

# SYNLETT Spotlight 74

## *N*-Tosyl Imines

Compiled by Mukut Gohain



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Mukut Gohain was born in Tinsukia, Assam, India in 1975. He received a B.Sc. (Chemistry) degree in 1997 from Dibrugarh University, Dibrugarh and M.Sc. (Chemistry) degree in 2000 from Assam University, Silchar. After completion of his M.Sc. degree he joined the Medicinal Chemistry Division of Regional Research Laboratory (CSIR), Jorhat 785006 to pursue a Ph.D. under the guidance of Dr. J. S. Sandhu, FNA. Presently he is working in the same laboratory under the supervision of Dr. Dipak Prajapati, Sc.E(II). His research interest is synthesis of potent bioactive molecules and development of new synthetic methods.

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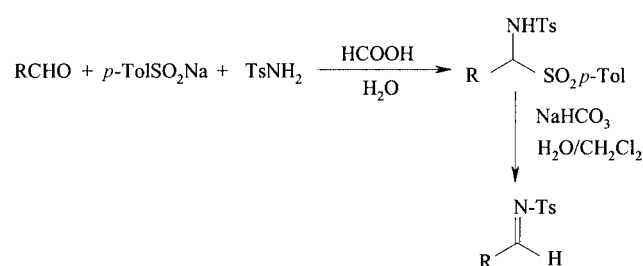
### Introduction

*N*-Tosyl imines are versatile synthetic intermediates in organic synthesis.<sup>1</sup> These are activated imines where the limitations of aldimine functionality such as low electrophilicity of azomethine carbon and the tendency of enoliz-

able imines to undergo deprotonation rather than addition can be circumvented.<sup>2,3</sup> They are used in olefination reactions and various C–C bond forming reactions.

### Preparation

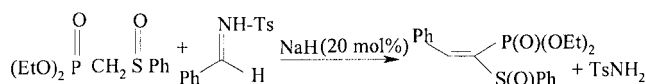
*N*-Tosyl imines can be prepared<sup>4</sup> by the reaction of aldehyde, *p*-toluene sulfonamide and sodium *p*-toluene sulfinate in aqueous formic acid, and subsequent treatment of the generated sulfonamide sulfone intermediate with sodium bicarbonate (Scheme 1).



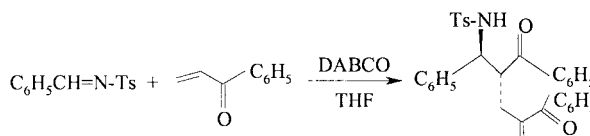
Scheme 1 R = Aliphatic/aromatic

### Abstracts

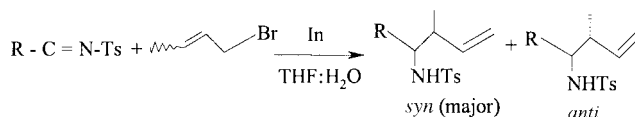
(A) The reaction of diethyl benzene sulfinyl methylphosphonate with *N*-tosyl imine in the presence of a catalytic amount of NaH (20 mol%) at 70 °C gives substituted (*E*)- $\alpha$ -benzene sulfinyl vinylphosphonates in 68–85% yields.<sup>5</sup>



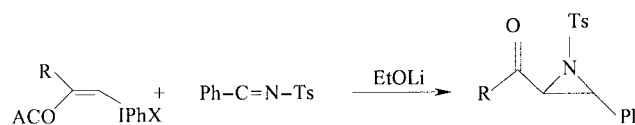
(B) The aza-Baylis–Hillman reaction of *N*-tosylimine with phenyl vinyl ketone gives the double aza-Baylis–Hillman adduct in good yields with excellent stereoselectivity in the presence of Lewis base DABCO<sup>6</sup> in THF.



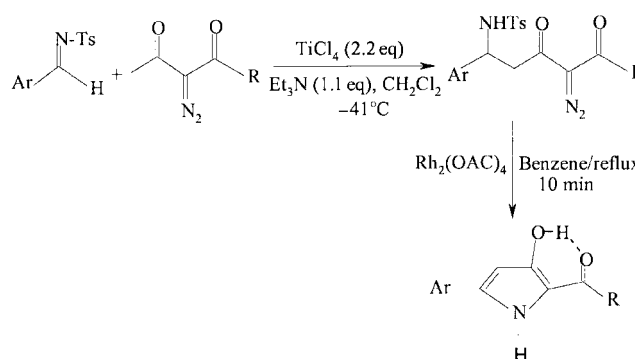
(C) Reaction of *N*-tosylimines having proximal chelating groups with crotyl bromide and indium in aqueous media give  $\alpha$ -crotylation products stereoselectively with *syn* selectivity.<sup>7</sup>



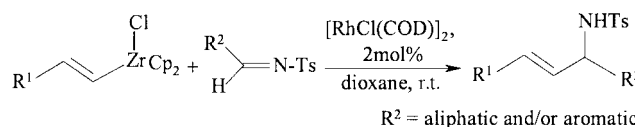
(D) Monocarbonyl iodonium ylides generated in situ from (*Z*)-(2-acetoxyvinyl) iodonium salts via an ester exchange reaction with EtOLi undergo alkylidene transfer reactions to *N*-tosyl imine yielding 2-acyl aziridines in good yields.<sup>8</sup>



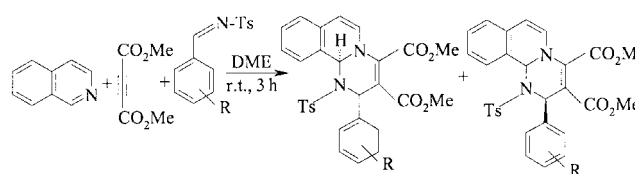
(E) Dengs et al. have used *N*-tosyl imines to prepare functionalized pyrrole derivatives. This approach is based on nucleophilic condensation of an  $\alpha$ -diazo- $\beta$ -ketoester or an  $\alpha$ -diazo- $\beta$ -ketoester with *N*-tosyl imine followed by Rh(II)-catalysed diazodecomposition.<sup>9</sup>



(F) Treatment of alkenylzirconocene chloride complexes to *N*-tosylimines in the presence of [RhCl(COD)]<sub>2</sub> (2 mol%) catalyst in dioxane at room temperature gives allylic amine derivatives in excellent yield.<sup>10</sup> This is the first example of the catalytic addition reactions of alkenyl zirconocene chloride complexes to aldimine derivatives.



(G) The formation of a 1,4-dipole from isoquinoline and dimethyl acetylene dicarboxylate (DMAD) and its trapping by phenyl isocyanate, diethyl mesoxalate and dimethyl azodicarboxylate were reported by Huisgen,<sup>11</sup> the utility of this reaction for the synthesis of six-membered heterocycles has not been explored so far. Nair et al.<sup>12</sup> have reported that the 1,4-dipole derived from isoquinoline and DMAD has been shown to react readily with *N*-tosyl imines resulting in the diastereoselective synthesis of 2*H*-pyrido[2,1-*a*]isoquinoline derivatives.



## References

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