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ISSN : 2348 - 5612 | Volume : 05 , Issue : 02 | January – March 2018

Solvent-free synthesis of tosyloxybenzalacetones: A Green Chemistry Aspect

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Abstract: The solvent free synthesis of α-tosyloxybenzalacetones by grinding the bezalacetones with [hydroxy(tosyloxy)iodo]benzene with a mortar and pestle at room temperature is described. This new method allows higher yields, reduced reaction times, ease of handling and follows principles of green chemistry.

Keywords: Solvent free synthesis, green chemistry, [hydroxy(tosyloxy)iodo]benzene, benzalacetones, α-tosyloxybenzalacetones.

ISSN : 2348-5612 © URR
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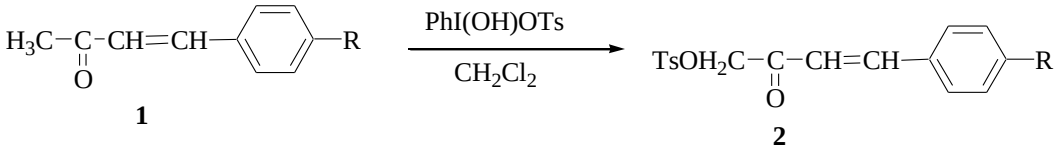
Introduction

In recent years, with the emphasis on adoption of cleaner green chemistry processes, a tremendous interest has been observed in carrying out various chemical transformations under heterogeneous conditions owing to simplicity in operation. The toxicity and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in huge amounts for organic reactions have posed a serious threat to the environment. Thus, design of solventless reaction has received tremendous attention in recent times in the area of green synthesis. In the previous communication, the synthesis and chemistry of α-tosyloxybenzalacetones **2**, obtained from the reaction of (*E*)-4-arylbut-3-en-2-ones (benzalaccetones) with HTIB in dichloromethane has been reported.[1]

Solvent-free reactions have many advantages and their important aspects are reduced pollution, lower cost and the simplicity of the processes.[2-3] Many organic solvents are ecologically harmful, thus it is required to develop benign chemical technologies having minimized usages of these solvents.[4] Concurrently, there is recent interest in the development of hypervalent iodine mediated methods in solid state. Literature survey revealed that organohypervalent iodine(III) reagents are versatile reagents to bring about a variety of useful transformations. One of the most interesting features of hypervalent iodine reagents is their use in the direct α-functionalization of ketones and of some other carbonyl compounds.[1-12] Moriarty and Prakash have developed a particularly useful methodology for the oxidative α-functionalization of enolizable carbonyl compounds or their enol ethers using hypervalent iodine oxidants.[13-23] α-Functionalized ketones are extremely useful and versatile precursors in organic synthesis.

Encouraged by these observations, the present study illustrates an environmentally benign strategy that proceeded under solvent free conditions. Just by grinding benzalacetones **(1a-1h)** and HTIB at room temperature using a solid state reaction afforded the desired product α-tosyloxybenzalacetones **(2a-2h)**. The reaction was smooth, clean and occurred at room temperature with short span of time.

The reaction was conducted following the procedure outlined here. 1.1 eq. of HTIB was added to benzalacetone **1a**. After being blended thoroughly in a pestle mortar at room temperature for about 5-10 minutes followed by work up the reaction afforded a single solid product, α-tosyloxybenzalacetone **(2a) (Scheme 1)** in 79% yield. The structure of the product was confirmed on the basis of elemental analysis and spectral data. The IR spectrum displayed carbonyl stretch at 1695 cm^{-1}. The ^1H NMR spectrum of **2a** showed a characteristic singlet at 4.74 due to methylene group which was further confirmed by DEPT-135 due to a negative peak.



1 **2**

Scheme 1 R = H, CH_3, OCH_3, Br, Cl, F, NO_2, 2-thienyl

Encouraged by the successful results, we studied the scope of new method for the synthesis of various aryltosyloxybenzalacetones **(2b-h)**. The reaction of various benzalacetone derivatives **(1b-h)** with HTIB under solvent free conditions afforded the corresponding tosyloxybenzalacetones **(2b-h)** in good yields **(Scheme 2**; **Table 1)**.
The physical data of products, 4-aryl-1-tosyl-but-3-en-2-ones **(2a-h)** is given in **Table 1.**

Table-1: Physical data of 4-aryl-1-tosyl-but-3-en-2-ones (2a-h)

Comp.	R	M.pt. (°C)	*Yield (%)
2a	H	60-61	79
2b	CH_3	132-134	77
2c	OCH_3	94-95	76
2d	Br	65-66	78
2e	Cl	67-68	77
2f	F	68-70	78
2g	NO_2	130-131	76
2h	2-thienyl	89-90	75

*Yields (%) of the products were calculated with respect to the corresponding benzalacetones **1**.

Finally, the noteworthy features of the present study are:

- This study demonstrates that HTIB, a tosyloxylating agent possesses selectivity for ketones in the presence of α,β-unsaturated conjugated double bond.
- The reaction involves the mild conditions, simple and high yielding procedure.
- The HTIB mediated solid state procedure is ecofriendly as it reduces the amount of solvents used in liquid phase and subsequent pollution due to solvents.

Experimental:
Melting points were taken in open capillaries and are uncorrected. IR spectra were recorded on Perkin-Elmer IR spectrophotometer. The ^{1}H NMR spectra were recorded on Brucker 300 MHz instrument. The chemical shifts are expressed in ppm units downfield from an internal TMS standard. Benzalacetones were prepared according to literature procedure by condensation of acetone with substituted aldehydes in 10% aq. NaOH.[28]

General procedure for Preparation of α-tosyloxybenzalacetones (2) in soild state (2a-g):
A mixture of benzalacetone (**2a**, 0.73 g, 5 mmol) and HTIB (1.98 g, 5.5 mmol) was blended thoroughly in a pestle mortar. The resulting homogenous mixture was ground at room temperature for 5-10 minutes. The resulting residue was basified with saturated solution of $NaHCO_3$ and extracted with dichloromethane (3×20 ml). The combined organic phase was dried (anhyd. Na_2SO_4) and concentrated to give crude gummy product which on recrystallization from acetonitrile afforded the pure product **a** (2.37 g, 75%).

4-Phenyl-1-tosyl-but-3-en-2-one (2a)
IR (ν_{max}, in KBr): 1695 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.43 (s, 3H, CH_3), 4.74 (s, 2H, CH_2), 6.91 (d, 1H, CH, *J* = 16.04 Hz), 7.38-7.56 (m, 5H, Ar-H), 7.36 (d, 2H, Ar-H, *J* = 8.1 Hz), 7.66 (d,

1H, CH, *J* = 16.04 Hz), 7.85 (d, 2H, Ar-H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 21.70, 71.60, 120.10, 128.15, 128.79, 129.05, 130.06, 131.34, 132.41, 145.45, 191.40. Anal. Cald. $C_{17}H_{16}O_4S$: C, 64.56; H, 5.06. Found : C, 64.35; H, 4.99. Mass, m/z: 316

4-(4-Methylphenyl)-1-tosyl-but-3-en-2-one (2b)

IR (ν_{max}, in KBr): 1695 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.44 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 4.73 (s, 2H, CH_2), 6.92 (d, 1H, CH, *J* = 16.04 Hz), 7.34-7.51 (m, 4H, Ar-H), 7.41 (d, 2H, Ar-H, *J* = 8.3), 7.65 (d, 1H, CH, *J* = 16.04 Hz), 7.84 (d, 2H, Ar-H, *J* = 8.3). Anal. Cald. $C_{18}H_{18}O_4S$: C, 65.45; H, 5.45. Found : C, 65.30; H, 5.29.

4-(4-Methoxyphenyl)-1-tosyl-but-3-en-2-one (2c)

IR (ν_{max}, in KBr): 1696 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.34 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 4.73 (s, 2H, CH_2), 6.92 (d, 1H, CH, *J* = 16.04 Hz), 7.36-7.54 (m, 4H, Ar-H), 7.39 (d, 2H, Ar-H, *J* = 8.3), 7.63 (d, 1H, CH, *J* = 16.04 Hz), 7.84 (d, 2H, Ar-H, *J* = 8.3).

Anal. Cald. $C_{18}H_{18}O_5S$: C, 62.43; H, 5.20. Found : C, 62.40; H, 4.98.

4-(4-Bromophenyl)-1-tosyl-but-3-en-2-one (2d)

IR (ν_{max}, in KBr): 1697 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.45 (s, 3H, CH_3), 4.75 (s, 2H, CH_2), 6.93 (d, 1H, CH, *J* = 16.02 Hz), 7.28 (d, 2H, Ar-H, *J* = 8.1), 7.36-7.53 (m, 4H, Ar-H), 7.61 (d, 1H, CH, *J* = 16.02 Hz), 7.86 (d, 2H, Ar-H, *J* = 8.1). Anal. Cald. $C_{17}H_{15}BrO_4S$: C, 51.65; H, 3.79. Found : C, 51.60; H, 3.79. Mass, m/z: 394.

4-(4-Chlorophenyl)-1-tosyl-but-3-en-2-one (2e)

IR (ν_{max}, in KBr): 1697 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.45 (s, 3H, CH_3), 4.73 (s, 2H, CH_2), 6.91 (d, 1H, CH, *J* = 15.9 Hz), 7.34-7.51 (m, 4H, Ar-H), 7.41 (d, 2H, Ar-H, *J* = 8.4), 7.63 (d, 1H, CH, *J* = 15.9 Hz), 7.86 (d, 2H, Ar-H, *J* = 8.4); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 21.65, 72.20, 126.3, 127.8, 128.80, 129.00, 129.60, 130.60, 133.3, 133.50, 142.29, 199.50. Anal. Cald. $C_{17}H_{15}ClO_4S$: C, 58.20; H, 4.27. Found : C, 58.06; H, 4.16. Mass, m/z: 350

4-(4-Fluorophenyl)-1-tosyl-but-3-en-2-one (2f)

IR (ν_{max}, in KBr): 1698 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.45 (s, 3H, CH_3), 4.74 (s, 2H, CH_2), 6.93 (d, 1H, CH, *J* = 16.00 Hz), 7.36-7.55 (m, 4H, Ar-H), 7.39 (d, 2H, Ar-H, *J* = 8.3), 7.61 (d, 1H, CH, *J* = 16.00 Hz), 7.84 (d, 2H, Ar-H, *J* = 8.3). Anal. Cald. $C_{17}H_{15}FO_4S$: C, 61.08; H, 4.49. Found : C, 61.05; H, 4.31.

4-(4-Nitrophenyl)-1-tosyl-but-3-en-2-one (2g)

IR (ν_{max}, in KBr): 1700 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.45 (s, 3H, CH_3), 4.74 (s, 2H, CH_2), 6.93 (d, 1H, CH, *J* = 16.00 Hz), 7.39 (d, 2H, Ar-H, *J* = 8.3), 7.61 (d, 1H, CH, *J* = 16.00 Hz), 7.84 (d, 2H, Ar-H, *J* = 8.3), 8.21-8.45(m, 4H, Ar-H).

4-(2'-Thienyl)-1-tosyl-but-3-en-2-one (2h)

IR (ν_{max}, in KBr): 1683 cm^{-1} (C=O str.); ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.45 (s, 3H, CH_3), 4.71 (s, 2H, CH_2), 6.83 (d, 1H, CH, *J* = 15.6 Hz), 7.07-7.15 (m, 3H); 7.31-7.44 (m, 4H), 7.65 (d, 1H, CH, *J* = 15.6 Hz); Anal. Cald. $C_{15}H_{14}O_4S_2$: C, 55.90; H, 4.35; Found: C, 55.88; H, 4.32.

Acknowledgment:

I am very thankful to Kurukshetra University, Kurukshetra for the award of University Research Scholarship to me for carrying out this work.

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