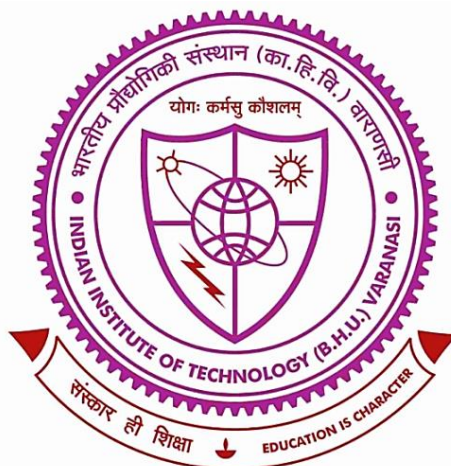


Synthesis and Applications of *N*-Nitrosamines and *N*-Nitrosamides in Different Organic Transformations



Thesis submitted in partial fulfilment for the

Award of Degree

Doctor of Philosophy

by

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Year of Submission
2023

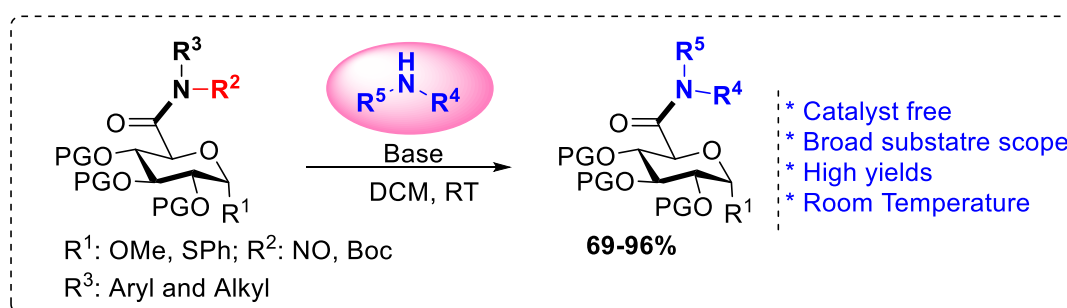
CHAPTER-6

Summary and Conclusions

6.1 Summary and Conclusions

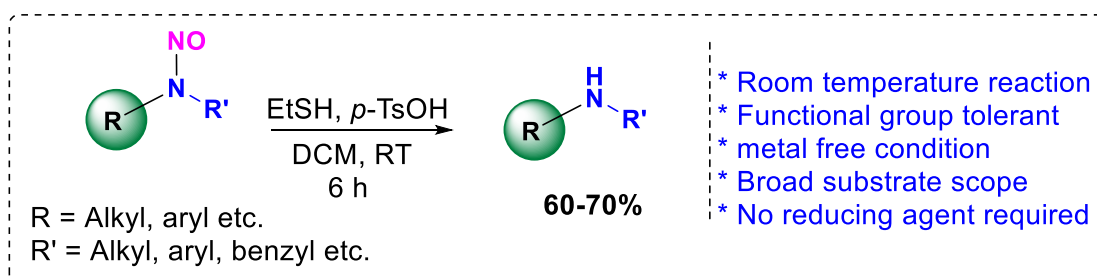
The present thesis entitled “**Synthesis and Applications of *N*-Nitrosamines and *N*-Nitrosamides in Different Organic Transformations**” described the synthesis of *N*-nitrosamines and their different reactions and applications. **Chapter 1** provided a general introduction to different nitroso compounds such as *C*-nitroso compounds, *S*-nitroso compounds, *O*-nitroso compounds and *N*-nitroso compounds and their synthetic applications. Apart from that, the focus of the thesis work has been briefed in this chapter.

Chapter 2 described the synthesis of glycouronamides via transamidation approach using *N*-nitrosamide intermediates under mild conditions. *N*-Nitroso uronamides underwent transamidation with various primary and secondary amines (alkyl amines, benzyl amines and anilines) in presence of triethylamine at room temperature. On the other hand, transamidation of *N*-Boc uronamides was successfully achieved with primary amines in the presence of DBU. In general, *N*-nitroso uronamides were found to be more reactive than *N*-Boc uronamides in terms of reaction time and yields. The developed protocol is highly efficient and does not require any catalyst or high-temperature conditions (**Scheme 6.1**).



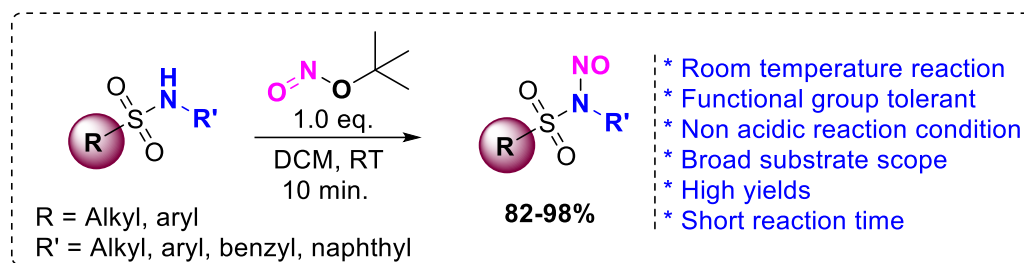
Scheme 6.1 Pictorial presentation of Chapter 2

Chapter 3 disclosed an efficient and practical method for the denitrosation of *N*-nitrosamines using ethanethiol with PTSA (*p*-toluenesulfonic acid) *via* trans-nitrosation strategy (**Scheme 6.2**). Denitrosation of *N*-nitroso *N*-alkyl and *N*-aryl anilines were achieved in good to excellent yields within 3 hours. This method was found to be very selective and efficient which tolerates many reactive functional groups during the denitrosation.



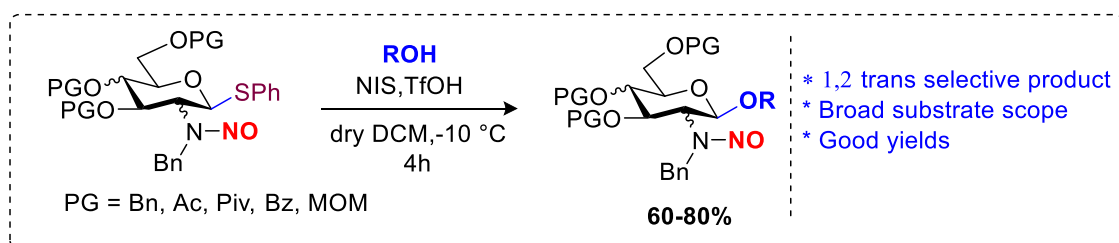
Scheme 6.2 Pictorial presentation of Chapter 3

Chapter 4 described the synthesis of *N*-nitroso sulfonamides from sulfonamides and tert-butyl nitrite (TBN) and their synthetic applications in nitroso transfer reactions under mild reaction conditions (**Scheme 6.3**). Various aryl *N*-methyl sulfonamides were prepared and subjected to the *N*-nitrosation reaction with TBN under optimization conditions. Aryl groups bearing various electron-donating functional groups such as methyl, methoxy, and tert-butyl groups underwent *N*-nitrosation within 10 min and provided the desired products good to excellent yields. Similarly, the electron-withdrawing groups such as nitro and cyano-containing substrates also underwent *N*-nitrosation smoothly and gave the desired product in excellent yields. The application of *N*-nitroso sulfonamides was explored for the nitrosation of secondary amines under mild reaction conditions. The developed methodology is attractive in terms of reaction conditions, yields, and execution of the reactions.



Scheme 6.3 Pictorial presentation of Chapter 4

Chapter 5 described the stereoselective synthesis of *O*-glycosides from 2-amino thioglycosides using *N*-nitroso group as directing group. The reaction was activated by using NIS/TfOH system in dichloromethane at $-10\text{ }^\circ\text{C}$ (Scheme 6.4). Various sugar and non-sugar acceptors were successfully glycosylated with 2-amino 1-thiogluco- and 2-amino 1-thiogalactoside under mild reaction conditions. These reactions provided β -glycosides in good to excellent yields.



Scheme 6.4 Pictorial presentation of Chapter 5

All the demonstrated synthetic protocols in the thesis are comparable to most of the existing protocols in terms of reaction condition and yield. Innocuous reagent, convenient procedure and high yield make these methods more attractive in organic synthesis. Hence, the developed methodologies will find wide applications in organic synthesis.