Poly{[4-(hydroxy)(tosyloxy)iodo]styrene}-promoted direct α-hydroxylation of ketones to α-hydroxyketones

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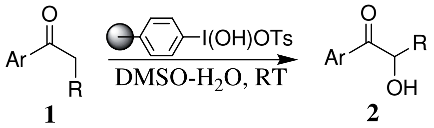
Poly{[4-(hydroxy)(tosyloxy)iodo]styrene} was efficient in the α-hydroxylation reaction of ketones to afford α-hydroxyketones in dimethyl sulfoxide-water. The polymer reagent could be regenerated and reused.

Keywords: poly{[4-(hydroxy)(tosyloxy)iodo]styrene}, α-hydroxylation, α-hydroxyketones

Polymer-supported organic reagents have been rapidly applied in the preparation of the organic molecules.[1] The most important point is that the regeneration and reuse of the recovered polymer-supported reagents are possible, thus providing an environmentally benign system.[2] In recent years, some polymer-supported trivalent iodine reagents have been synthesised and used in organic synthesis in the chemical and pharmaceutical industries.[3] Among them, poly{[4-(hydroxy)(tosyloxy)iodo]styrene is an important reagent in the synthesis of α-tosyloxyketones.[4]

The conversion of enolizable ketones to their corresponding α-hydroxyderivatives is an important synthetic transformation and has received a great deal of attention.[5] Recently, hypervalent iodine reagents were used in the direct hydroxylation of ketones for the synthesis of α-hydroxyketones.[6] Among them, the method of using [hydroxy(tosyloxy)iodo]benzene (Koser's reagent) is the most simple and efficient one,[6d] but the by-product, iodobenzene can not be reused. On the base of our study of poly{[4-(hydroxy)(tosyloxy)iodo]styrene},[7] we herein reported a simple and efficient α-hydroxylation reaction of ketones for the preparation of α-hydroxyketones (Scheme 1). The present method has the advantages such as mild reaction conditions, convenient manipulation and good yields. And the polymer reagent could be regenerated and reused.

Reaction of ketones **1** with poly{[4-(hydroxyl)(tosyloxy)iodo]styrene} in DMSO–H_2O at room temperature overnight gave α-hydroxyketones **2** in moderate to good yields (Table 1, Entries 1–7). The recovered poly(4-iodostyrene) was dissolved in CH_2Cl_2 and precipitated by the addition of diethyl ether to purify the resin. The recovered resin was converted to poly{[4-(hydroxy)(tosyloxy)iodo]styrene} according to the literature method.[7] Then we used the regenerated poly{[4-(hydroxy)(tosyloxy)iodo]styrene} in the α-hydroxylation reaction of **1a** and found that it had the same reactivity as the fresh prepared resin (Table 1, Entry 8).



Scheme 1

In conclusion, we have developed a simple and efficient method for the α-hydroxylation reaction of ketones with poly{[4-(hydroxy)(tosyloxy) iodo]styrene} in moderate to good yields. The polymer reagent could be regenerated and reused.

Experimental

Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ with TMS as the internal standard. IR spectra were recorded on a Shimadzu IR-408 spectrometer. Poly{[4-(hydroxy)(tosyloxy)iodo]styrene} was prepared as the literature method[7] and the functional group loading was 1.90 mmol/g determined by sulfur elemental analysis.

Typical procedure for synthesis of α-hydroxyketones (**2a**)

To a stirred solution of acetophenone **1a** (0.12 g, 1 mmol) in DMSO–H_2O (10 ml-0.5 ml) was added poly{[4-(hydroxy)(tosyloxy)iodo]styrene} (1.1g, 2 mmol) at room temperature in one portion. When the reaction was finished (monitored by TLC), the mixture was poured into ice-water to cause precipitation and the precipitate was collected by filtration for reusing. The filtrate was extracted with CH_2Cl_2 (3×20 ml). The organic phases were combined, washed with water (2×15 ml) and dried over $MgSO_4$. After evaporation, the residue was purified via chromatography on silica gel (ether/petroleum ether = 2:3 as an eluent) to afford **2a**.

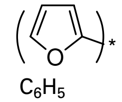
2a: IR (cm^{-1}): 3430 (O–H), 1681 (C=O). ^1H NMR (400MHz, $CDCl_3$): $\delta = 2.91$ (s, 1H), 4.92 (s, 2H), 7.51–7.95 (m, 5H).

2b: IR (cm^{-1}): 3432 (O–H), 1682 (C=O). ^1H NMR (400MHz, $CDCl_3$): $\delta = 2.46$ (s, 3H), 3.32 (s, 1H), 4.85 (s, 2H), 7.28–7.84 (m, 4H).

2c: IR (cm^{-1}): 3418 (O–H), 1674 (C=O). ^1H NMR (400MHz, $CDCl_3$): $\delta = 3.41$ (s, 1H), 3.91 (s, 3H), 4.84 (s, 2H), 6.97–7.94 (m, 4H).

2d: IR (cm^{-1}): 3428 (O–H), 1684 (C=O). ^1H NMR (400MHz, $CDCl_3$): $\delta = 3.45$ (s, 1H), 4.84 (s, 2H), 7.47–7.88 (m, 4H).

Table 1 The synthesis of α-hydroxyketones

Entry	Ar	R	Product	Yield[a]/%	M.p./°C	Lit. m.p. (°C)
1	C_6H_5	H	**2a**	73	83–84	86–87[6b]
2	p-$CH_3C_6H_4$	H	**2b**	81	87–88	89–90[6d]
3	p-$CH_3OC_6H_4$	H	**2c**	68	99–100	100[8]
4	p-ClC_6H_4	H	**2d**	84	119–120	122.4[9]
5	p-BrC_6H_4	H	**2e**	80	134–135	136.6[9]
6		H	**2f**	78	80–81	82–83[6b]
7	C_6H_5	C_6H_5	**2g**	62	127–128	126-128[6d]
8	C_6H_5	H	**2a**[b]	73	83–84	86–87[6b]

[a]Isolated yields. [b]Using the regenerated resin.

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2e: IR (cm^{-1}): 3426 (O–H), 1685 (C=O). ^{1}H NMR (400MHz, $CDCl_3$): δ = 3.28 (s, 1H), 4.85 (s, 2H), 7.65–7.85 (m, 4H).

2f: IR (cm^{-1}): 3426 (O–H), 1682 (C=O). ^{1}H NMR (400MHz, CDCl3): δ = 2.81 (s, 1H), 4.76 (s, 2H), 6.61–7.66 (m, 3H).

2g: IR (cm^{-1}): 3420 (O–H), 1715 (C=O). ^{1}H NMR (400MHz, $CDCl_3$): δ = 3.92 (s, 1H), 5.96 (s, 1H), 7.28–7.94 (m, 10H).

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