supposedly containing the nickel catalyst. This limitation is however of no relevance, considering the extremely small amounts of the catalyst system required (10^{-5} mol %).

3.3. Mechanistic study of the cleavage reaction

Among the useful procedures to aid in the distinction between homogeneous and heterogeneous catalysts, the results from the addition of particular additives and poisons in substoichiometric and overstoichiometric amounts can provide significant evidences in support of one or other type of catalysis [63-64] In this context, the ability of Hg (0) to poison metal-particle heterogeneous catalysts by amalgamating the metal or adsorbing on the metal surface, has been known for more than 90 years and is a widely used test. In our case, when a drop of Hg (0) was added to the POMB and submitted to the reaction conditions, no inhibition was observed (negative mercury drop test), as displayed in Table 1, entry 1.

The amount of poison required to suppress the catalytic activity is also indicative of the catalysis involved. More than one equivalent of poison per catalytic metal is expected for a molecular or monometallic catalyst, while nanoclusters or heterogenous catalysts, with only a fraction of metal atoms exposed at their surface, can be readily deactivated with low amounts of such poisoning additives. Indeed, nickel catalysts are particularly sensitive to low levels of site-blocking poisons such as reduced sulfur or phosphorus species [65-68] that bind strongly to metal centers, thereby blocking the access of the substrate to the active site. No inhibition was observed when sub- and overstoichiometric amounts of PPh_3 and CS_2 were added to the reaction (Table 1, entries 2-6), thus providing a strong evidence for the participation of homogeneous catalysts.

Metal hydride complexes have been employed in aerobic oxidation of several compounds [69-70]. In addition, thermal oxidative degradation of polyethylene glycol derivatives has been described in aerobic conditions to provide formate residues [71]. We tentatively propose that such formate residues from the oxidative partial degradation of PEG-400 might release hydride anions to generate nickel hydride complexes which would be the real catalytically active species. This proposal would explain the induction time of approximately 9 h observed in the conversion rate *vs* time kinetic plot (Figure 6). In fact, addition of a 10^{-4} mol% of sodium formate accelerated the reaction, as a conversion rate of 42% was observed after 3h. However, the addition of sodium formate in amounts higher than 10^{-3} mol% had a deleterious effect in the reaction outcome. Further attempts to prove the participation of nickel hydride species failed due to the very small amounts of catalyst and to the nature of the solvent employed.

Formation of pentyl benzoate (PB) by a nickel-catalyzed benzylic C-H oxidation [72] is proposed as the key step of the reaction mechanism, followed by hydrolysis of the above intermediate by water released in the previous step. As a matter of fact, PA and BA were easily isolated with good yields (77 and 76% respectively) by treatment of readily available PB [73] under the same aerobic reaction conditions. Interestingly, blank experiments in the absence of $NiBr_2$ and/or MBTB were performed and no cleavage of PB was observed. Moreover, PB was detected in variable amounts from the cleavage of POMB when shorter reaction times (15-20h) or slightly lower temperatures (115ºC) were employed.

4. Conclusion

After a systematic study of reaction conditions including evaluation of nickel sources, ligands, solvents, temperature, reaction time and catalyst amount, a highly efficient procedure for the nickel-catalyzed debenzylation of benzyl ether POMB is presented. This protocol may be complementary approach to debenzylation mediated by dihydrogen, with the advantages that much lower catalyst loadings, and a safer and more abundant reagent, molecular oxygen at atmospheric pressure, are required. In addition, it is a valid alternative to the recently reported vanadium-based aerobic method. Evidences in favour of the homogeneous nature of the catalytically active species derived from $NiBr_2$/MBTB are provided from several poisoning experiments, and the participation of benzoate intermediate PB is suggested on account of the detection and reactivity of this intermediate. Further exploration of substrate scope is now under progress.

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Appendix A. Supplementary material

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.apcata.XXXXXX

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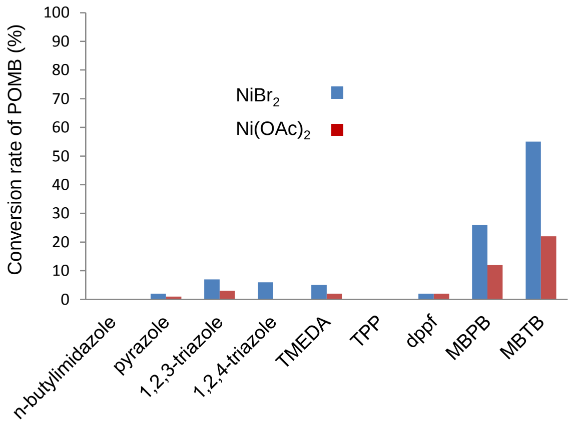

Fig. 1. Conversion rate of POMB as a function of the ligand employed. Reaction conditions: $NiBr_2$ or $Ni(OAc)_2$ (0.0001 mmol), POMB (1 mmol), ligand (0.0001 mmol), 1,4-dioxane (1 mL), O_2 (1 atm), 120 °C, 96 h. Conversion rate determined by GC-MS.

dppf: 1,1′-Ferrocenediyl-bis(diphenylphosphine); MBPB: Methyl 3,5-bis((1H-pyrazol-1-yl)methyl)benzoate; MBTB: Methyl 3,5-bis((1H-1,2,4-triazol-1-yl)methyl)benzoate.

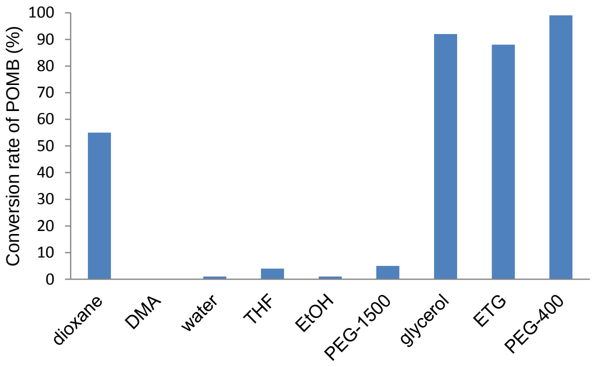

Fig. 2. Conversion rate of POMB as a function of the solvent. Reaction conditions: $NiBr_2$ (0.0001 mmol), POMB (1 mmol), MBTB (0.0001 mmol), NaOAc (0.1 mmol), solvent (1 mL), O_2 (1 atm), 120 °C, 96 h. Conversion rate determined by GC-MS.

DMA: *N*,*N*-Dimethylacetamide; PEG: Polyethylene glycol; ETG: Ethylene glycol.

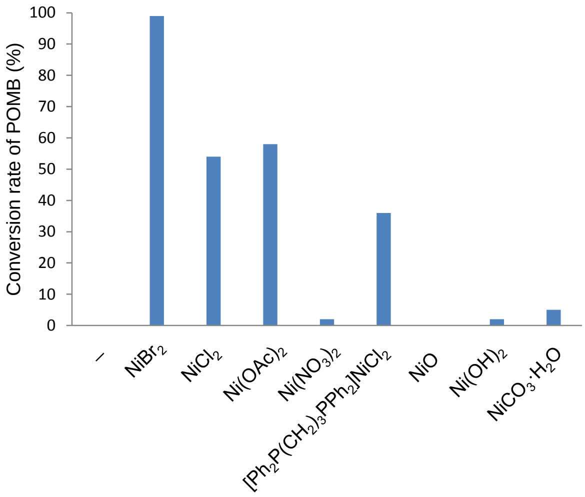

Fig. 3. Conversion rate of POMB as a function of the nickel source. Reaction conditions: Nickel salt or complex (0.0001 mmol), POMB (1 mmol), MBTB (0.0001 mmol), NaOAc (0.1 mmol), PEG-400 (1 mL), O_2 (1 atm), 120 °C, 96 h. Conversion rate determined by GC-MS.

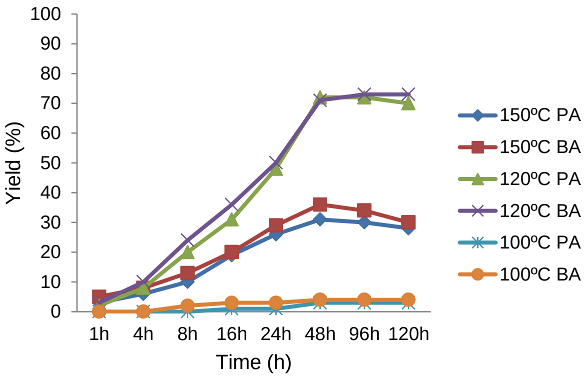

Fig. 4. Isolated yields of PA and BA as a function of temperature and reaction times, in the reaction of POMB (1 mmol), O_2 (1 atm), $NiBr_2$ (0.0001 mmol), MBTB (0.0001 mmol), NaOAc (0.1 mmol) and PEG-400 (1 mL).

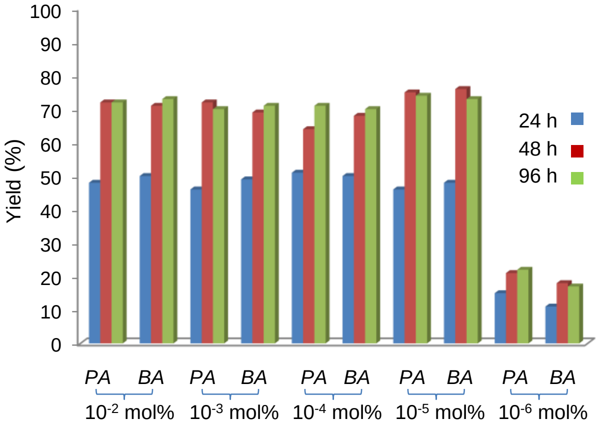

Fig. 5. Isolated yields of PA and BA as a function of the amount of the catalyst ($NiBr_2$/MBTB) and reaction time, in the reaction of POMB (1 mmol), O_2 (1 atm), $NiBr_2$, MBTB, NaOAc (0.1 mmol) and PEG-400 (1 mL) at 120 ºC.

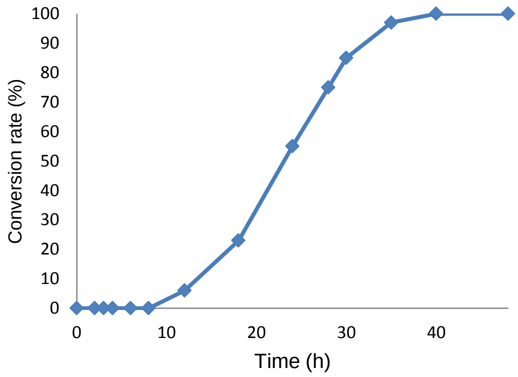

Figure 6. Conversion rate (%) of POMB *vs* time.

Table 1. Summary of poisoning experiments

Entry	Additive	Conversion (%)[a]
1	Hg (one drop)	97 (PA *74*/BA *75*)
2	CS_2 (0.5 eq. per metal atom)	99 (PA *76*/BA *78*)
3	CS_2 (2 eq. per metal atom)	99 (PA *75*/BA *78*)
4	PPh_3 (0.03 eq. per metal atom)	96 (PA *73*/BA *73*)
5	PPh_3 (0.3 eq. per metal atom)	98 (PA *74*/BA *76*)
6	PPh_3 (4 eq. per metal atom)	99 (PA *76*/BA *78*)

Conditions: POMB (1 mmol), O_2 (1 atm), $NiBr_2$ (0.0000001 mmol), MBTB (0.0000001 mmol), NaOAc (0.1 mmol), PEG-400 (1 mL), 120 ºC, 48 h.

[a] Conversion rate determined by gas chromatography analysis. GC-MS yields (PA %/BA %) are shown in italics. Anisole was used as internal standard.