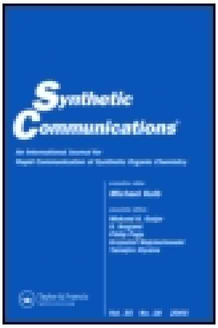

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HYPERVALENT IODINE IN SYNTHESIS XXVIII: THE PREPARATION AND UTILITY OF POLYMER-SUPPORTED PHENYLIODINE(III) DIACETATE

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Abstract: The polymer-supported phenyliodine(III) diacetate has been developed, which has been used effectively to oxidize a variety of organic compounds with good yield.

Our interest has recently been focused on the applications of hypervalent iodine compounds in organic synthesis[1]. The phenyliodine(III) diacetate (PID) is the most frequently used and easily available reagent in the family of hypervalent iodine compounds. It is not only a key precursor to prepare other hypervalent iodine compounds, but it is also an effective reagent to oxidize many kinds of compounds. [2] As a reagent, phenyliodine(III) diacetate has some advantages such as mild reaction conditions, easy handling, high selectivity and low toxicity. But it also has a major disadvantage, the desired oxidation product is contaminated with

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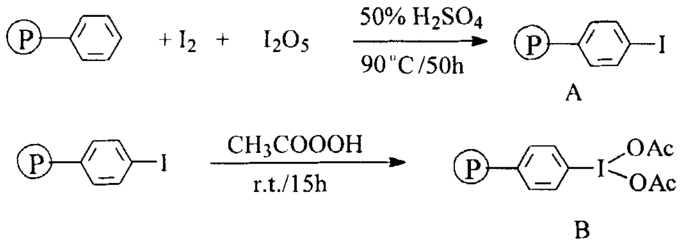
the iodobenzene by-product after reaction. Sometimes, complex chromatographic techniques have to be used for isolating the product. A strategy that completely avoids generating product containing the iodobenzene is the use of a polymer-supported reagent. The advantages of polymer-supported reactive species are now widely recognized by organic chemists, and increasing exploitation of these system is occurring both in academic and industry laboratories.[3]

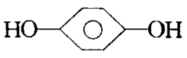
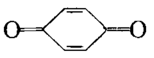
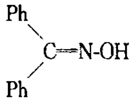
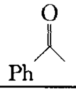
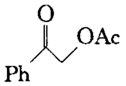
In view of this, we have prepared the polymer-supported phenyliodine(III) diacetate and studied its reactivity with various organic compounds.[4]

For any successful polymer-supported strategy optimal loading is essential, therefore we chose linear polystyrene as a suitable matrix which can be iodinated at the benzene ring. There are two steps for the preparation of polymer-supported phenyliodine(III) diacetate. First, in the presence of 50% sulfuric acid, linear polystyrene(MW=250,000) reacted with iodine and iodine pentoxide in nitrobenzene at 90^0C for 50 hours to give iodinated polystyrene(A). Then the iodinated polystyrene was oxidized by peracetic acid in methylene chloride to form polymer-supported phenyliodine(III) diacetate(B). The loading capacity of the polymer was obtained by iodometry and determined to be 2.96 mmol/g. Because it is a soluble polymer-supported reagent, the reaction with substance can be carried out under homogeneous conditions.



As a polymer-supported reagent, B was found to have the same oxidative properties as PID. Table I represents oxidation results for a variety of organic

Table I

Entry	substance	condition^{a}	product	m. p(℃)		Yield
				found^{b}	Lit.	(%)^{p}
1	PhSH	r. t. /40min	PhSSPh	59	59-60^{c}	93
2	PhSH	r. t. /40min	PhSSPh	59	59-60^{c}	91^{q}
3	p-$CH_3C_6H_4SH$	r. t. /40min	(p-$CH_3C_6H_4S)_2$	44-45	46^{d}	89
4	$PhCH_2SH$	r. t. /40min	$PhCH_2SSCH_2Ph$	69-71	71-72^{e}	90
5	PhSPh	reflux/4h	PhS(O)Ph	68-69	70. 5^{f}	80
6	(P-$CH_3C_6H_4)_2S$	reflux/4h	(p-$CH_3C_6H_4)_2S{=}O$	94-96	95^{g}	71
7	$PhCH_2SCH_2Ph$	reflux/4h	$(PhCH_2)_2S{=}O$	135-136	134^{h}	65
8	Ph_3P	reflux/6h	$Ph_3P{=}O$	154	156^{i}	72
9		r. t. /30min		114	115. 5^{j}	63
10	p-$CH_3C_6H_4CH{=}NNHTs$	r. t. /2h	p-$CH_3C_6H_4CHO$	Oil	/	78
11	 $Ph_2C{=}N\text{-}OH$	r. t. /5h	PhCOPh	48-49	48-48. 5^{k}	71
12	p-$NO_2C_6H_4CH{=}NNHPh$	r. t. /8h	p-$NO_2C_6H_4CHO$	106-107	106^{l}	78
13	PhTeTePh	r. t. /40min	 $Ph\overset{O}{\overset{\|}{Te}}O\overset{O}{\overset{\|}{C}}CH_3$	148-150	150-152^{m}	72
14	(p-$CH_3C_6H_4)_2Te$	r. t. /30min	(p-$CH_3C_6H_4)_2Te(OAc)_2$	183	180^{n}	71
15		$AcOH/Ac_2O$/6h/30°		47-48	48-49^{o}	52

a. The reaction was considered complete when no starting material was detected by TLC. b. Melting points were uncorrected. c—l: from Beilsteins: (c: **6** 324; d: **6** 425; e: **6** 465; f: **6** 300; g: **6** 419; h: **6** 456; i: **16** 783; j: EII **7** 567; k: **7** 410; l: **7** 256). m: Otsubo, T. J. Org. Chem. 1989, **54**, 4398. n: Liu, Z. D.; Chen, Z. C. Heteroat. Chem. 1992, **3**, 559. o: Beilsteins: **8** 92. p: Isolated yield. q: The reagent has been recycled five times.

compounds. Thiophenols (entry 1, 2, 3, 4) were oxidized to yield disulfides. A particularly useful reaction is the oxidation of sulfides (entry 5, 6, 7) to sulfoxides. This reaction has high selectivity and no further oxidation to produce sulfones was observed. Triphenylphosphine (entry 8) was transformed into triphenylphosphine oxide and the phenol (entry 9) was oxidized to p-benzoquinone. Oxidation of hydrazone and similar carbonyl derivatives (entry 10, 11, 12) with B leaded to regeneration of the carbonyl function under very mild conditions. B can oxidatively cleave the Te-Te bond in diphenyl ditelluride (entry13) to form benzenetellurinic mixed anhydride. Diaryltelluride (entry 14) reacted with B to afford diaryltellurium diacetate. Another use is reaction of B with enolizable ketone such as acetophenone (entry 15) leading to α-acetoxy ketone.

In general, the reaction of B with those substance readily occurred in an appropriate solvent. After the reaction was completed, ether was added to the reactive mixture to precipitate the polymer which contain A and some remains of B . Then, filtration of the polymer followed by evaporation of the filtrate gave the desired product. The recovered polymer can be regenerated and used repeatly.

In summary, we have shown that a soluble polymer-supported phenyliodine(III) diacetate can be readily prepared and its utility in the oxidations of various organic compounds . The work-up is very easy . The use of B offers considerable advantages over PID because the side-product is removed by simple filtration after precipitation of A. No chromatography is necessary. Furthermore , an excess of the reagent can be used without subsequent problems during purification . Finally this soluble polymer-supported reagent may be a suitable precursor to prepare other polymer-supported hypervalent iodine reagents. Further developments in this area will be reported in due course.

Experimental Section

Proton nuclear magnetic resonance (^{1}H,NMR)spectra was recorded at 60 MHz on a Varian EM 360. Infrared spectra was recorded on a PE-683 Infrared spectraphotometer .Elemental analyses was operated on a Carlo Erbal 1106 instrument .

Materials :

Thiophenol, triphenylphosphine, 1,4-dibenzendiol and polystyrene(MW=250,000) were bought from Arcon chemical corporation, the others were prepared according to methods presented in the literatures .

1. Preparation of B.

The iodination of polystyrene [5]: A 500 mL three-necked round-bottomed flask was charged with 20 g polystyrene , 20 g iodine , 8 g I_2O_5 in mixture of 40 mLCCl_4 , 40 mL50% H_2SO_4 and 120 mL of nitrobenzene . The reaction was carried out under reflux at 90℃for total 50 hours . The polymer was precipitated by pouring the reaction mixture into ethyl acetate. The solid was isolated and dissolved in CH_2Cl_2 and precipitated again by adding ethyl acetate. 38 g of iodinated polystyrene was obtained : C% 45.08 , H% 3.24, I% 51.68. About 93% benzene ring was iodinated. IR:1000, 810,750, 690cm^{-1}. 5 g of iodinated polystyrene was dissolved in 30 mL CH_2Cl_2 and 20 mL peracetic acid(CH_3COOOH) was slowly added dropwise . When the addition of peracetic acid was completed, continue to stir the mixture for 10 hours. After adding ether to the yellowish solution a white polymer was isolated, washed with ether, then dried at 40℃ for about 4 hours to obtain 7 g of B IR :1650,1500,1410, 1360, 1280,1000,810,710,660,cm^{-1}.The loading was determined by iodometry and was 2.96 mmol/g and about 96% A was turned to B.

2. General oxidation procedures:

(1). Oxidation of thiophenol (entries 1,2,3,4)

In a 100 mL round-bottomed flask , B (2 g,5.92 mmol) was dissolved in 20 mL

CH_2Cl_2 and 3 mmol thiophenol was added at room temperature . After 40 min, the resulting solution became reddish , then 15 mL ether was added and the resulting precipitate filtered off . The filtrate was washed with 5% NaOH (10 mL), then washed with water (10 mL x 2) and dried (Na_2SO_4). Removal of the solvent gave corresponding product.

(2). Oxidation of sulfide (entries 5,6,7)

In a 100 mL round-bottomed flask, B(2 g,5.92 mmol) was dissolved in 20 mL CH_2Cl_2 , then 2 mmol sulfide was added. After refluxing for about 4 hours , the resulting solution became yellowish, then 15 mL ether was added and the resulting precipitate filtered off . The filtrate was washed with 5% NaOH (10 mL), then washed with water (10 mL x 2) and dried (Na_2SO_4). Removal of the solvent gave corresponding product.

(3). Oxidation of triphenylphosphine (entry 8)

B(2 g, 5.92 mmol) was dissolved in 20 mL CH_2Cl_2, then 1.5 mmol Ph_3P was added. After reflux for about 6 hours, Ph_3P could not be detected by TLC, then 15 mL ether was added and the resulting precipitate filtered off . The filtrate was washed with 5% NaOH (10 mL), then washed with water (10 mL x 2) and dried (Na_2SO_4). Removal of the solvent gave corresponding product.

(4). Oxidation of 1,4-benzenediol (entry 9)

B (1.5 g,4.44 mmol) was dissolved in 20 mL CH_2Cl_2 ,then 1 mmol 1,4-benzenediol in 5 mL CH_2Cl_2 was added dropwise . After stirring for about 25 min , a black substance was generated,then 15 mL ether was added and the resulting precipitate filtered off . The filtrate was washed with 5% NaOH (10 mL), then washed with water (10 mL x 2) and dried (Na_2SO_4). Removal of the solvent gave corresponding product.

(5). Oxidation of carbonyl derivative (entries 10,11,12)

B(2 g,5.92 mmol) was dissolved in 20 mL CH_2Cl_2, carbonyl derivative (1 mmol) and 2 mL water was added , stirred for 5 min at room temperature . The solution immediately turned green , which gradually changed to yellow(about 40 min), and was further stirred for a few hours,then 15 mL ether was added and the resulting precipitate filtered off . The filtrate was washed with 5% NaOH (10 mL), then washed with water (10 mL x 2) and dried (Na_2SO_4). Removal of the solvent gave corresponding product.

(6). Oxidation of diaryltelluride or diarylditelluride (entries 13,14)

B(2 g,5.92 mmol) was dissolved in 20 mL CH_2Cl_2.Then 1 mmol diaryltelluride or diarylditelluride was added and the mixture stirred at room temperature for about 30 min,then 15 mL ether was added and the resulting precipitate filtered off . The filtrate was washed with 5% NaOH (10 mL), then washed with water (10 mL x 2) and dried (Na_2SO_4). Removal of the solvent gave corresponding product.

(7). Oxidation of acetophenone (entry 15)

B(2 g,5.92 mmol) was put in 20 mL $AcOH/Ac_2O$, then acetophenone(2 mmol) was added and was stirred at 30℃ for about 6 hours ,then 15 mL ether was added and the resulting precipitate filtered off . The filtrate was washed with 5% NaOH (10 mL), then washed with water (10 mL x 2) and dried (Na_2SO_4). Removal of the solvent gave corresponding product.

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