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Synthesis of Alkylammonium Tosylates with Poly{[4-Hydroxy(Tosyloxy)lodo]Styrene}

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Synthesis of Alkylammonium Tosylates with Poly{[4-Hydroxy(Tosyloxy)Iodo]Styrene}

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Abstract: Several primary carboxamides (RCONH₂) were converted to the corresponding alkylammonium tosylates ($RN^+H_3^-OTs$) with poly{[4-hydroxy (tosyloxy) iodo]styrene} (PSHTIB) in yields ranging from 60% to 90%.

Keywords: Alkylammonium tosylate, carboxamide, Hofmann rearrangement, poly{[4-hydroxy(tosyloxy)iodo]styrene}

Applying hypervalent iodine reagents in the synthetic processes could avoid the use of toxic compounds containing heavy metals, such as lead, mercury, and chromium. Generally, the reaction conditions are exceedingly simple, especially without special precautions to the solvents for the exclusion of oxygen or humidity. Moreover, polymer-supported hypervalent iodine reagents also provided simplicity of workup. Thus, polymer-supported hypervalent iodine reagents have been intensively applied in various synthesis.^[1]

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Poly{[4-Hydroxy(Tosyloxy)Iodo]Styrene} (PSHTIB) as a polymersupported reagent was found to have the same properties as [hydroxyl (tosyloxy)iodo]benzene (HTIB). It is a readily available and stable crystalline compound, which can be handled under ambient conditions.^[2] Gerald F. Koser reported aliphatic carboxamides converted to alkylammonium tosylates with HTIB.^[3] We have explored the utility of PSHTIB as a Hofmann reagent, and the results of the study are described in this communication.

PSHTIB was prepared from the commercial linear polystyrene (average MW = 250,000) by the reported method.^[2,4] The exact loading capacity of PSHTIB was 1.91 mmol/g, which was measured by element analysis (Scheme 1).

When PSHTIB was mixed with primary carboxamide in acetonitrile, the reaction took place at reflux. After the reaction, the mixtures were hot-filtrated. Then, they were kept below 10°C and the corresponding alkylammonium tosylates were separated. Iodinated polystyrene was recovered by simple filtration and was converted to PSHTIB according to the reported method.^[2,4] The loading capacity of the reagent was 1.88 mmol/g. We used this reagent with the propionamide and got good results. This result showed the reagent had almost the same functional group as the original prepared reagent (Table 1).

Hexylammonium tosylate. White powder, IR (KBr): 3433, 1490, 1189, 817 cm⁻¹; ¹H NMR (δ, CDCl₃, 300 MHz): 0.80 (t, J = 6.3 Hz, 3H), 1.11 (m, 6H), 1.40 (m, 2H), 2.36 (s, 3H), 2.72 (m, 2H), 7.20 (d, 2H, J = 8 Hz), 7.70 (s, 3H), 7.98 (d, 2H, J = 8 Hz). ¹³C NMR (δ CDCl₃, 75 MHz): 13.89, 21.29, 22.33, 25.99, 27.36, 31.08, 39.33, 125.90, 128.99, 140.70, 141.26. Anal. calcd. for C₁₃H₂₃NO₃S: C, 57.11; H, 8.48; N, 5.12. Found: C, 57.04; H, 8.57; N, 4.94.

Heptadecylammonium tosylate. White powder, IR (KBr): 3432, 1470, 1189, 817 cm⁻¹, ¹H NMR (δ , CDCl₃, 300 MHz): 0.90 (t, J = 6.9 Hz), 1.15–1.49 (m, 30H), 2.37 (s, 3H), 2.75 (s, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.60 (s, 3H), 7.75 (d, J = 7.9 Hz, 2H). ¹³C NMR (δ CDCl₃, 75 MHz): 14.08, 21.30, 22.67, 24.75, 26.38, 27.45, 29.01, 29.34, 29.43, 29.59, 29.71, 31.91, 39.92, 110.13, 125.91, 129.00, 140.68, 141.24. Anal. calcd. for C₂₄H₄₅NO₃S: C, 67.40; H, 10.61; N, 3.27. Found: C, 67.57; H, 10.67; N, 2.99.

Naphthylmethylammonium tosylate. White powder, IR (KBr): 3436, 1182, 814 cm^{-1} ; ¹H NMR (δ , DMSO, 300 MHz): 2.35 (s, 3H), 4.20–4.55

$$RCONH_2 + PS - I < OH - CH_3CN - RN^+H_3OTs + PS - I$$

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Scheme 1.

Table 1. Results for the Hofmann reac

R	Reflux (h)	Products ^b	Mp (°C)		Yields (%)	
			Found	Lit.	PSHTIB	HTIB
Me	12	CH ₃ N ⁺ H ₃ ⁻ OTs	142-143	146-147 ^[5]	82	93
Et	2	$CH_3CH_2 N^+H_3^-OTs$	115-116	118 ^[5]	89 (87 ^{<i>a</i>})	90
n-Pr	1	$CH_3(CH_2)_2 N^+H_3^-OTs$	133-134	139 ^[5]	60	
n-Hex	3	$CH_3(CH_2)_5 N^+H_3^-OTs$	114-117		82	
n-Hep	3	$CH_3(CH_2)_6 N^+H_3^-OTs$	127-129	131-133 ^[3]	70	93
n-Und	1	CH ₃ (CH ₂) ₁₀ N ⁺ H ₃ ⁻ OTs	102-115	$102 - 130^{[3]}$	70	57
n-Ole	2	CH ₃ (CH ₂) ₁₆ N ⁺ H ₃ ⁻ OTs	72-78		89	
Benzyl	3	PhCH ₂ N ⁺ H ₃ ⁻ OTs	177-180	185.5 ^[5]	90	89
$C_{10}H_7CH_2$	3	$C_{10}H_7CH_2 N^+H_3^-OTs$	170-177		88	

^{*a*}By applying poly{[4-hydroxy(tosyloxy)iodo]styrene} recycled. ^{*b*}IR, ¹H NMR spectra were identical with the literature.

(q, J = 5.6 Hz, 2H), 7.10~8.16 (m, 11H), 8.28 (s, 3H). ¹³C NMR (δ , DMSO, 75 MHz): 21.22, 43.00, 123.89, 125.83, 125.96, 126.75, 127.23, 127.76, 128.48, 129.15, 129.64, 130.37, 131.12, 133.72, 138.00, 146.29. Anal. calcd. for C₁₈H₁₉NO₃S: C, 65.63; H, 5.81; N, 4.25. Found: C, 65.21; H, 5.63; N, 4.12.

CONCLUSIONS

Several alkylammonium tosylates ($RN^+H_3^-OTs$) were obtained from corresponding primary carboxamides ($RCONH_2$) with PSHTIB in acetonitrile at reflux. The reaction is mild and has operational simplicity, good yields, and the possibility of recycling, according with green chemistry's requirement.

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