

Notes

Synthetic Use of Poly[4-hydroxy(tosyloxy)iodo]styrenes

Seiichiro Abe,[†] Kenji Sakuratani,[‡] and Hideo Togo^{*,†,‡}

Graduate School of Science and Technology and Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan

togo@scichem.s.chiba-u.ac.jp

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Introduction

Recently, the study and synthetic use of organohypervalent iodine compounds have been extensively carried out.¹ Among these compounds, (diacetoxyiodo)benzene has been well-used in organic synthesis. On the basis of the high utility of (diacetoxyiodo)benzene, we have recently reported the first synthetic use of poly[4-(diacetoxyiodo)styrene] for the iodination of aromatics, oxidative 1,2-aryl migration of alkyl aryl ketones, oxidation of hydroquinones and sulfides, and radical cyclization of *N*-methyl (2-aryl)ethanesulfonamides.² Moreover, the recyclic use of poly[4-(diacetoxyiodo)styrene] has established this compound as an environmentally benign reagent. After this first report, the synthetic use of poly[4-(diacetoxyiodo)styrene] became popular.³ Today, [hydroxy(tosyloxy)iodo]benzene is another useful hypervalent iodine reagent for organic synthesis, similar to (diacetoxyiodo)benzene, especially for the α -tosyloxylation of ketones and esters, *vic*-ditosyloxylation of alkenes, and formation of 1-alkynyliodonium, 1-alkenyliodonium, and aryliodonium salts.⁴ Thus, two types of new polymer reagents, poly[4-hydroxy(tosyloxy)iodo]styrene (high average MW) and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]

styrene} (low average MW), were prepared from polystyrene (average MW = 45 000) and poly(α -methylstyrene) (average MW = 6200), respectively. Poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} were prepared by the reaction of the corresponding poly[4-(diacetoxyiodo)styrene] and poly{ α -methyl[4-(diacetoxyiodo)styrene]}, respectively, with *p*-toluenesulfonic acid monohydrate. Quantitative analysis by NMR of the acetic acid formed in the exchange reactions from the diacetoxyiodo groups into hydroxy(tosyloxy)iodo groups with *p*-toluenesulfonic acid monohydrate in poly[4-(diacetoxyiodo)styrene] and poly{ α -methyl[4-(diacetoxyiodo)styrene]}, respectively, suggested that the conversion of the [4-(diacetoxyiodo)]phenyl groups to [4-hydroxy(tosyloxy)iodo]phenyl groups proceeded quantitatively. Elemental analysis also indicates that ~80% of the phenyl groups in polystyrene and poly(α -methylstyrene) bear a hydroxy(tosyloxy)iodo group and the other ~20% are iodo phenyl groups. These results were also supported by comparing the IR spectra of these polymer-supported reagents with the IR spectrum of [hydroxy(tosyloxy)iodo]benzene.

The solubility of these polymer-supported reagents in chloroform, as a typical organic solvent, was then studied. The solubilities of poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} are 11.0 and 46.4 mg/mL at 15 °C, respectively. Poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene}, which has a low average MW, is more soluble than poly[4-hydroxy(tosyloxy)iodo]styrene in chloroform.

α -Tosyloxylation of Ketones. α -Sulfonyloxy ketones are useful building blocks for organic synthesis.⁵ α -Tosyloxylation of ketones with poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} was carried out, and the reactivities were compared with that of [hydroxy(tosyloxy)iodo]benzene, on the basis of the literature method.⁴ The results are shown in Table 1 and suggest that poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} show the same reactivity as [hydroxy(tosyloxy)iodo]benzene. However, there is not a large difference in reactivity between poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene}, despite the considerable difference in average MW and solubility.

Oxidative α -Tosyloxylation of Alcohols. The oxidation of alcohols with a Dess–Martin reagent or *o*-iodoxybenzoic acid, which are pentavalent iodine re-

[†] Graduate School of Science and Technology.

[‡] Department of Chemistry.

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Table 1. α -Tosyloxylation of Ketones
$$\text{R}-\text{C}(=\text{O})-\text{CH}_2-\text{R}' \xrightarrow[\text{CH}_3\text{CN, reflux}]{\text{Ar-I(OH)OTs}} \text{R}-\text{C}(=\text{O})-\text{CH}(\text{OTs})-\text{R}'$$

Entry	R-	R'-	Ar-		
			Ph-	PS	PMS
1		H-	91	69	85
2		CH ₃ -	67	57	71
3		H-	68	59	55
4		H-	70	66	66
5	-(CH ₂) ₄ -		30	48	45
6	CH ₃ -	CH ₃ CO-	73	66	66

agents, is a well-known method for the oxidation of alcohols in organic synthesis.⁶ However, to our knowledge, oxidation with trivalent iodine reagents is extremely limited and, normally, the formed aldehydes are oxidized further to carboxylic acids.^{3c,7} Thus, the oxidation of *sec*-alcohols with poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} was studied. Surprisingly, the oxidation proceeded effectively to form the corresponding α -tosyloxyketone in good to moderate yields. The reaction in chloroform gave the products in slightly better yields than that in acetonitrile. However, the same reaction with [hydroxy(tosyloxy)iodo]benzene gave the α -tosyloxyketone in low yields. Moreover, the oxidation of *prim*-alcohols with poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} gave the corresponding α -tosylaldehydes in good yields, though the same reaction with [hydroxy(tosyloxy)iodo]benzene did not give α -tosylaldehydes at all. This direct conversion of alcohols to α -tosyloxyketones and α -tosylaldehydes is shown in Table 2.

With regard to the substituent effect on the aromatic ring of α -arylethanol, it was found that an electron-withdrawing group at the aromatic ring in alcohols increased the reactivity, while an electron-donating group retarded the reaction. The poor reactivity of an electron-donating group such as a methoxy group is attributed to the direct reaction of the aromatic ring of α -anisylethanol with the trivalent iodine atom of the hydroxy(tosyloxy)iodo phenyl group in polymer-supported reagents to form the corresponding anisylidonium species. The reaction of [hydroxy(tosyloxy)iodo]benzene with electron-rich aromatics such as anisole and thiophene to form the corresponding phenyl arylidonium tosylates is known.⁴

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Table 2. Oxidative α -Tosyloxylation of Alcohols
$$\text{R}-\text{CH}_2-\text{CH}(\text{OH})-\text{R}' \xrightarrow[\text{CHCl}_3, \text{ reflux}]{\text{Ar-I(OH)OTs (2.0 eq.)}} \text{R}-\text{C}(=\text{O})-\text{CH}(\text{OTs})-\text{R}'$$

Entry	R-	R'-	Ar-		
			Ph-	PS	PMS
1	CH ₃ -	H-	18	45	67
2	Cl-	H-	59	98	96
3		H-	62	80	94
4		CH ₃ -	40	94	86
5	CH ₃ O-	H-	4	5	15
6	-(CH ₂) ₄ -		0	42	33
7	H-	PhCH ₂ CH ₂ -	0	67	58
8	H-	PhCH ₂ CH ₂ CH ₂ -	0	69	50

Table 3. Reaction with Regenerated Polymer Reagents
$$\text{Ph}-\text{C}(=\text{O})-\text{C}_2\text{H}_5 \xrightarrow[\text{CH}_3\text{CN, reflux}]{\text{Ar-I(OH)OTs (2.0 eq.)}} \text{Ph}-\text{C}(=\text{O})-\text{CH}(\text{OTs})-\text{CH}_3$$

Times	Ar-	
	PS	PMS
1	57	71
2	60	75

$$\text{Ph}-\text{CH}(\text{OH})-\text{C}_2\text{H}_5 \xrightarrow[\text{CHCl}_3, \text{ reflux}]{\text{Ar-I(OH)OTs (2.0 eq.)}} \text{Ph}-\text{C}(=\text{O})-\text{CH}(\text{OTs})-\text{CH}_3$$

Times	Ar-	
	PS	PMS
1	94	86
2	91	94

Regeneration and Reuse. In these reactions, the reaction mixtures became homogeneous solutions under refluxing conditions in acetonitrile and chloroform, respectively. However, after the reactions with poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene}, the formed poly(4-iodostyrene) and poly(α -methyl-4-iodostyrene) were quantitatively recovered, respectively, by the addition of a 1/1 mixture of hexane and chloroform, or ether. Here, the recovered poly(4-iodostyrene) and poly(α -methyl-4-iodostyrene) were again oxidized with peracetic acid to form poly[4-(diacetoxy)iodo]styrene and poly{ α -methyl-

[4-(diacetoxy)iodo]styrene} and then converted to poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene}, respectively. These regenerated polymer reagents showed the same reactivity that was observed in the first use with poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} in the α -tosyloxylation of ketones and oxidative α -tosyloxylation of alcohols.

Ultrasonic enhancement of α -tosyloxylation of ketones with the present polymer reagents was not observed, though α -tosyloxylation of ketones with [hydroxy(tosyloxy)iodo]benzene was accelerated by ultrasonic irradiation.⁸

In conclusion, poly[4-hydroxy(tosyloxy)iodo]styrene and poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} have enough reactivity for the α -tosyloxylation of ketones and the oxidative α -tosyloxylation of alcohols; moreover, these polymer reagents can be regenerated and reused as environmentally benign reagents.

Experimental Section

General. All reactions were carried out under an argon atmosphere. ¹H NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane (TMS) in δ units. Values of *J* are given in hertz. IR spectra were recorded on a FT/IR-200 spectrometer. Microanalyses were performed with Perkin-Elmer 240B and 240 elemental analyzers at the Chemical Analysis Center of Tsukuba University. Melting points were determined on a Yamato melting point apparatus in open capillary tubes and are shown uncorrected. Silica Gel 60 (Kanto Kagaku Co.) was used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for p-TLC.

Materials. Polystyrene (Aldrich 33165-1), poly(α -methylstyrene) (Aldrich 41794-7), ketones, and most of the alcohols are commercially available.

Preparation of Poly[4-(diacetoxyiodo)styrene]. A mixture of 16 g (153 mmol) of polystyrene, 18 g (71 mmol) of iodine, 7 g (21 mmol) of iodine pentoxide, 40 mL of carbon tetrachloride, and 35 mL of 50% sulfuric acid in 200 mL of nitrobenzene was kept at 90 °C for 72 h. After the reactions were completed, the reaction mixture was diluted with 100 mL of chloroform and precipitation occurred upon the addition of methanol (1500 mL). The precipitates were collected by filtration to give poly(4-iodostyrene). IR peaks of 700 and 760 cm⁻¹ in polystyrene and poly(α -methylstyrene), respectively, disappeared, and a new peak at 820 cm⁻¹ appeared in poly(4-iodostyrene) and poly(α -methyl-4-iodostyrene). Hydrogen peroxide (30%, 40 mL) was added dropwise to an acetic anhydride solution (145 mL) at 0 °C. The solution was slowly warmed to room temperature and stirred overnight. To this solution was added poly(4-iodostyrene) (8 g). Then, the solution was kept at 48 °C overnight. At the end of the reaction, diethyl ether was added to the solution to cause precipitation. The product (ca. 9 g) was collected by filtration: IR (KBr) 1630 (br), 1560 (br), 1480, 1450, 1410, 1260, 1180, 1000, 770 (br) cm⁻¹. Anal. Found: C, 36.33; H, 3.66; I, 39.19.

Poly{ α -methyl[4-(diacetoxy)iodo]styrene} was prepared under the same conditions as those described above: IR (KBr) 1640 (br), 1560 (br), 1480, 1400, 1050, 1000, 760 (br) cm⁻¹. Anal. Found: C, 43.61; H, 4.27; I, 34.21.

Preparation of Poly[4-hydroxy(tosyloxy)iodo]styrene. Poly[4-(diacetoxyiodo)styrene] (10 mmol) was added to the solution of *p*-toluenesulfonic acid monohydrate (20 mmol) in chloroform (20 mL) and stirred for 24 h at room temperature under dark conditions. After the reaction was completed, diethyl ether (50 mL) was added to the reaction mixture. The mixture was filtered, and the solid was washed with diethyl ether: IR

(KBr) 3430 (br), 2920, 1480, 1400, 1210, 1180, 1130, 1040, 1010, 820, 765, 700, 570 cm⁻¹. Anal. Found: C, 36.33; H, 3.66.

Poly{ α -methyl[4-hydroxy(tosyloxy)iodo]styrene} was prepared under the same conditions as those described above: IR (KBr) 3440 (br), 2920, 1480, 1400, 1210, 1190, 1130, 1040, 1010, 820, 690, 570 cm⁻¹. Anal. Found: C, 39.45; H, 4.07.

Typical Procedure for α -Tosyloxylation of Acetophenone. To a solution of acetophenone (0.5 mmol) and acetonitrile (3 mL) was added poly[4-hydroxy(tosyloxy)iodo]styrene (0.401 g, 0.75 mmol). The mixture was refluxed for 3 h under an argon atmosphere. A mixture of hexane (15 mL) and chloroform (15 mL) was added to the reaction mixture, and the solution was filtered. The formed poly(4-iodostyrene) was recovered as a solid quantitatively. The filtrate was evaporated, and the residue was chromatographed on silica gel using a 4/1 mixture of hexane and ethyl acetate as an eluent to give α -tosyloxyacetophenone.

Typical Procedure for Direct, Oxidative α -Tosyloxylation of α -Methylbenzyl Alcohol. To a solution of α -methylbenzyl alcohol (0.5 mmol) in chloroform (3 mL) was added poly[4-hydroxy(tosyloxy)iodo]styrene (0.530 g, 1.0 mmol). The mixture was refluxed for 16 h under an argon atmosphere. A mixture of hexane (15 mL) and chloroform (15 mL) was added to the reaction mixture, and the solution was filtered. The formed poly(4-iodostyrene) was recovered as a solid quantitatively. The filtrate was evaporated, and the residue was chromatographed on silica gel using a 4/1 mixture of hexane and ethyl acetate as an eluent to give α -tosyloxyacetophenone.

α -Tosyloxyacetophenone: mp 90 °C (lit.^{4b} 90–91 °C); IR (KBr) 1715, 1360, 1180, 820, 750, 680 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 2.45 (s, 3H), 5.27 (s, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.85 (t, *J* = 7.2 Hz, 4H).

α -Tosyloxypropiofenone: mp 68 °C (lit.^{4b} 68–69 °C); IR (KBr) 1700, 1370, 1170, 830, 760, 660 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 1.60 (d, *J* = 7.0 Hz, 3H), 2.41 (s, 3H), 5.79 (q, *J* = 7.00 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.60 (tt, *J* = 7.4, 2.7 Hz, 1H), 7.75 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.88 (dt, *J* = 8.6, 1.3 Hz, 1H).

α -Tosyloxycyclohexanone: mp 72 °C (lit.^{4b} 74–76 °C); ¹H NMR (400 MHz, CDCl₃) 1.64–1.76 (m, 3H), 1.85–2.01 (m, 3H), 2.26–2.34 (m, 3H), 2.44 (s, 2H), 4.90 (ddd, *J* = 10.8, 5.9, 1.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 6.5 Hz, 2H).

α -Tosyloxy-2,4-pentadione: mp 82 °C (lit.^{4b} 82–83 °C); IR (KBr) 3060, 1600, 1370, 1200, 1180, 800 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 1.96 (s, 6H), 2.49 (s, 3H), 4.49 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H).

α -Tosyloxy-*p*-chloroacetophenone: mp 122 °C (lit.^{4b} 125 °C); IR (KBr) 1710, 1360, 1190, 810 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 2.46 (s, 3H), 5.21 (s, 3H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.45 (dt, *J* = 8.9, 2.3 Hz, 2H), 7.80 (dt, *J* = 9.0, 2.2 Hz, 2H), 7.84 (dt, *J* = 7.2, 2.3 Hz, 2H).

α -Tosyloxy-*p*-methylacetophenone: mp 80 °C (lit.⁹ 82–83 °C); IR (KBr) 1700, 1350, 1170, 810 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 2.41 (s, 3H), 2.45 (s, 3H), 5.24 (s, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H).

(Tosyloxy)methyl 2-thienyl ketone: mp 92–93 °C (lit.¹⁰ 94–96 °C); IR (KBr) 1685, 1370, 1180, 730 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 2.45 (s, 3H), 5.09 (s, 2H), 7.16 (dd, *J* = 4.8, 3.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.73 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.79 (dd, *J* = 3.9, 1.0 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H).

(Tosyloxy)methyl 2-furanyl ketone: mp 63–64 °C (lit.¹⁰ 65–67 °C); IR (KBr) 1695, 1370, 1170, 810, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 2.45 (s, 3H), 5.09 (s, 2H), 6.58 (dd, *J* = 3.7, 1.7 Hz, 1H), 7.33 (dd, *J* = 3.7, 0.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.61 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H).

4-Phenyl-2-tosyloxybutanal: oil; IR (neat) 1740, 1360, 1180, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 1.91–1.62 (m, 2H), 2.48 (s, 3H), 2.54 (t, *J* = 7.8 Hz, 2H), 4.59 (ddd, *J* = 6.8, 6.0, 1.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 7.15–7.31 (m, 3H), 7.37 (q, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 9.55 (d, *J* = 1.5 Hz, 1H).

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Anal. Calcd for C₁₇H₁₈O₄S: C, 64.13; H, 5.70. Found: C, 64.20; H, 5.64.

5-Phenyl-2-tosyloxypentanal: oil; IR (neat) 1740, 1370, 1240, 1180, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 1.52–1.65 (m, 2H), 1.75 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.51 (t, *J* = 7.6 Hz, 2H), 4.61 (ddd, *J* = 7.0, 5.8, 1.3 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 7.19 (q, *J* = 6.3 Hz, 2H), 7.25 (q, *J* = 6.2 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 9.54 (d, *J* = 1.5 Hz, 1H). Anal. Calcd for C₁₈H₂₀O₄S: C, 65.04; H, 6.06. Found: C, 64.71; H, 6.32.

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Supporting Information Available: ¹H NMR spectra for all α-tosyloxyketones and α-tosyloxyaldehydes and IR spectra of poly[4-hydroxy(tosyloxy)iodo]styrene and poly{α-methyl[4-hydroxy(tosyloxy)iodo]styrene}. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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