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Preparation of resin-bound alkynyl iodonium salts and their application in organic synthesis as alkynyl transfer reagents

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Abstract—We have synthesized polymer-supported alkynylphenyl iodonium salts. They served as effective alkynyl transfer reagents for the preparation of acetylenic sulfones; the by-product, polymer supported (4-iodostyrene), could be reactivated for reuse numerous times. © 2001 Elsevier Science Ltd. All rights reserved.

Supported reagents on organic polymers have rapidly become an area of intense research activity.¹ One of the key advantages is the ease of separation from the product mixture at the end of a reaction, and polymer recycling. Hypervalent iodine compounds have attracted wide attention due to their unique chemical properties.² During continuing efforts to develop new polymer supported hypervalent iodine compounds,^{3–5} we became interested in the synthesis of resin-bound alkynyl iodonium salts.

Alkynylphenyl iodonium salts⁶ are very important reagents in organic synthesis which can be used to synthesize heterocycles.⁷ Above all, they have been recognized to be useful as synthons of alkynyl cations.⁸ However, to the best of our knowledge, no examples of polymer-supported alkynylphenyl iodonium salts have been reported. In this paper, we report the preparation of polymer-supported alkynylphenyl iodonium salts, and their application as alkynyl transfer reagents to synthesize acetylenic sulfones and phenylbenzotriazoles.

The polymer support chosen for immobilization of the alkynyliodonium salts was commercially available polystyrene (MW=250,000, Acros). The resin was first converted into poly[(4-diacetoxyiodo) styrene] by known methods.⁹ Poly[(4-diacetoxyiodo) styrene] was dissolved in CH₂Cl₂ and *p*-toluenesulfonic acid added. After a few minutes, poly{[4-hydroxy (tosyloxy)iodo]styrene} precipitated as a yellow solid. Elemental analysis showed that the resin contained 1.91 mmol per gram. This resin and alkynes were refluxed in dry CHCl₃ for a few hours. The resulting solution was evaporated in vacuo and diethyl ether was added to precipitate the white polymeric alkynyl iodonium salts¹⁰ (Scheme 1). The conversion was established by IR spectroscopy, by the shifting of the characteristic peaks of SO₂ from 1186 to 1178 cm⁻¹, and the appearance of a peak at 2156 cm⁻¹ (C=C, 1a) or 1364 cm⁻¹ (t-Bu, 1b)



Scheme 1.

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and 2170 cm⁻¹ (C=C, 1b). The functional group loading was estimated as 1.21 (1a) or 1.41 (1b) mmol/g of resin by elemental analysis of the sulfur component. The polymer bound alkynyliodonium salts are stable in air, and no decomposition was noted over a period of two weeks at room temperature, but the resin products were best stored away from direct sunlight and in a refrigerator.

Acetylenic sulfones are important well-known synthetic intermediates.¹¹ Chen et al. reported¹² that alkynyl phenyliodonium salts could be used to synthesize acetylenic sulfones. On recognition that polymeric reagents have the same reactivity as their small molecule counterparts, the polymeric alkynylphenyl iodonium salts were employed as alkynyl transfer reagents to prepare acetylenic sulfones¹³ (Scheme 2).

To a solution of the sodium sulfinates (2) in water was added the polymer-supported alkynylphenyl iodonium salts (1) in CHCl₃. The reactions were carried out in the presence of a catalytic amount of tetraethylammonium bromide (TEBA) at room temperature. After the reaction was complete, the organic layer was separated and dried over anhydrous MgSO₄. The solvent was removed under vacuum and CH₃CN was added to the resulting oil to precipitate poly(4-iodostyrene). The solution was submitted to column chromatography on silica gel to give pure

 Table 1. S-Alkynylation of sodium sulfinates (2) with
 with

 polymer-supported alkynylphenyl iodonium salts (1)
 iodonium salts (1)

Entry	R	Ar	Time (min)	Yield (%) ^a
1	Ph	Ph	15	61
2	t-Bu	Ph	20	70
3	Ph	$p-CH_3C_6H_4$	15	59
4	t-Bu	$p-CH_3 C_6H_4$	20	65
5	Ph	p-Cl C ₆ H ₄	15	62
6	t-Bu	p-Cl C ₆ H ₄	20	65
7	Ph	$m-NO_2 C_6 H_4$	15	64
8	<i>t</i> -Bu	$m - NO_2 C_6 H_4$	20	72

^a Isolated yields.

products. The reactions were efficient and high yielding. (Table 1)

Functionalized benzotriazoles are considered to be important substances in organic synthesis.¹⁴ We prepared phenylethynyl benzotriazole by using the polystyrene supported phenyliodonium salts. After the potassium salt of benzotriazole was dissolved in *t*-BuOH and CH_2Cl_2 , **1a** was added. After stirring the reaction mixture for 24 h, the product mixture was extracted and submitted to column chromatography on silica gel to give phenylethynyl benzotriazole.¹⁵ (Scheme 3)

After the reactions, poly(4-iodostyrene), to which the polymeric alkynylphenyl iodonium salts had been converted, was dissolved in CH_2Cl_2 and precipitated by the addition of ether to purify the resin. The recovered resin was converted to polymer supported alkynyliodonium salts according to the above methods. The alkynylation of sodium sulfonates (2a) with polymer-supported alkynylphenyl iodonium salts (1a) was repeated four times using the same batch of 1a. As seen in Table 2, the yields remained constant.

In conclusion, our research group has first prepared the polymer-supported alkynylphenyl iodonium salts. They can serve as effective alkynyl transfer reagents for the preparation of acetylenic sulfones by a solid-phase organic synthesis. The regeneration of polymeric hypervalent iodine salts that show the same activity as newly prepared reagents has been discussed. Further applications of polymeric alkynylphenyl iodonium salts are under study.

 Table 2. Reusability of resin-bound alkynylphenyl iodonium salts

Experiment	Yields using 1a (%)	
1	61	
2	59	
3	60	
4	58	



Scheme 2.



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- 10. Preparation of polymer-supported alkynylphenyl iodonium salts 1: To a solution of poly{[4-hydroxy(tosyloxy)iodo]styrene} (2 mmol, 1.05 g) in 10 mL CHCl₃, phenylacetylene (12 mmol, 2.09 g) or *t*-butylacetylene (8 mmol, 0.66 g) was added. The mixture was refluxed for 1 or 6 h, respectively. After the reaction was complete, the CHCl₃ was evaporated in vacuum to give an oily residue. Diethyl ether (10 mL) was added to precipitate the products, which were filtered off and washed with ether (10 mL×2) and acetone (10 mL×2) to afford the products. Compound 1a: white powder; 1.2 g; S%: 3.87%; IR (KBr)

v (cm⁻¹): 2921, 2156, 1483, 1178, 1031, 1006, 816, 680. Compound **1b**: white powder; 1.1 g; S%: 4.51%; IR (KBr) v (cm⁻¹): 2922, 2170, 1482, 1364, 1177, 1032, 1005, 815, 681.

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- 13. Preparation of acetylenic sulfones 3: A solution of polymer-supported alkynylphenyl iodonium salt (1) 1 mmol in 10 mL CHCl₃ was added to a solution of sodium sulfinate (2) 1 and 0.05 mmol TEBA in 10 mL H₂O, and the mixture stirred at room temperature. After the reaction was complete, the organic layer was separated and the water layer was extracted with CHCl₃ (10 mL×2). The combined organic layer was washed with water (10 mL× 2) and dried over MgSO₄. After removal of the solvent, 5 mL CH₃CN was added to separate poly (4-iodostyrene) and the product. Further purification could be achieved by column chromatography using 2:1 hexane/ dichloromethane as eluent (R_f =0.2).
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- 15. Preparation of phenylethynyl benzotriazole **4**: 1 mmol of the potassium salt of benzotriazole was dissolved in 10 mL mixed solvent of *t*-BuOH and CH₂Cl₂ (1:1), and 1.2 mmol polymer-supported alkynylphenyl iodonium salt **1a** was added to the solution. After stirring for 24 h at room temperature, the product mixture was poured into 10 mL water. The organic layer was separated and the aqueous layer extracted with CHCl₃ (10 mL×2). The combined organic layer was washed with water (10 mL×2), and dried over MgSO₄. After removal of the solvent, 5 mL CH₃COOC₂H₅ was added to separate poly (4iodostyrene) and the product. Further purification could be achieved by chromatography using 1:1 hexane/ dichloromethane as eluent (R_f =0.26).

Compound 4: white solid; mp 77–78°C (lit¹⁶ 77–78°C); ¹H NMR (CDCl₃): δ 7.44–7.52 (m, 4H); 7.64–7.69 (m, 3H); 7.77 (d, J=8 Hz, 1H); IR (film) ν (cm⁻¹): 2259, 1611, 1483, 1306, 1286, 1005, 780, 761, 754, 689.

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