Amberlyst A-26: an efficient and reusable heterogeneous catalyst for a one-pot oxidation–Cannizarro reaction

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Amberlyst A-26 catalyses the efficient synthesis of α-hydroxy-arylacetic acids from aryl methyl ketones in the presence of SeO_2. After simple separation, the catalyst does not lose its activity and can be reused without significant loss in activity for at least four cycles.

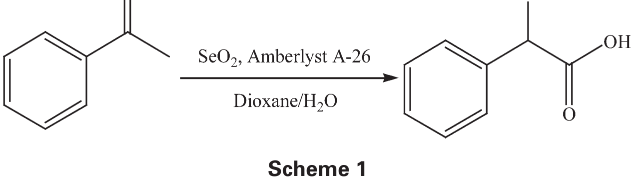
Keywords: α-hydroxy-arylacetic acids, Amberlyst A-26, heterogeneous catalyst, reusable catalyst

α-Hydroxy-arylacetic acids are very useful intermediates for the development of molecules of pharmaceutical or biological interest. They are important synthons of many natural and semisynthetic biologically active compounds such as prostaglandins,[1] β-lactams,[2,3] vanillic acid metabolites[4] and homatropine.[5]

Some classical methods for the synthesis of α-hydroxy-arylacetic acids are reported in the literature. These include the cyanidation of aromatic aldehydes,[6] reaction of aromatic aldehyde with chloroform,[7] chlorination of aryl methyl ketones[8] and reaction of glyoxylic acids with benzene.[9] In contrast to the drastic reaction conditions, low yields and severe side reactions of these methods, it is reported that ytterbium triflate[10] and rare earth perfluoroctanesulfonates[11] can separately catalyse the synthesis of α-hydroxy-arylacetic acid from aryl methyl ketones in good to excellent yields. However, reusing the ytterbium triflate required tedious work up procedures such as filtration, purification and drying; as to rare earth perfluoroctanesulfonate, the reuse procedure involved the use of fluorous solvents.

From the environmental point of view, several practical and economical aspects of organic reactions have to be developed for their industrialisation. Therefore, the development of highly active and easily reusable immobilised catalysts is of great interest to chemists.[12] To date, numerous reactions on polymer-supported catalysts suggest that the polymer-supported catalytic system is promising (see ref. 13 and refs therein). Ideally, the catalytic synthesis is efficiently carried out, and the catalyst can be easily separated from the reaction mixture by simple filtration. Recently, Amberlyst resins such as A-15[14–19] with the functional group [$-SO_3H$] and A-27[20] with the functional group [$-N(CH_3)_3^+$] have been widely reported in organic synthesis because of their ease of handling, recoverability and enhanced reaction rates.

We now report an efficient way to synthesise α-hydroxy-arylacetic acids from aryl methyl ketones catalysed by the reusable heterogeneous catalyst Amberlyst A-26, a macroreticular anionic resin with [$-N(CH_3)_3^+$] as functional group (Scheme 1).



Scheme 1

Initially, the effects of catalyst amount and solvent were examined. The results are summarised in Table 1. Acetophenone was selected as a model reactant for this study. We found that treating acetophenone (10 mmol) and SeO_2 (20 mmol) in a solution of dioxane/H_2O (3/1, 4 mL) with A-26 (1g) as catalyst at 90 °C for 24 h gave the product in 95% yield (Table 1, entry 1).

Under similar conditions, lower product yields of 88% and 73% were obtained when decreasing the catalyst amount from 1 g to 0.75 g and 0.5 g (Table 1, entries 2 and 3). No reaction was observed in the absence of Amberlyst A-26 after 48h (Table 1, entry 4). In contrast, other solvents were less effective and lower product yields of 35–80% were obtained for reactions in dioxane, MeCN, H_2O, toluene (Table 1, entries 5–8). The mixture of dioxane and H_2O on 3:1 ratio as solvent proved to be the most efficient and was selected as the solvent for subsequent investigations.

The reaction was extended to the synthesis of other α-hydroxy-arylacetic acids as summarised in Table 2. Moderate to excellent yields (70–95%) of α-hydroxy-arylacetic acids were obtained. The product from entry 1 was isolated and identified as mandelic acid. When the reaction was finished, and the reaction mixture was cooled to room temperature, the solid phase containing catalyst Amberlyst A-26 and selenium powder can be separated by filtration. Selenium powder can be further removed by soaking with dilute nitric acid. Amberlyst A-26 can be recycled by washing with dilute hydrochloric acid and can be reused in the reaction. The recycled results (Table 2, entry 1) indicate that the catalyst does not lose its activity and can be reused without significant loss in activity for up to four cycles. This one-pot oxidation-Cannizarro reaction comprises two steps. In the first step, the methyl group is oxidised to an aldehyde group by SeO_2. In the second step,a Cannizaro-type reaction forms the α-hydroxy acid. These two reactions could be carried out in the same reaction vessel [10]. Amberlyst A-26 is an ideal catalyst for efficiently promoting the two steps.

Table 1 The effect of catalyst amount and solvent[a]

Entry	Catalyst/g	Solvent (vol/vol)	Time/h	Yield/%[b]
1	1	Dioxane/H_2O (3/1)	24	95
2	0.75	Dioxane/H_2O (3/1)	24	88
3	0.5	Dioxane/H_2O (3/1)	24	73
4	–	Dioxane/H_2O (3/1)	48	–
5	1	Dioxane	24	40
6	1	CH_3CN	24	52
7	1	H_2O	24	80
8	1	PhMe	24	35

[a] Reaction conditions: Amberlyst A-26, acetophenone (10 mmol), solvent (4 mL), SeO_2 (20 mmol), 90 °C.
[b] Isolated yield.

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Table 2 Amberlyst A-26 catalysed synthesis of α-hydroxy-arylacetic acids[a]

Entry	Reactant	Product	Yield[b]/%	M.p./°C
1	$PhCOCH_3$	$PhCH(OH)COOH$	95, 94, 93, 93[c]	120–122 (lit.[10] 120–122)
2	$4\text{-}ClC_6H_4COCH_3$	$4\text{-}ClC_6H_4CH(OH)COOH$	92	118–120 (115–121)[d]
3	$3\text{-}ClC_6H_4COCH_3$	$3\text{-}ClC_6H_4CH(OH)COOH$	89	112–114 (lit.[10] 112–114)
4	$2\text{-}ClC_6H_4COCH_3$	$2\text{-}ClC_6H_4CH(OH)COOH$	90	78–80 (lit.[11] 78–80)
5	$2\text{-}BrC_6H_4COCH_3$	$2\text{-}BrC_6H_4CH(OH)COOH$	85	178–180 (lit.[11] 179–180)
6	$4\text{-}BrC_6H_4COCH_3$	$4\text{-}BrC_6H_4CH(OH)COOH$	88	114–116 (lit.[10] 114–116)
7	$4\text{-}CH_3C_6H_4COCH_3$	$4\text{-}CH_3C_6H_4CH(OH)COOH$	82	120–122 (lit.[10] 120–122)
8	$3,4\text{-}(CH_3)_2C_6H_3COCH_3$	$3,4\text{-}CH_3C_6H_3CH(OH)COOH$	81	126–128 (lit.[11] 126–128)
9	$2,4\text{-}(CH_3)_2C_6H_3COCH_3$	$2,4\text{-}CH_3C_6H_3CH(OH)COOH$	81	120–122 (lit.[11] 120–122)
10	2-Acetonaphthone	Hydroxy(2-naphthyl)acetic acid	80	124 (lit.[10] 125–126)
11	2-Acetylthiopene	Hydroxy(thien-2-yl)acetic acid	70	92–94 (lit.[11] 92–94)

[a] The reaction condition: Amberlyst A-26 (1 g), aryl methyl ketone (10 mmol), 1,4-dioxane (3 mL), H_2O (1 mL), SeO_2 (20 mmol), 90 °C, 24 h.

[b] Isolated yield.

[c] Recycled results.

[d] Across organics.

In conclusion, Amberlyst A-26 is an efficient and reusable heterogeneous catalyst for preparation of α-hydroxy-arylacetic acids. The catalyst can be separated by simple filtration and the reaction can be repeated many times.

Experimental

Chemicals used were obtained from commercial suppliers and used without further purification. IR spectra were recorded on a Bomem MB154S IR analyser. ^1H NMR spectra were recorded with a Bruker Advance RX500 spectrometer. Mass spectra were recorded on a Saturn 2000GC/MS instrument.

CAUTION: SeO_2 and selenium are very toxic and dangerous for the environment. Due precautions should be taken.

Typical procedure for preparation of α-hydroxy-arylacetic acids: A mixture of Amberlyst A-26 (1 g), the aryl methyl ketone (10 mmol), 1,4-dioxane (3 mL), H_2O (1 mL) and SeO_2 (20 mmol) was stirred at 90 °C for 24 h. Then the mixture was cooled to room temperature. The solid phase containing the Amberlyst A-26 and selenium powder was filtered off, the filtrate was filtered again through a short pad of celite in order to immobilise the unreacted SeO_2. The filtrate was diluted with 1% aq. NaOH (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The aqueous solution was acidified to pH 1 with 10% aq. HCl and extracted with EtOAc (3 × 20 mL). The combined organic phases were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and a yellowish crude product was obtained. The crude product was purified by column chromatography on silica gel column to give a white crystalline (eluent: $CH_2Cl_2/MeOH = 90/10$). All of the products are known compounds and were characterised by comparison of their spectroscopic data with those of authentic samples. Selected data for mandelic acid (Table 2, entry 1): 95% yield. White solid; m.p. 120–122 °C; IR (KBr): ν 3400 (OH), 1714 (C=O) cm^{-1}; ^1H NMR (500 MHz, TMS, $CDCl_3$) δ 5.27 (s, 1H, –CH), δ 7.37–7.48 (m, 5H, –Ar), –OH resonances were broad and weak; ^{13}C NMR (75MHz): δ =71.6, 125.6, 127.8, 127.9, 136.5, 175.8; MS (EI) *m/z* 152 (M+).

The solid phase containing the catalyst Amberlyst A-26 and selenium powder, which had been separated by filtration, could be treated with dilute nitric acid (50 mL, 1 M) to remove selenium powder. The Amberlyst A-26, which remained, could then be washed with dilute hydrochloric acid (50 mL, 1 M) and reused in the reaction.

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