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Water as an Efficient Solvent for Oxygenation Transformations with 34% Hydrogen Peroxide Catalyzed by some Heteropolyoxometalates

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Summary. A highly efficient, selective, fast, and cheap protocol is developed for oxidation of aromatic amines and alcohols utilizing 34% hydrogen peroxide in water catalyzed by some W- and Mo-based heteropolyoxometalates. Findings showed that dodecatungstophosphoric acid, $H_3PW_{12}O_{40}$, was the most efficient catalyst in the examined oxidation reactions. This methodology may prove to be a valuable alternative for eco-friendly green oxidation. Inherent simplicity, easy work up, and using regenerable catalysts were other key aspects of this oxidation protocol.

Keywords. Oxidation; Heteropolyacid; Catalysis; Hydrogen peroxide.

Introduction

Waste minimization is a very important aspect of an environmentally benign protocol [1, 2]. Practically, this means performing reactions with high conversions, using green reagents, and a green reaction medium followed by an efficient recycling program. Although, several effective protocols based on reusing of the reaction medium have been introduced, the recycling of organic solvents is complex and requires purification by distillation. Whereas the use of water (without co-solvents) as reaction medium makes recycling processes very easy and cheap. In addition, the aqueous medium allows one-pot multistep processes to be performed [3–7].

Despite the vast array of homogeneously catalyzed reactions that has been developed in the past decades, industrial fine chemical manufacture still heavily depends on classical organic chemistry based on stoichiometric reagents. Development of highly active homogeneous catalysts that meet industrial demands is a challenging task. Considerable research, most of quite recent vintage, on homogeneous catalysis by heteropolyoxometalates as early transition metal oxygen anion clusters is a rapidly growing area, in part as a consequence of the unusual versatility of these catalysts and their compatibility with environmentally friendly conditions [8–11].

Heteropolyoxometalates are an extraordinarily versatile class of complexes with potential catalytic applications for a variety of attractive processes. These include O_2- and H_2O_2-based oxidations and processes that take place under environmentally benign conditions. The selected examples reviewed show the broad scope of potentially promising applications of heteropolyoxometalates as acid and redox catalysts in liquid phase organic reactions including epoxidation, oxidative dehydrogenation, and oxidative cleavage processes [12–20]. Due to their unique physicochemical properties, heteropolyoxometalates can be profitably used in homogeneous, biphasic, or heterogeneous systems, providing a broad operational choice [21–23].

Selective oxidation of arylamines and alcohols to their corresponding oxygenated products are of the most fundamental functional transformations through-

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out chemistry and have been a challenge for many years [24–30]. A variety of stoichiometric and catalytic routes have been reported for preparation of these crucial industrial precursors. The nature of the oxidation products formed in these reactions depends on the type of the oxidant used and the reaction conditions. Various reagents, including metal compounds, organic peroxides, and hydrogen peroxide, have been utilized to form oxygen containing derivatives of many organic precursors [27–30, 32–52, 57–59]. However, some of the homogeneous and heterogeneous catalysts disclosed in the literature are often required in stoichiometric amounts. Many of these methods are usually toxic and hazardous and suffer from harsh reaction conditions, over-oxidation, low yields of the desired products, and cause environmental problems [53, 54]. Therefore, designing a catalytic formulation using environmentally benign oxidants by the mediation of simple water soluble metal complexes in aqueous reaction media are desirable in organic chemistry, biochemistry, and atmospheric chemistry.

Herein, we wish to report a simple, clean, efficient, and eco-friendly process for oxygenation of anilines and alcohols with 34% hydrogen peroxide catalyzed by some simple heteropolyoxometalates. Indeed, in contrast to almost all presently employed processes, reactions were performed in water effectively.

Results and Discussion

Oxygenation of Aniline and Cyclohexanol in Water with H_2O_2 Catalyzed by Different Heteropolyoxometalates

Table 1 introduces an efficient new methodology for catalytic oxygenation of aniline and cyclohexanol with 34% H_2O_2 in drinking water using simple heteropolyoxometalates.

Among the examined catalysts for the oxygenation of aniline with hydrogen peroxide, $K_4SiW_9Mo_2O_{39}$, and $H_3PW_{12}O_{40}$ showed the best results. They provided 67% of product with >97% selectivity after 60 min. Previously, it has been demonstrated that nitrosobenzene was the sole product of aniline oxidation with aqueous hydrogen peroxide by the mediation of dodecatungstophosphoric acid [31].

The results of oxygenation of cyclohexanol with H_2O_2 in water demonstrated that $H_3PW_{12}O_{40}$ and $K_5Na_2PW_{11}O_{39}$ were the best catalysts in this oxidation system and they led to complete conversion of cyclohexanol to cyclohexanone after 2.5 h. $H_3PMo_{12}O_{40}$ and its ammonium salt $[(CH_3)_4N]_3PMo_{12}O_{40}$ showed less catalytic activity and resulted in 30 and 13% yields, respectively, under the same reaction conditions. Other mixed metal substituted *Keggin*-type heteropolyanions revealed moderate reactivity and provided 67–70% of cyclohexanone under

Table 1. Oxidation of aniline and cyclohexanol in normal drinking water with 34% H_2O_2 catalyzed by different heteropolyoxometalates[a]

Entry	Catalyst	Substrate	Product	Conv./%	Sel./%	Time/min
1	$H_3PW_{12}O_{40}$	*Ph*-NH_2 (**1**)	*Ph*-NO (**2**)	67	100	60
2		$C_6H_{11}OH$ (**3**)	$C_6H_{10}O$ (**4**)	100	98	150
3	$H_3PMo_{12}O_{40}$	**1**	**2**	56	97	60
4		**3**	**4**	30	100	180
5	$Na_3PW_9Mo_3O_{40}$	**1**	**2**	64	98	60
6		**3**	**4**	70	95	210
7	$K_4SiW_9Mo_2O_{39}$	**1**	**2**	67	97	60
8		**3**	**4**	67	92	210
9	$K_5Na_2PW_{11}O_{39}$	**1**	**2**	53	100	60
10		**3**	**4**	100	98	150
11	$(TBA)_3PMo_{12}O_{40}$	**1**	**2**	54	96	60
12		**3**	**4**	13	100	180

[a] To a solution of catalyst (0.015 mmol for aniline and 0.018 mmol for cyclohexanol) and 34% H_2O_2 (8 mmol for aniline and 5 mmol for cyclohexanol) in water (4 cm^3 for aniline and 5 cm^3 for cyclohexanol) as solvent was added substrate (4 mmol for aniline and 0.94 mmol for cyclohexanol). The reaction mixture was stirred at room temperature for the required time. Progress of the reactions was followed by aliquots withdrawn directly and periodically from the reaction mixture and analyzed by gas chromatography. Products were isolated as described in the experimental section

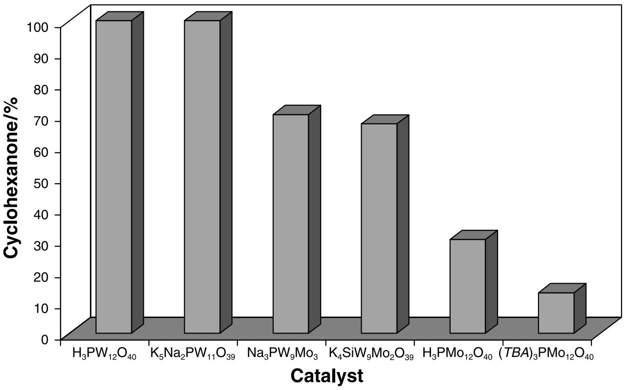

Fig. 1. Oxygenation of cyclohexanol in drinking water with H_2O_2 catalyzed by different heteropolyoxometalates

the reaction conditions reported here (Fig. 1 and Table 1).

Effects of Different Solvents on the Oxygenation of Aniline and Cyclohexanol with 34% H_2O_2 Catalyzed by $H_3PW_{12}O_{40}$

To test the range of solvents that may promote oxidation reactions, a number of usual solvents were screened. Table 2 presents the results of catalytic oxygenation of aniline and cyclohexanol with H_2O_2 mediated by $H_3PW_{12}O_{40}$ in different solvents. Water (electrical conductivity, 550 S; total dissolved solids, 350 mg/dm^3; and *pH*, 8.3) turned out as the best solvent for these oxygenation transformations. Findings clearly approved that water was more effective than dichloromethane.

According to the results in Table 2, 69% of nitrosobenzene was produced in water, whereas 27% of conversion was observed in CH_2Cl_2 under the same reaction conditions within 60 min. It seems that inorganic impurities in the water do not interfere into the reaction progress. Ethanol was also capable of aniline oxygenation with 71% yield at the same time. Other organic solvents revealed less reactivity than water in the oxygenation of aniline. Acetone, dichloromethane, and chloroform produced 12–27% of conversions to the corresponding products after 60 min. Meanwhile, ^{t}*Bu*OH was the most efficacious organic solvent and led to 50% yield at the same time.

Table 2 also shows results of oxidation of cyclohexanol with H_2O_2 catalyzed by $H_3PW_{12}O_{40}$ in different solvents. As in the oxygenation of aniline, water was the best solvent for selective oxidation of cyclohexanol. Complete conversion of cyclohexanol to cyclohexanone was obtained in water with 100% selectivity after 2.5 h. Fortunately, inorganic impurities in water had no effect on the efficiency of cyclohexanol oxidation. Other organic solvents such as chloroform, ethanol, and acetone were not suitable for the oxygenation system. These solvents gave rise to 5, 15, and ~10% of cyclohexanone, respectively, within 2.5 h (Fig. 2).

Different reactivity patterns observed for the introduced catalysts in different solvents may in part be explained considering solubility of them. For example, $K_5Na_2PW_{11}O_{39}$ and $(TBA)_3PMo_{12}O_{40}$, which are slightly soluble in CH_2Cl_2, revealed little

Table 2. Effect of different solvents on the oxidation of aniline and cyclohexanol with 34% H_2O_2 catalyzed by $H_3PW_{12}O_{40}$

Entry	Solvent	Substrate	Product	Conv./%	Sel./%	Time/min
1	Water	*Ph*-NH_2 (**1**)	*Ph*-NO (**2**)	69	100	60
2		$C_6H_{11}OH$ (**3**)	$C_6H_{10}O$ (**4**)	100	100	150
3	Ethanol	**1**	**2**	98	71	60
4		**3**	**4**	15	95	150
5	Acetone	**1**	**2**	12	93	60
6		**3**	**4**	<10	>95	150
7	*t*-Butanol	**1**	**2**	50	95	60
8		**3**	**4**	3	>97	150
9		**5**	**6**	85	100	300
10	Dichloromethane	**1**	**2**	27	93	60
11		**3**	**4**	6	>95	150
12	Chloroform	**1**	**2**	25	92	60
13		**3**	**4**	5	>95	150

Reactions were carried out as described below Table 1

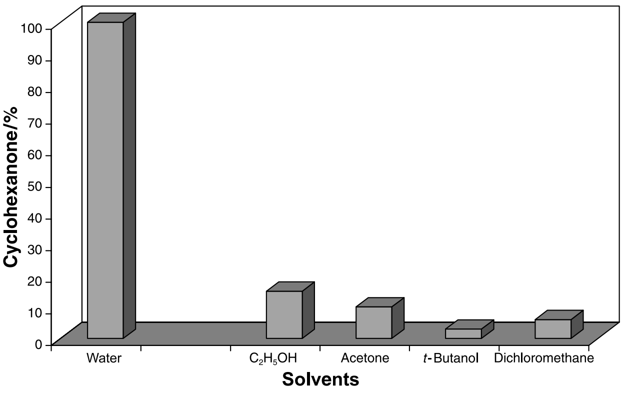

Fig. 2. Effect of different solvents on the oxygenation of cyclohexanol with H_2O_2 catalyzed by $H_3PW_{12}O_{40}$

catalytic activity, whereas good yields were obtained with these two catalysts in water.

As a fortuitous extension of the solvent study, the oxidation of aniline and cyclohexanol with hydrogen peroxide in water has cleanly and selectively provided nitrosobenzene and cyclohexanone.

Oxygenation of some Anilines and Alcohols into the Corresponding Oxygenated Products

Treatment of some aromatic amines with hydrogen peroxide in the presence of dodecatungstophosphoric acid as catalyst in water gave the corresponding nitroso derivatives with good to excellent yields and with 100% selectivities (Table 3). These results showed that phenylenediamine was the most reactive substrate toward oxidation, whereas electron deficient 4-NO_2-aniline led to only 32% of the nitroso product.

This methodology provided a new environmentally friendly route to the conversion of alcoholic functions to carbonyl groups with excellent selectivities. Table 3 shows the results of oxygenation of different alcohols with H_2O_2 under the influence of $H_3PW_{12}O_{40}$ in water at 70°C. Findings showed that 3-NO_2-benzyl alcohol and 1-phenylethanol were the most reactive substrates in the oxygenation system. They produced 90 and 85% yields of the corresponding ketones after 2.5 h, whereas 3-O*Me*-benzyl alcohol, benzyl alcohol, and isopropanol resulted in 67–78% conversions after the required times. *n*-Butanol and *n*-heptanol, as linear primary alcohols, showed little reactivity toward oxidation. They exhibited 30 and 9% conversions after 2.5 and 4.5 h, respectively.

Effect of Different Oxidants on the Oxygenation of Cyclohexanol

A large number of oxidants have been extensively investigated in context with homogeneous catalytic oxidation processes. The primary characteristics that define the attractiveness of an oxidant are the active oxygen percent (the higher the better) and the selectivity associated with its use, in addition to the pragmatic issues of cost and effect on the environment. While the oxidants such as OCl^-, Cl_2, and ClO_2 lead in varying yields to chlorinated organic compounds, including the highly toxic and carcinogenic dioxins, and are rapidly becoming environmentally unacceptable, many other oxidants that produce only minimally toxic inorganic waste as by-products, such as sulfate from persulfate, are also becoming environmentally and hence politically and economically

Table 3. Oxidation of some aromatic amines and alcohols with 34% H_2O_2 in water catalyzed by $H_3PW_{12}O_{40}$

Entry	Class	Substrate	Product	Conv./%	Sel./%	Time/min
1	Anilines*	*Ph*-NH_2	C_6H_5–NO	71	100	60
2		4-NO_2-Aniline	4-NO_2–C_6H_4–NO	32	100	60
3		4-*Me*-Aniline	4-*Me*–C_6H_4–NO	77	100	60
4		1,2-Phenylenediamine	1-NO-2-(NH_2)C_6H_4	100	92	30
5	Alcohols	Isopropanol	C_3H_6O	67	100	180
6		4-O*Me*-Benzyl alcohol	4-O*Me*–C_7H_5O	73	100	120
7		Benzyl alcohol	C_7H_6O	78	100	150
8		*n*-Butanol	$CH_3(CH_2)_2CHO$	30	75	150
		n-Heptanol	$CH_3(CH_2)_5CHO$	9	60	270
9		1-*Ph*-Ethanol	*Ph*-$COCH_3$	85	100	150
10		3-NO_2-Benzyl alcohol	3-NO_2–C_7H_5O	90	100	150

* Water:^{t}*Bu*OH (3:1) mixture was used as solvent. Reactions were carried out as described below Table 1

Table 4. Oxidation of cyclohexanol to cyclohexanone with different oxidants catalyzed by $H_3PW_{12}O_{40}$

Entry	Oxidant	Yield/%	Sel./%	Time/h
1	H_2O_2	70	100	4
2	H_2O_2	0*	–	4
3	$KMnO_4$	72	90	3.5
4	$KMnO_4$	30*	95	3.5
5	$K_2S_2O_8$	43	93	5
6	$K_2S_2O_8$	44*	93	5
7	$K_2Cr_2O_7$	<10	100	7
8	$K_2Cr_2O_7$	<5*	–	7

Reactions were carried out as described below Table 1
* In the absence of catalyst at 70°C

unacceptable. The most attractive oxidants with respect to the criteria articulated above are O_2 and H_2O_2. Hydrogen peroxide readily transfers one of its oxygen atoms to a substrate to produce as a by-product a 'green' substance, water, which is a great advantage of this oxidant in comparison with all other oxidants [55–56].

Table 4 describes oxygenation of cyclohexanol with some important oxidants catalyzed by $H_3PW_{12}O_{40}$. Findings demonstrated that hydrogen peroxide was the best oxidant in this catalytic oxygenation system. It gave rise to 70% of cyclohexanone in the presence of a catalyst within 4 h, whereas no conversion occurred in the absence of the catalyst with this oxidant at the same time. Sodium permanganate was also suitable for oxidation of cyclohexanole. It led to 72 and 30% of cyclohexanone in the presence and in the absence of the acid catalyst within 3.5 h. Other oxidants, potassium persulfate and potassium dichromate, showed less reactivity in the oxygenation system and their reactivities were independent into the presence of catalyst. Potassium persulfate and potassium dichromate led to ~44 and <10% of cyclohexanone in this oxygenation system (Fig. 3 and Table 4).

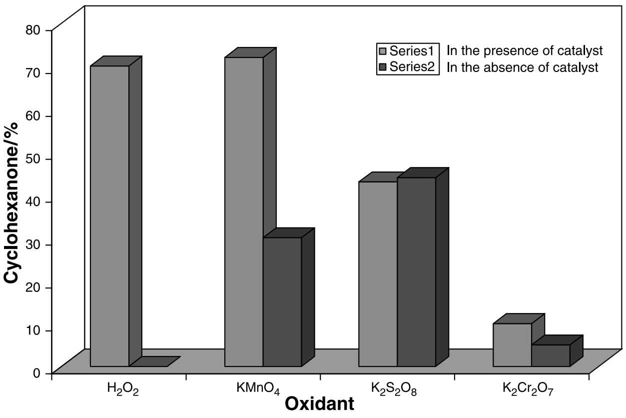

Fig. 3. Oxygenation of cyclohexanol to cyclohexanone with different oxidants in presence or absence of $H_3PW_{12}O_{40}$

Conclusion

In conclusion, we have demonstrated an efficient, eco-friendly, and effective one-pot protocol to oxidize aromatic amines and alcohols directly into their corresponding oxygenated products in water. These reactions were facile, high-yielding, and easy to work up and should provide a mild oxidative alternative for organic chemists. We have shown that mentioned water-soluble heteropolyoxometalates were effective, stable, and recyclable catalysts in biphasic reaction media. The *in situ* prepared catalysts were as active as the recycled ones. Simple polyoxotungstophosphates used in this protocol can be readily synthesized on a large scale from cheap salts and are degraded at a very slow rate [60–62].

Experimental

Materials and Instrumentation

Solvents, reagents, and other chemicals used in this study were of the highest grade available and were purchased from SD Fine Chemicals (India). The reagents were stored at 5°C and purified just before use. Silica gel 60 (70–230 mesh, purchased from E-Merck A.G., Darmstadt, West Germany) was used for column chromatography. Purity of the substances and progress of the reactions were monitored by gas chromatography. GLC analyses were performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector using 25 m × 0.25 mm CPB 5-20 and fused silica WCOT 25 m × 0.23 mm capillary columns. The heteropolyoxometalates $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $(TBA)_3PMo_{12}O_{40}$, $Na_3PW_9Mo_3O_{40}$, and $K_5Na_2PW_{11}O_{39}$ were prepared and characterized according to literature procedures [60–67].

Synthesis of $Na_3PW_{12}O_{40} \cdot 7H_2O$

$Na_2WO_4 \cdot 2H_2O$ (30 mmol, 10 g) was slowly added to 20 cm^3 distilled water and the mixture was warmed to 60°C with complete stirring. Then, 1 cm^3 85% H_3PO_4 (15 mmol) and 8 cm^3 HCl (100 mmol) were added and the resulting mixture was stirred for 1 h. The white afforded precipitate was washed with water and was recrystallized twice from hot water.

Synthesis of $Na_2HPMo_{12}O_{40} \cdot 14H_2O$

To 420 cm^3 of a 2.85 *M* aqueous solution of Na_2MoO_4 were added successively 6.8 cm^3 85% H_3PO_4 and 284 cm^3 70%

HClO. The disodium salt was precipitated from the yellow lukewarm solution. After the mixture was cooled to room temperature, the microcrystalline powder was filtered off and air-dried. Recrystallization in a mixture of 40 cm^3 *Et*OH/200 cm^3 H_2O gave 180 g of greenish microcrystals.

Synthesis of $H_3PMo_{12}O_{40} \cdot 14H_2O$

$H_3PMo_{12}O_{40} \cdot 14H_2O$ was obtained from a solution of 250 g $Na_2HPMo_{12}O_{40} \cdot 14H_2O$ in 200 cm^3 H_2O, acidified by 50 cm^3 12 *M* HC1, and extracted by 400 cm^3 Et_2O. The heavy layer (300 cm^3), to which 150 cm^3 H_2O were added, gave 190 g of yellow crystals after desiccation.

Synthesis of $(TBA)_3PMO_{12}O_{40}$

$H_3PMo_{12}O_{40} \cdot 14H_2O$ (10 g) was dissolved in 20 cm^3 water, 5 g $[(n\text{-}C_4H_9)N]_4Br$ were dissolved in 50 cm^3 CH_2C1_2, and the mixture was poured into the molybdophosphate solution with vigorous stirring. Three phases were formed: a yellow solid one, a lower liquid one (CH_2C1_2), yellow colored, and an aqueous upper one, poorly colored. The solid was washed with Et_2O, providing 8.5 g of product. A further yield of 2.5 g was obtained by addition of Et_2O to the CH_2C1_2 phase. Recrystallization was performed in CH_2C1_2.

Synthesis of $Na_7PW_9MO_2O_{39}$

$Na_5HPW_9O_{34} \cdot 24H_2O$ (11 g) was dissolved in a mixture of 20 cm^3 1 *N* aqueous sodium molybdate and 16 cm^3 1 *N* aqueous hydrochloric acid. Then about 12 cm^3 1 *N* hydrochloric acid were added drop wise until the *pH* lies between 6 and 6.5. The sodium salt $Na_7PW_9MO_2O_{39} \cdot 19H_2O$ was precipitated by addition of solid sodium chloride.

Synthesis of $Na_3PW_9Mo_3O_{40}$

Dioxane (20 cm^3), 30 cm^3 5.45 *N* aqueous hydrochloric acid, and 10 cm^3 1 *N* aqueous sodium molybdate are mixed. Upon addition of 10 g $Na_7PW_9MO_2O_{39} \cdot 19H_2O$ to this solution, the yellow salt $Na_3PW_9MO_3O_{40} \cdot 25H_2O$ precipitates. This compound, unstable in aqueous solution, is stable in hydro-organic mixtures, as water/dioxane, 1/1 in volume.

General Procedure for Oxidation of Anilines to Nitrosoderivatives in Water

To a solution of 0.015 mmol catalyst and 8 mmol 34% H_2O_2 in 4 cm^3 water as solvent was added 4 mmol amine and the reaction mixture was stirred at room temperature for the required time. Progress of the reaction was followed by aliquots withdrawn directly and periodically from the reaction mixture, which were analyzed by gas chromatography using a CPB 10 capillary column. Eventually, the organic phase was resolved using a decantor. The extract was dried over anhydrous sodium sulfate, filtered, and was concentrated under reduced pressure. The products were purified by column chromatography on silica gel (1/5, ethyl acetate/hexane). The boiling point and spectral data of each product were compared with those of authentic samples and literature values. After fifteen runs using the recycled catalyst, efficiency of the oxygenation system was ~10% decreased.

General Procedure for Oxidation of Alcohols in Water

To a solution of 0.018 mmol catalyst and 5 mmol 34% H_2O_2 in 5 cm^3 drinking water as solvent, was added 0.94 mmol alcohol and the reaction mixture was allowed to stir at 65–70°C for the required time. Progress of the reaction was followed by aliquots withdrawn directly from the reaction mixture, which were analyzed by gas chromatography using an internal standard. After completion of the reaction, the products were resolved from water. The extract was dried over anhydrous sodium sulfate, filtered, and was concentrated under reduced pressure. Finally, the concentrated filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound. After five runs using the recycled catalyst, efficiency of the oxygenation system was ~10% decreased.

Recycling of the Catalyst

At the end of the reaction, to regenerate the catalyst and decompose the excess hydrogen peroxide, the aqueous phase (~7 cm^3) of the reaction mixture was dried slowly at 50°C under intense light for 2 h and then at 130°C for 3 h. The regenerated solid acid catalyst was washed with dichloromethane and dried at 130°C for 1 h. Usual spectroscopic methods showed no changes in the purity of the recycled catalyst after several apes without considerable loss of activity. Further experiments are on the way to check this protocol in large scale synthesis.

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