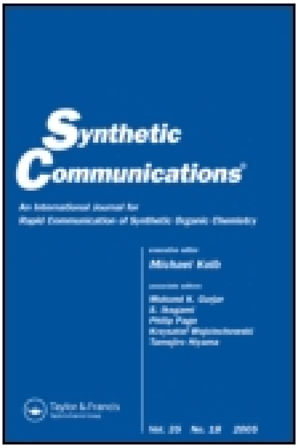

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Abstract: Arenecarbaldehyde-4-arylthiazol-2-ylhydrazones underwent ring closure with poly[(4-diacetoxyiodo)styrene] (PSDIB) to 3,5-diarylthiazolo[2,3-c]-s-triazoles in dichloromethane.

Keywords: Arenecarbaldehyde-4-arylthiazol-2-ylhydrazone, 3,5-diarylthiazolo[2,3-c]-s-triazole, poly[(4-diacetoxyiodo)styrene]

Because thiazolo[2,3-c]-s-triazoles possess particular biological activities, their synthesis and physiological activities have received attention.[1] Hypervalent iodine reagents have an important role in the synthesis of heterocyclic compounds.[2] Om Prakash and coworkers have synthesized a series of thiazolo[2,3-c]-s-triazoles with phenyliodine diacetate(IBD).[3]

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Recently we successfully prepared thiazole[2,3-c]-s-triazoles with poly[(4-diacetoxyiodo)-styrene] (PSDIB), and the results of the study are described in this article.

PSDIB was prepared from the commercial linear polystyrene (average molecular weight (MW) = 250,000) and 1% cross-linked polystyrene by the reported method.[4] The exact loading capacity of PSDIB was measured by iodometry and determined to be 2.62 mmol/g (linear) and 2.03 mmol/g (1% cross-linked).

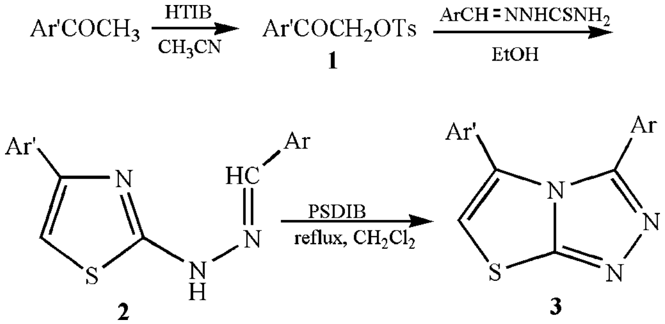
The α-tosyloxy-acetophenones (**1**) (Table 1, Scheme 1), which were prepared from corresponding acetophenones by [hydroxy(tosyloxy)iodo]benzene (HTIB) in acetonitrile,[5] reacted with arenecarbaldehyde of thiosemicarbazone to give arenecarbaldehyde-4-arylthiazol-2-ylhydrazones (**2**) (Table 2, Scheme 1).[3]

The reaction of arenecarbaldehyde-4-arylthiazol-2-ylhydrazone and PSDIB (linear) in refluxing dichloromethane resulted in the formation of 3,5-diarylthiazolo[2,3-c]-s-triazoles (**3**) (Table 2, Scheme 1). The PSDIB (linear) could be reused and the yield was still excellent. The experimental results showed PSDIB (recycled) had almost the same functional group as the originally prepared PSDIB. We also applied 1% cross-linked PSDIB and got the same results; furthermore, its treatment is much simpler than linear reagent after reaction. The yields of thiazole[2,3-c]-s-triazoles are approximately 70%. Probably the short time resulted in the low yield. If the reaction time is lengthened, the yield may be improved.

Polystyrene-supported hypervalent iodine reagent has these distinguishing features: the polyiodobenzen that is formed from PSDIB easily separated from products after reaction by simple filtration; the inconvenient operation of separating and refining iodobenzene that is formed from phenyliodine diacetate(IBD) is avoided; the polystyrene-supported

Table 1. Results of the formation of **1** and **2**

Entry	Ar′	Ar	Mp (°C) Found	Mp (°C) Lit.	Yield (%)
1a	Ph		91–92	91–92[5]	95
1b	*p*-ClPh		122–123	122[5]	90
1c	*p*-MePh		81–82	82[5]	92
2a	Ph	Ph	192–193[3]		90
2b	Ph	*p*-MeOPh	193–194	194[6]	92
2c	*p*-ClPh	Ph	200–203	194[7]	87
2d	*p*-ClPh	*p*-MeOPh	195–196[3]		90
2e	*p*-MePh	Ph	200–202	197[8]	94
2f	*p*-MePh	*p*-MeOPh	166–168	165–6[9]	89



Scheme 1.

hypervalent iodine reagent can be recycled and this recycling is environmentally safe.[4,10]

EXPERIMENTAL

Linear polystyrene was purchased from J&K Chemical Ltd. and 1% cross-linked polystyrene (200–400 mesh) was purchased from Nankai Share Group. The melting points were determined by the capillary method and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively on a Bruker AV-300 instrument. Elemental analyses were performed on a CYB 08.35-91. IR spectra were recorded at FT-IR 1730. MS spectra were recorded at HP 1100 LC/MSD 1946A.

Table 2. Results of the formation of **3**

				Mp (°C)		
Entry	Ar′	Ar	Time (h)	Found	Lit.[3]	Yield (%)
3a	Ph	Ph	2	165–166	164–165	68[a]
3b	Ph	*p*-MeOPh	1	140–141	139–141	63
3b	Ph	*p*-MeOPh	1	140–141	139–141	62[b]
3c	*p*-ClPh	Ph	2	190–192		65
3d	*p*-ClPh	*p*-MeOPh	1	187–188	187–188	72
3d	*p*-ClPh	*p*-MeOPh	1	187–188	187–188	70[b]
3e	*p*-MePh	Ph	2	155–156		68
3f	*p*-MePh	*p*-MeOPh	1.5	165 (decomp.)		72[a]

[a] By applying 1% cross-linked PSDIB.

[b] By applying recycled PSDIB (linear).

General Procedure for Synthesis of Arenecarbaldehyde-4-arylthiazol-2-ylhydrazones

A suspension of arenecarbaldehyde of thiosemicarbazone (534 mg, 3 mmol) and α-tosyloxy-acetophenone (870 mg, 3 mmol) in ethanol (30 ml) were refluxed for 1–3 h. During the reaction, the starting material disappears when the temperature of the mixture reached 55°C or so, and a new solid appears at once. It dissolved in dichloromethane, which was washed with 2% Na_2CO_3 and water; the organic layer was dried over Na_2SO_4 and evaporated in vacuo to give a solid.

Preparation of 3,5-Diaryl 1,2,4-thiazolo [2,3-c]-s-triazoles

To a solution of arenecarbaldehyde-4-arylthiazol-2-ylhydrazone (1 mmol) in 20 ml of dichloromethane was added linear PSDIB (0.7 g). The contents were refluxed for 1–2 h. The resulting dark brown solution was evaporated, the remainder was poured into 80 ml of anhydrous ethanol in stirring conditions, and the linear iodinated polystyrene was filtrated. The ethanol was evaporated. The residue was dissolved in dichloromethane, washed with 2% $NaHCO_3$ and water, and dried over Na_2SO_4. The crude product was purified by column chromatography using a petroleum ether–ethyl acetate mixture followed by crystallization to afford 3,5-diaryl-l,2,4-thiazolo[2,3-c]-s-triazoles.

3c, 3-Phenyl-5-*p*-chlorophenyl-1,2,4-thiazolo[2,3-c]-s-triazole

IR (KBr): ν max 1650 (C=C, C=N), 1610, 1575 (C-N) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.54 (m, 5H), 7.93 (d, $J = 8.20$ Hz, 2H), 8.49 (d, $J = 8.80$ Hz, 2H), 8.76 (s,1H). ^{13}C NMR (δ, $CDCl_3$): 127.0, 129.0 (2), 129.5 (2), 129.6 (2), 132.2 (2), 133.2, 137.1, 140.2, 165.2, 167.9, 168.0, 190.1. MS: M/Z 310.0 $(M-1)^+$. Anal. calcd. for $C_{16}H_{10}ClN_3S$: C, 61.63; H, 3.20; N, 13.47. Found: C, 62.04; H, 3.15; N, 13.74.

3e, 3-Phenyl-5-*p*-methylphenyl-1,2,4-thiazolo[2,3-c]-s-triazole

IR (KBr): ν max 1650 (C=C, C=N), 1610, 1575 (C-N) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 2.47 (s, 3H), 7.29–7.37 (m, 2H), 7.50–7.56 (m, 3H), 7.91–7.94 (m, 2H), 8.43 (d, $J = 8.30$ Hz, 2H), 8.75 (s, 1H).^{13}C NMR (δ, $CDCl_3$): 21.9, 126.4, 128.9 (2), 129.5 (2), 129.9 (2), 131.1 (2), 132.6, 133.3, 145.3, 164.7, 167.7, 168.8, 190.1. MS: M/Z 290.1 $(M-1)^+$. Anal. calcd. for $C_{17}H_{13}N_3S$: C, 70.07; H, 4.50; N, 14.42. Found: C, 69.55; H, 4.37; N, 15.22.

3f, 3-*p*-Methoxyphenyl-5-*p*-methylphenyl-l,2,4-thiazolo[2,3-c]-s-triazole

IR (KBr): ν max 1650 (C═C, C═N), 1610, 1575 (C-N) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 2.47 (s, 3H), 3.91 (s, 3H), 7.01 (d, $J = 8.80$ Hz, 2H), 7.34 (d, $J = 8.20$ Hz, 2H), 7.88 (d, $J = 8.80$ Hz, 2H), 8.43 (d, $J = 8.20$ Hz, 2H), 8.72 (s, 1H). ^{13}C NMR (δ, $CDCl_3$): 21.9, 55.5, 114.5 (2), 125.0, 126.2, 126.5, 129.8 (2), 130.6 (2), 131.5 (2), 145.0, 164.3, 167.2, 168.0, 190.1. MS: M/Z 320.1$(M-1)^+$. Anal. calcd. for $C_{18}H_{15}N_3OS$: C, 67.27; H, 4.70; N, 13.07. Found: C, 67.30; H, 4.00; N, 13.12.

Regeneration of Linear Poly[(4-diacetoxyiodo)styrene]

Recovered iodinated polystyrene (2.5 g) was added to 40 ml of CH_2Cl_2 and heated to make it dissolve. The solution then was put in 200 ml of methanol and 2.1 g of puried iodinated polystyrene, from which 2.9 g of poly[(4-diacetoxyiodo)styrene] was prepared by the reported method,[4] too. Its exact loading capacity was 2.51 mmol/g.

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