

p-Toluenesulfonyl Azide

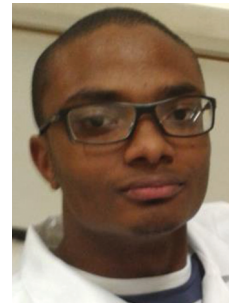
João Victor Santiago

Instituto de Química de São Carlos, Universidade de São Paulo, CEP 13560-970, São Carlos, SP, Brazil
 jvss@usp.br
 jvss.qpa@gmail.com

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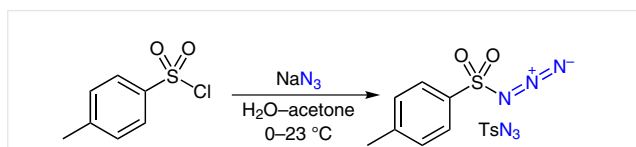
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João Victor Santiago was born in 1991 in Brasília, Brazil. He obtained his B.Sc. in Chemistry (2012) and his M.Sc. in Organic Chemistry (2014) from the University of Brasília-UnB. Currently, he works towards his Ph.D. under the guidance of Professor Antonio C. B. Burlon. His research focuses on the synthesis of hexahydro-pyridazines, 1,2-oxazinanes, and substituted cyclohexanes from α,β -unsaturated diazoketones.



Introduction

p-Toluenesulfonyl azide (TsN₃, CAS: 941-55-9) can be prepared in good yield from the reaction of *p*-toluenesulfonyl chloride (TsCl) and sodium azide (NaN₃) (Scheme 1).¹ TsN₃ is a colorless oil with a melting point of 21–22 °C and boiling point of 110–115 °C at 0.001 mmHg.²

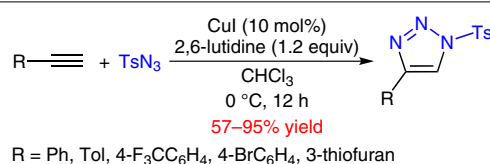


Scheme 1 Classic preparation of *p*-toluenesulfonyl azide

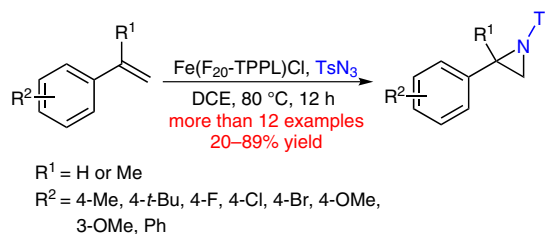
One of the most used applications of TsN₃ is the diazo transfer reaction. One of the first works to describe the concept of diazo transfer was published in 1910 by Dimroth.³ Since this date, the application of TsN₃ in diazo chemistry is frequently mentioned. Other applications for TsN₃ include cycloaddition reactions, especially the [3+2] cycloaddition with alkynes for the formation of substituted triazoles.⁴ Here, some recent examples of reactions employing TsN₃ are presented.

Table 1 Use of TsN₃

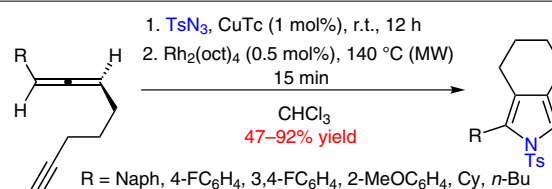
(A) Based on computational and mechanistic studies of copper-catalyzed azide–alkyne cycloaddition (CuAAC), Chang and co-workers⁵ have reported the regioselective synthesis of a series of *N*-sulfonyl-1,2,3-triazoles. CuI was employed as catalyst and 2,6-lutidine as an additive. *N*-Sulfonyl-1,2,3-triazoles were synthesized in 57–95% yield.



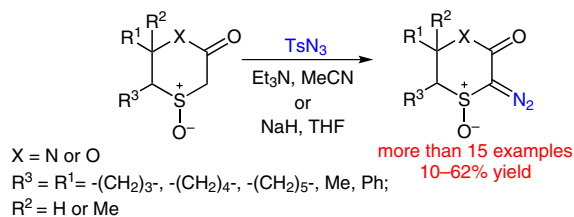
(B) Zhang and co-workers⁶ reported the use of iron porpholactones as catalysts for the aziridination of alkenes and for the amidation of alkanes. In the aziridination of alkenes, mainly styrene derivatives were utilized as substrates. TsN₃ acted as the nitrogen source. The authors synthesized a series of aziridines in 20–89% yield.



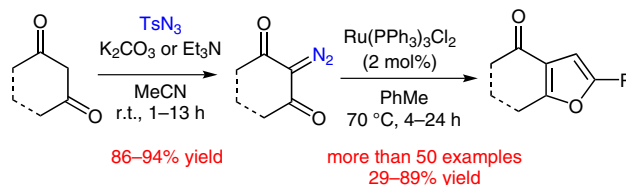
(C) The application of α -diazo-*N*-sulfonyl-imines as intermediates has often been reported.⁷ In 2013, Schultz and Sarpong⁸ performed the synthesis of 3,4-fused pyrroles using TsN₃ in the formation of α -Rh-imino-carbenoid as an intermediate by the reaction of α -diazo-*N*-tosyl-imines and a rhodium catalyst. In an one-pot methodology, the authors synthesized a series of 3,4-fused pyrroles in 47–92% yield.



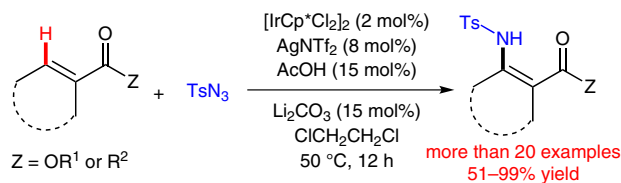
(D) Collins et al.⁹ reported the application of TsN₃ as a reagent in the synthesis of α -diazo- β -oxo-sulfoxides by a diazo-transfer reaction. In this work, the authors utilized sulfoxides containing monocyclic, bicyclic, or acyclic lactones and lactams. A series of α -diazo- β -oxo-sulfoxides were synthesized in 10–62% yield.



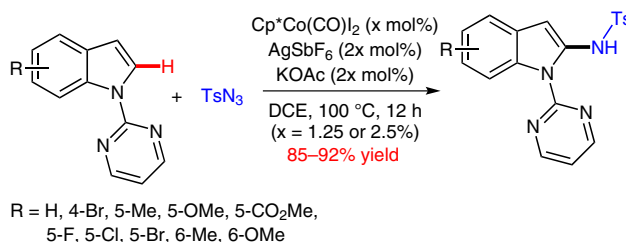
(E) Lee and Xia¹⁰ have reported the regioselective synthesis of a series of functionalized furans from the reaction of terminal alkynes and cyclic or acyclic diazocarbonyl compounds. The authors utilized TsN₃ in a diazo-transfer reaction, furnishing diazocarbonyl compounds in 86–94% yield.¹¹ The products were utilized in the synthesis of functionalized furans in 29–89% yield by a ruthenium-catalyzed [3+2] cycloaddition.



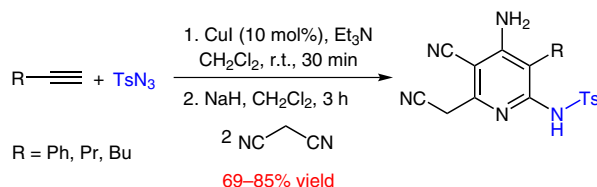
(F) C–H bond activation is versatility and has been widely applied in organic synthesis for the formation of functionalized bonds. In 2014, Chang and Kim¹² reported the iridium-catalyzed amidation of C–H bonds in α -aryl or α,β -unsaturated carbonyl compounds (esters or ketones). The authors propose that TsN₃ allows the formation of the C–N bond by insertion of the amide group, followed by the extrusion of molecular nitrogen. In this work, more than 20 products of C–H insertion were synthesized in 51–99% yield.



(G) Kanai and co-workers¹³ reported the directed selective amidation of C-2 carbons on an indole nucleus by C–H bond activation. The authors utilized an in situ generated cobalt catalyst for the transformation. TsN₃ was employed as the reagent for the insertion of *N*-tosyl into the C-2 carbon, furnishing the products in 85–92% yield.



(H) Yavari and co-workers¹⁴ synthesized a series of pentasubstituted pyridines by copper catalysis using a tandem process. Sulfonyl compounds, including TsN₃, were utilized for the formation of sulfonketenimides as key intermediates, which in one step furnished pentasubstituted pyridines with good yields (69–85%).



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