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Min Zhu [a], Cheng Gang Cai [a], Wei Ke [a] & Jing Shao [a]

[a] College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou, China

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CONVENIENT, SOLVENT-FREE METHOD FOR PREPARATION OF [HYDROXY(PHOSPHORYLOXY)IODO]ARENES

Min Zhu, Cheng Gang Cai, Wei Ke, and Jing Shao
College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou, China

A convenient, solvent-free method for preparation of [hydroxy(phosphoryloxy)iodo]arenes is reported. (Diacetoxyiodo)benzene or other hypervalent iodine reagents and phosphates are simply blended and ground for several minutes in an agate mortar, giving good yields of [hydroxy(phosphoryloxy)iodo]arenes with excellent purities.

Keywords: [Hydroxy(phosphoryloxy)iodo]arenas; preparation; solvent-free

The hypervalent iodine reagents, $ArIL_1L_2$, with one aryl and two heteroatom ligands are versatile reagents for the oxidation and functionallization of organic compounds.[1] Because hypervalent iodine reagents are nonmetallic oxidation reagents, they avoid the issues of toxicity common to many transition metals involved in such processes. Among them, [hydroxy(tosyloxy)iodo]benzene (Koser's reagent, HTIB) is a good reagent for introducing tosylate ligand into ketones, alkenes, and alkenoic acids to give corresponding α-tosyloxy ketones, *vic*-ditosyloxyalkanes, and tosyloxy lactones.[2] It is also a convenient precursor for the preparation of various iodonium salts.[3] Recently, Yusobov, and Wirth reported a solvent-free method for the synthesis of HTIB and other [hydroxy[(organosulfonyl)oxy]iodo]arenes by the ligand exchange reaction of (diacetoxyiodo)arenes with the corresponding organosulfonic acids (Scheme 1).[4]

As a useful reagent analogous to HTIB with iodine(III)-bound phosphate ligands, [hydroxy((bis(phenyloxy)-phosphoryl)oxy)iodo]benzene was the first reported member of [hydroxy(phosphoryloxy)iodo]arenes in 1988, which was prepared by the reaction of (diacetoxyiodo)benzene with diphenyl phosphate in aqueous acetonitrile.[5] It was found that various ketones and pentenoic acids can be converted directly into the respective products of α-phosphoryloxylation and phosphoryloxylactonization by [hydroxy((bis(phenyloxy)phosphoryl)oxy)iodo]benzene. The [hydroxy(phosphoryloxy) iodo]arenes also reacted easily with terminal alkynes to afford alkynyl phosphates via the intermediate formation of the respective alkynyl iodonium phosphates,[6]

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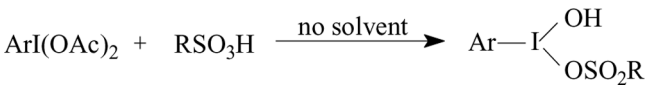
Address correspondence to Min Zhu, Zhejiang Shuren University, College of Biological and Environmental Sciences, Hangzhou, 310015, China. E-mail: hzzm60@163.com



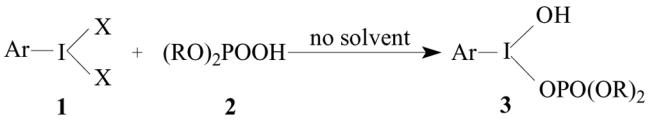
Scheme 1. A solvent-free method for the synthesis of [hydroxy[(organosulfonyl)oxy]iodo]arenes.

which were difficult to prepare with other methods. Alkynyl phosphates play a key role in mechanistic and bioorganic chemistry[7]; however, the applications of [hydroxy(phosphoryloxy)iodo]arenes in organic chemistry are limited in comparison with [hydroxyl[(organosulfonyl)oxy]iodo]arenes.

To explore their applications in synthesis, we first investigated the simple route for preparation of [hydroxy(phosphoryloxy)iodo]arenes and got a good result. In this article, we report a fast, convenient, and solvent-free method for preparation of [hydroxy(phosphoryloxy)iodo]arenes (Scheme 2).

Initially, we used diphenyl phosphate (**2a**) as the representative of dialkanyl phosphate to react with an equivalent of (diacetoxyiodo)benzene (**1a**); we found **that** when they were mixed and ground in an agate mortar for only 5 min, the desired [hydroxy((bis(phenyloxy)phosphoryl)oxy)iodo]benzene (**3a**) was afforded by a ligand exchange reaction in a yield of 87% with excellent purity. According to this protocol, a serious of experiments were carried out, and the known and unknown [hydroxy(phosphoryloxy)iodo]arenes (**3**) were prepared in good yields in short times, shown in Table 1. All formed [hydroxy(phosphoryloxy)iodo]arenes were characterized by ^{1}H NMR, ^{13}C NMR, infrared (IR), mass spectra (MS), and melting points.

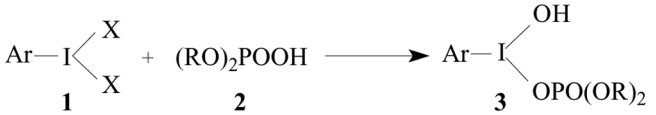
It is notable from Table 1 that all the reactions were completed in 10 min and provided products in good to excellent yields. When (diacetoxyiodo)benzene (**1a**) and (diacetoxyiodo)-*p*-Cl-benzene (**1b**) were used, the reactions gave products in excess of 86% yields (entries 1–5). When [bis(trifluoroacetoxy)iodo]benzene (**1c**) was used in place of **1a** and **1b**, the yields of the reactions were somewhat less than the previous reactions (entries 6–8). We also found that iodosylbenzene (**1d**) can react with phosphate; however, the reactions needed longer times, and the yields were not as good as others (entries 9 and 10). (*R*)-(–)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate can react with **1a** and **1c**, giving the new corresponding chiral hypervalent iodine reagent **3c** in excellent yields (entries 3 and 8). Now we are investigating the applications of **3c** in organic chemistry, especially in asymmetry synthesis, which will be reported in due course.



Ar=Ph, *p*-Cl-C_6H_4
X=OAc, $OCOCF_3$, =O
R=Ph, Bz, (R)-(-)-1,1'-Binaphthyl-2,2'-diyl-

Scheme 2. A convenient, solvent-free method for preparation of [hydroxy(phosphoryloxy)iodo]arenes.

Table 1. Synthesis of [hydroxy(phosphoryloxy)iodo]arenas



Entry	1	2: R	Product 3	Time (min)	Yield (%)[a]
1	$PhI(OAc)_2$ **1a**	Ph **2a**	**3a**	5	87
2	**1a**	$PhCH_2$ **2b**	**3b**	5	86
3	**1a**	(*R*)-(-)-1,1′-Binaphthyl-2,2′-diyl **2c**	**3c**	10	94
4	*p*-Cl-$C_6H_4I(OAc)_2$ **1b**	**2a**	**3d**	5	98
5	**1b**	**2b**	**3e**	5	94
6	$PhI(OCOCF_3)_2$ **1c**	**2a**	**3a**	5	83
7	**1c**	**2b**	**3b**	5	81
8	**1c**	**2c**	**3c**	10	85
9	PhI=O **1d**	**2a**	**3a**	10	67
10	**1d**	**2b**	**3b**	10	70

[a]Isolated yield.

In summary, a rapid and convenient method for preparation of [hydroxy (phosphoryloxy)iodo]arenes is afforded by the simple, solvent-free ligand exchange reaction in an agate mortar. It is simple and fast, and it affords good to excellent yields. Furthermore, the range of useful applications of [hydroxy(phosphoryloxy) iodo]arenes in organic synthesis will be extended.

EXPERIMENTAL

Melting points were determined on a digital melting-point apparatus and were not corrected. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Aavance III500-MHz NMR spectrometer, IR spectra were recorded on a FT-170 SX instrument, and MS were determined on an HP5989A mass spectrometer. Hypervalent iodine reagents were prepared according to literature procedures.[8–11] All phosphates are commercially available.

General Procedure for Synthesis of [Hydroxy(phosphoryloxy)iodo]-arenes

(Diacetoxyiodo)benzene **1a** (183 mg, 0.568 mmol, 1.0 equiv) and diphenyl phosphate **2a** (143 mg, 0.568 mmol, 1.0 equiv) was gently blended in an agate mortar. The resulting homogeneous mixture was then ground for 5 min. The formed residue was washed with diethyl ether (5 mL) and dried under high vacuum to afford [hydroxy((bis(phenyloxy)-phosphoryl)oxy)iodo]benzene **3a** (231 mg, 87% yield).

Selected Data

[Hydroxy((bis(phenyloxy)phosphoryl)oxy)iodo]benzene (3a). Mp 101–103 °C (lit.[5] 102–105 °C); ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.05–7.09 (m, 6H), 7.20–7.28 (m, 6H), 7.39–7.42 (m, 1H), 7.89 (d, $J = 5.5$ Hz, 2H); ^{13}C NMR (125 MHz), δ: 120.3, 124.2, 124.3, 130.0, 131.1, 131.8, 132.7, 151.9; IR (KBr), ν/cm^{-1}: 3370, 3058, 1743, 1450, 1295, 1192, 1043.

[Hydroxy[(bis(benzoyloxy)phosphoryl)oxy]iodo]benzene (3b)[5]. Mp 72–73 °C; ^{1}H NMR (500 MHz, DMSO-d_6), δ: 4.74 (d, $J = 7.0$ Hz, 4H), 7.27–4.34 (m, 10H), 7.49–7.52 (m, 2H), 7.56–7.58 (m, 1H), 8.12 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR (125 MHz), δ: 68.0 (d, $J = 5.0$ Hz), 124.5, 127.6, 127.9, 128.4, 130.7, 131.2, 132.5, 137.3 (d, $J = 6.3$ Hz); IR (KBr), ν/cm^{-1}: 3369, 3061, 2951, 1454, 1268, 1215, 1024; MS m/z (%): 498 (M^+, 100).

(*R*)-[Hydroxy((1,1′-binaphthyl-2,2′-diylphosphoryl)oxy)iodo]benzene (3c). Mp 157–160 °C; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.20 (t, $J = 2.5$ Hz, 2H), 7.24–7.32 (m, 3H), 7.33–7.36 (m, 4H), 7.43 (t, $J = 2.5$ Hz, 2H), 7.86 (t, $J = 8.0$ Hz, 4H), 7.94 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (125 MHz), δ: 120.5 (d, $J = 2.5$ Hz), 121.4, 125.7, 126.7, 127.1, 127.5, 128.5, 130.2, 131.3, 131.8, 132.2, 137.5, 146.8 (d, $J = 8.8$ Hz); IR (KBr), ν/cm^{-1}: 3414, 3068, 1465, 1256, 1231, 1107, 1074; MS, m/z (%): 568 (M^+, 100). HRMS: calcd. for $C_{26}H_{18}IO_5P$: 567.9932; found: 567.9921.

[Hydroxy[(bis(phenyloxy)phosphoryl)oxy]iodo]-4-Cl-benzene (3d). Mp 95–97 °C; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.05–7.11 (m, 6H), 7.16 (d, $J = 9.0$ Hz, 2H), 7.22–7.26 (m, 4H), 7.74 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (125 MHz), δ: 120.2 (d, $J = 5.0$ Hz), 124.9, 129.6, 130.9, 133.9, 138.1, 151.0 (d, $J = 7.5$ Hz); IR (KBr), ν/cm^{-1}: 3392, 3063, 1489, 1268, 1207, 1109, 1084; MS, m/z (%): 504 (M^+, 100); HRMS: calcd. for $C_{18}H_{15}ClIO_5P$: 503.9387; found: 503.9381.

[Hydroxy[(benzoyloxy)phosphoryl)oxy]iodo]-4-Cl-benzene (3e). Mp 70–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 4.83 (d, $J = 8.0$ Hz, 4H), 7.13 (dd, $J = 7.0$, 2.0 Hz, 2H), 7.24–7.26 (m, 4H), 7.28–7.32 (m, 6H), 7.84 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz), δ: 68.3 (d, $J = 6.3$ Hz), 127.6, 128.1, 128.5, 130.8, 133.5, 136.8 (d, $J = 7.5$ Hz), 137.8, 138.7; IR (KBr), ν/cm^{-1}: 3463, 3058, 1422, 1386, 1222, 1100, 1039; EIMS, m/z (%): 532 (M^+, 100); HRMS: calcd. for $C_{20}H_{19}ClIO_5P$: 531.9699; found: 531.9679.

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