SHORT PAPER

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Oxidative conversion of aldoximes into carboxylic acid esters catalysed by polystyrene-bound phenylseleninic acid

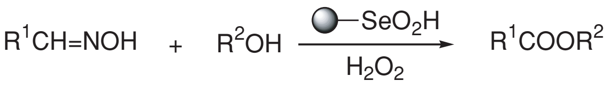
Shou-Ri Sheng[a, b] and Xian Huang[a]*

[a]Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou, 310028, P.R.. China
[b]Department of Chemistry, Jiangxi Normal University, Nanchang, 330027, P.R. China

Aromatic and aliphatic aldoximes were catalytically oxidised to carboxylic acid esters in good to moderate yields with hydrogen peroxide as oxidant using polystyrene-bound phenylseleninic acid as catalyst.

Keywords: polystyrene-bound phenylseleninic acid, catalytic oxidation, aldoxime, ester

Organoselenium reagents have attracted much attention in synthetic organic chemistry.[1] The phenylseleninic acid/hydrogen peroxide oxidation system is widely known. It has been used in the epoxidation of olefins and in the Baeyer—Villiger reaction of ketones,[2-4] in the oxidation of allylic alcohols,[5] in the oxidation of sulfides,[6] in the oxidation of aldehydes[7] and phenolic system.[8] The oxidative conversion of aldoximes into carboxylic acid esters[9] catalysed by 2-nitrobenzeneseleninic acid also has been reported. However, arylseleninic acid and its reduced species are very often toxic and moderately expensive. The use of polymer-bound phenylseleninic acid would provide significant advantages, including decreased volatility, easy of recovery and recycle of the spent reagent and simplification of product work-up. Taylor and Flood[10] once reported the use of polystyrene-bound phenylseleninic acid as a catalyst for oxidation of olefins, ketones and aromatic systems. However, the synthesis of the functionalised polymer in that context is not convenient. It used mercurated polystyrene and selenium dioxide and the reaction was very long. Another method of the preparation of polystyrene-bound phenylseleninic acid with Ag_2SeO_4 is also not easy.[11] In our previous work, polystyrene-bound phenylseleninic acid was obtained as a by-product during the elimination of a polystyrene-bound phenylselenoxide followed by reacting further with hydrogen peroxide.[12] Herein, We wish report that aldoximes undergo directly oxidative conversion into carboxylic acid esters in alcohols with hydrogen peroxide as oxidant using polystyrene-bound phenylseleninic acid as catalyst (Scheme 1).



Scheme 1

To a solution of the aldoximes in alcohols is added 30% aqueous hydrogen peroxide and catalytic amounts of polystyrene-bound phenylseleninic acid[12] (9.85% Se, its IR spectrum was compatible with the previously reported material[11]), the corresponding carboxylic acid esters were

Table 1 Esters prepared from aldoximes with polystyrene-bound phenylseleninic acid as catalyst

R^1	R^2	Reaction time	Yield/ %[a, b]	^1H NMR δ/ppm	ν max (C=O)
C_6H_5	CH_3	5h	80	8.10—7.90 (m, 2H), 7.38—7.40 (m, 3H), 3.81 (s, 3H)	1722
C_6H_5	CH_2CH_3	5h	81	8.10—7.85 (m, 2H), 7.15—7.45 (m, 3H), 4.50 (q, 2H), 1.20 (t, 3H)	1718
C_6H_5	$CH_3(CH_2)_2$	8h	83	8.02—7.95 (m, 2H), 7.15—7.55 (m, 3H), 4.20 (t, 2H), 1.61—1.80 (m, 2H), 1.20 (t, 3H)	1716
C_6H_5	$CH(CH_3)_2$	8h	83	8.12—7.92 (m, 2H), 7.10—7.55 (m, 3H), 5.10—5.40 (m, 1H), 1.33 (d, 6H)	1716
C_6H_5	$CH_2C_6H_5$ [c]	12h	68	8.10—7.80 (m, 2H), 7.05—7.48 (m, 8H), 5.20 (s, 2H)	1726
p-$CH_3C_6H_4$	CH_3	4h	86	7.89 (d, 2H), 7.15 (d, 2H), 3.81 (s, 3H), 2.30 (s, 3H)	1725
p-ClC_6H_4	CH_3	5h	83	7.95 (d, 2H), 7.35 (d, 2H), 3.80 (s, 3H)	1718
p-$NO_2C_6H_4$	CH_3	5h	87	8.25 (d, 2H), 7.65 (d, 2H), 3.90 (s, 3H)	1720
m-$NO_2C_6H_4$	$CH(CH_3)_2$	10h	84	8.50—8.68 (m, 1H), 8.38—8.30 (m, 2H), 7.68—7.60 (m, 1H), 3.91 (s, 3H)	1718
$PhCH_2$	CH_3	4h	78	8.05—7.90 (m, 2H), 7.35—7.42 (m, 3H), 3.81 (s, 3H), 3.50 (s, 2H)	1730
$PhCH_2$	$CH_2C_6H_5$ [c]	12h	68	7.10—7.42 (m, 10H), 5.00 (s, 2H), 3.51 (s, 2H)	1735
$CH_3(CH_2)_2$	CH_3	8h	75	3.45 (s, 3H), 2.01 (t, 2H), 1.35—1.45 (m, 2H), 0.88 (t, 3H)	1740

[a]Isolated yield.
[b]Products were characterised by comparison of their physical data, IR, ^1H NMR spectra with known samples.
[c]The reaction temperature is 100°C when benzyl alcohol was used.

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* To receive any correspondence. E-mail: huangx@mail.hz.zj.cn

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

obtained in good to moderate yields at refluxing temperature for 4–12h (Table 1).

In our experiments, the reaction occured slowly at room temperature (only 20% of the product was obtained after two days). Furthermore, no reaction between aldoximes and alcohols took place on treatment with methanolic 30% hydrogen peroxide without polystyrene-bound phenylseleninic acid at room temperature for several days or refluxing for 72h. However, the addition of catalytic amounts of polystyrene-bound phenylseleninic acid to this system activated the oxidant and brought about the formation of methyl esters. When tertiary alcohols were used, the corresponding esters were not formed. In all cases, the recovered polymer could be used in subsequent oxidations with no further treatment and no significant loss of reactivity.

In summary, polystyrene-bound phenylseleninic acid and aqueous hydrogen peroxide was shown to be an efficient and mild reagent for the directly conversion of both aromatic and aliphatic aldoximes into the corresponding carboxylic acid esters of primary and secondary alcohols.

Experimental

^{1}H NMR spectra were recorded on Varian EM-360 and FX–90Q instruments using $CDCl_3$ as the solvent and with TMS as an internal standard. Infrared spectra were obtained on Bruker-22 spectrophotometer. Aldoximes[9] were prepared according to the literature methods.

General procedure for aldoximes conversion to carboxylic acid esters: Polystyrene-bound phenylseleninic acid 0.5 g (1.24 mmol/g loading) was added to a solution of aldoxime (5 mmol) in the appropriate alcohol (25 ml) and then an aqueous 30% H_2O_2 solution (2 ml, 17.7 mmol) was added. The mixture was stirred at refluxing temperature until TLC indicated almost the disappearance of aldoxime. The reaction mixture was filtered through a Büchner funnel to remove the polymeric reagent. A saturated $NaHCO_3$ solution was added to the filtrate and excess of alcohol was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the product was purified by column chromatography.

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