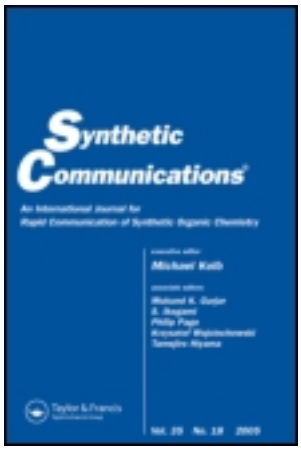

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CONVENIENT SYNTHESIS OF 2-ARYLBENZOXAZOLES MEDIATED BY SOLID-SUPPORTED PHENYLIODINE DIACETATE

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ABSTRACT

2-Arylbenzoxazoles were prepared in good yields through the intramolecular cyclization of phenolic Schiff's base in conjunction with poly[styrene(iodoso diacetate)], and the regenerated reagent kept the same activity in the reaction.

Recently Togo reported that the polymer supported phenyliodine diacetate could be used for the oxidative 1,2-aryl migration of alkyl aryl ketone.[1] For the benefits of the reagent, such as ease in handling and efficient regeneration without loss of activity,[1,2] poly[styrene(iodoso diacetate)] has attracted considerable attentions in recent years. Ley[2] and his cooperator applied this polymer supported reagent to synthesize quinones from quinols, prepare spirodienones by oxidative reactions of

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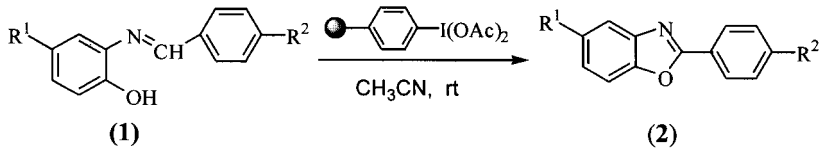
tyrosine derivatives. Togo et al.[3] later also reported that the α-hydroxylation of ketones, oxidation of sulfides and iodination of aromatic compounds. In view of our ongoing program on the application of cross-linked poly- [styrene(iodoso diacetate)][CPSID] in the formation of heterocyclic compounds,[4] we explored the intramolecular cyclization of phenolic Schiff's bases with CPSID.

The oxazole derivatives have been found wide application in agriculture and medicine.[5] It was also reported[6] that the benzoxazole ring is key part of the antitumor metabolite UK-1. Among the known methods for the synthesis of 2-arylbenzoxazoles, the general approach involved the oxidative cyclization of phenolic Schiff's base by oxidants such as barium manganate,[7] lead tetraacetate,[8] nickle peroxide.[9] Prakash[10] reported phenyliodine diacetate could be used to synthesize 2-arylbenzoxazoles via the oxidative intramolecular cyclization of phenolic Schiff's base. Here the cross-linked poly[styrene(iodoso diacetate)] could be applied into this reaction, and gage 2-arylbenzoxazoles in good yields. Additionally, CPSID has two advantages over phenyliodine diacetate: the poly(iodostyrene) as byproduct could be removed from the product just by filtration and the regenerated CPSID had the same activity in the reaction.

The 2% cross-linked poly[styrene(iodoso diacetate)] was prepared according to our previous work.[4] Commercially available 2% cross-linked polystyrene (200–400 mesh) reacted with iodine and iodine pentoxide to give iodinated polystyrene. Then poly(iodostyrene) was treated with peracetic acid at 40°C for one day to give cross-linked poly[styrene(iodoso diacetate)]. The loading of the polymer was determined to be 1.99 mmol/g.

To a stirred solution of Schiff's base (**1**) in acetonitrile, cross-linked poly[styrene(iodoso diacetate)] was added at room temperature. After several hours, the reaction was completed (monitored by TLC), and filtered to separate the resin. The solvent was removed under reduced pressure, and the residue was neutralized with aqueous sodium bicarbonate solution to give 2-arylbenzoxazoles (Scheme 1) in good yields (Table 1).

We also investigated the activity of the recycled cross-linked poly-[styrene(iodoso diacetate)] which could be reused for more than 4 times.



(1) **(2)**

Scheme 1.

Table 1. Formation of 2-Arylbenzoxazoles (**2**) from Schiff's Base (**1**) by Using CPSID

Entry	Compound (**1**)	R^1	R^2	Product (**2**)	Time (h)	Yield[a] (%)
1	1a	H	H	2a	1.5	71
2	1b	H	Me	2b	1	62
3	1c	H	MeO	2c	3	60
4	1d	H	Cl	2d	3	75
5	1e	H	NO_2	2e	2	78
6	1f	Me	H	2f	2	80
7	1g	Me	Me	2g	2	67
8	1h	Me	MeO	2h	3	70
9	1i	Me	Cl	2i	3	83
10	1j	Me	NO_2	2j	2	80
11[b]	1b	H	Me	2b	1	61
12[c]	1a	H	H	2a	0.5	83

[a]Isolated yield.
[b]By applying regenerated CPSID for 4 times.
[c]By applying phenyliodine diacetate.

The result (Table 1) showed the reagent could be regenerated and reused for the reaction without loss of the activity.

EXPERIMENTAL

Two percent cross-linked polystyrene was purchased from Aldrich. ^{1}H-NMR spectra were recorded at 60 MHz on a Varian EM-300 spectrometer of solutions in $CDCl_3$ or CCl_4. Infrared spectra were recorded on a Perkin Elmer 683 spectrophotometer in KBr. Phenolic Schiff's base was prepared by the literature method.[12]

Typical Procedure for the Preparation of 2-Arylbenzoxazoles (2)

Two percent cross-linked poly[styrene(iodoso diacetate)](1.4 mmol), which has been soaked in CH_3CN over night, was added to the solution of phenolic Schiff's base (**1**) in 8–20 mL CH_3CN at room temperature. After the reaction was completed (monitored by TLC), the resin was filtrated and washed with $CHCl_3$ (2×5 mL). The solvent was removed in vacuo and the

residue was neutralized with $NaHCO_3$ solution (5 mL). The crude product was extracted with CH_2Cl_2 (3×5 mL). The combined organic layer was washed with H_2O (5 mL), dried over $MgSO_4$ and evaporated. The residue was chromatographed on a column (silica gel, acetone : hexane = 1 : 9 as an eluent) to afford pure 2-arylbenzoxazole (**2**).

2a: White solid; m.p. 101–102°C (lit[10] m.p. 102°C); ^{1}H-NMR ($CDCl_3$) δ: 8.1–8.3 (m, 2H), 7.2–7.8 (m, 7H); IR (KBr) ν (cm^{-1}): 1625, 1555, 1460, 1450, 1340, 1240, 1050; MS: m/z (relative intensity) 195 (M^+ 100) 92 (8).

2b: White solid; m.p. 112–113°C (lit[10] m.p. 113–114°C); ^{1}H-NMR ($CDCl_3$) δ: 8.07–8.37 (m, 2H), 7.07–7.63 (m, 6H), 2.45 (s, 3H); IR (KBr) ν (cm^{-1}): 1630, 1545, 1455, 1240, 1050; MS: m/z (relative intensity) 209 (M^+ 100) 91 (8).

2c: White solid; m.p. 99–100°C (lit[10] m.p. 101); ^{1}H-NMR ($CDCl_3$) δ: 8.07–8.21 (m, 2H), 7.12–7.81 (m, 6H); 3.78 (s, 3H); IR (KBr) ν (cm^{-1}): 1630, 1590, 1450, 1350, 1250, 1240, 1055; MS: m/z (relative intensity) 225 (M^+ 100) 210 (41) 182 (34).

2d: White solid; m.p. 145–147°C (lit[10] m.p. 147°C); ^{1}H-NMR ($CDCl_3$) δ: 8.03–8.20 (m, 2H), 7.10–7.70 (m, 6H); IR (KBr) ν (cm^{-1}): 1620, 1555, 1455, 1345, 1240, 1045; MS: m/z (relative intensity) 231 ($M^+ + 2$, 33) 229 (M^+ 100) 194 (2) 92 (12).

2e: White solid; m.p. 263–266°C (lit[10] m.p. 266–268°C); ^{1}H-NMR ($CDCl_3$) δ: 9.05–9.10 (m, 2H), 6.8–8.1 (m, 6H); IR (KBr) ν (cm^{-1}): 1630, 1560, 1510, 1465, 1330,1240, 1050; MS: m/z (relative intensity) 240 (M^+ 100) 194 (28) 182 (22).

2f: White solid; m.p. 102–103°C (lit[10] m.p. 103°C); ^{1}H-NMR ($CDCl_3$) δ: 8.21–8.40 (m, 2H), 7.07–7.60 (m, 6H); 2.43 (s, 3H); IR (KBr) ν (cm^{-1}): 1640, 1555, 1470, 1330, 1250, 1050; MS: m/z (relative intensity) 209 (M^+ 100) 106 (20).

2g: White solid; m.p. 132–133°C; ^{1}H-NMR ($CDCl_3$) δ: 8.00–8.17 (m, 2H), 6.90–7.54 (m, 5H); 2.43 (s, 3H); IR (KBr) ν (cm^{-1}): 1620, 1560, 1470, 1255, 1050; MS: m/z (relative intensity) 223 (M^+ 100) 106 (9); Anal. calcd for $C_{15}H_{13}NO$: C, 80.72; H, 5.83; N, 6.28. Found: C, 80.63; H, 5.82; N, 6.18.

2h: White solid; m.p. 106–107°C; ^{1}H-NMR ($CDCl_3$) δ: 8.03–8.18 (m, 2H), 6.78–7.50 (m, 5H), 3.78 (s, 3H), 2.43 (s, 3H); IR (KBr) ν (cm^{-1}): 1615, 1530, 1450, 1250, 1240, 1060, 1055; MS: m/z (relative intensity) 239 (M^+ 100) 224 (35) 208 (1) 196 (24); Anal. calcd for $C_{15}H_{13}NO_2$: C, 75.31; H, 5.44; N, 5.86. Found: C, 75.43; H, 5.42; N, 5.68.

2i: White solid; m.p. 144–145°C; ^{1}H-NMR ($CDCl_3$) δ: 8.00–8.25 (m, 2H), 6.90–7.65 (m, 5H), 2.44 (s, 3H); IR (KBr) ν (cm^{-1}): 1630, 1550, 1460, 1260, 1050, 1000; MS: m/z (relative intensity) 245 ($M^+ + 2$, 33) 243 (M^+ 100)

208 (2) 106 (22). Anal. calcd for $C_{14}H_{10}ClNO$: C, 68.43; H, 4.07; N, 5.75. Found: C, 68.27; H, 4.02; N, 5.68.

2j: White solid; m.p. 209–211°C (lit[11] m.p. 211–212°C); ^{1}H-NMR ($CDCl_3$) δ: 8.37–8.40 (m, 2H), 7.2–7.6 (m, 5H), 2.45 (s, 3H); IR (KBr) ν (cm^{-1}): 1640, 1560, 1510, 1465, 1330, 1240, 1050; MS: m/z (relative intensity) 254 (M^+ 100) 224 (16) 208 (31) 196 (15) 106 (11).

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