

TABLE OF CONTENTS

	Page
	No.
Acknowledgements	v
List of Titles	viii
List of Schemes	xii
List of Figures	xiv
List of Tables	xvi
List of Abbreviations	xvii
General Experimental Considerations	xx
Preface	xxi

LIST OF TITLES

CHAPTER-1

Titles	Introduction	Page
		No.
1.1	Brief Introduction	1
1.2	C- Nitroso Compounds	2
1.3	S-Nitroso Compounds	5
1.4	O-Nitroso Compounds	8
1.5	N-Nitroso Compounds	9
	1.5.1 Properties and Spectroscopic Discussion	10
	1.5.2 Synthesis of <i>N</i> -nitrosamines	11
	1.5.3 Electrophilic Substitution at the α -carbon of <i>N</i> -Nitrosamines	17
	1.5.4 Sydnone formation	14
	1.5.5 Fischer-Hepp rearrangement	15
	1.5.6 Reduction of <i>N</i> -Nitrosamines	17
	1.5.7 Oxidation of <i>N</i> -Nitrosamines	18
	1.5.8 Denitrosation of <i>N</i> -Nitrosamines	20
	1.5.9 Photochemistry of <i>N</i> -nitrosamines	21
	1.5.10 <i>N</i> -Nitroso Directed C-H Activation	23
1.6	Conclusion	26
1.7	The Objectives of The Present Work	27
1.8	References	28

CHAPTER-2

An Efficient Synthesis of *N*-Nitrosamines Under Solvent, Metal and Acid Free Conditions Using *Tert*-Butyl Nitrite

2.1	Introduction	33
2.2	Results and Discussions	37
2.2.1	Optimization for <i>N</i> -nitrosation under different reaction conditions	37
2.2.2	Substrate scope	41
2.2.3	Synthesis of <i>N</i> -cyclohexylhydroxylamine	45
2.2.4	Restricted rotation of <i>N</i> -nitrosamines	46
2.2.5	Plausible mechanism	49
2.3	Other Related Applications of <i>tert</i> -Butyl Nitrite (TBN)	48
2.3.1	Conversion of hydrazides into aryl azides	49
2.3.2	Synthesis of carboxylic acid from corresponding primary amides	52
2.4	Conclusion	53
2.5	Experimental Section	54
2.5.1	Experimental procedure for <i>N</i> -nitrosation of secondary amines (2a-2w)	54
2.6	Analytical Data for Products	54
2.7	Procedure for Preparation of <i>N</i> -Nitroso Cyclohexylhydroxylamine	68
2.8	Procedure for the Synthesis of Aryl Azides from Aryl Hydrazines (4a-4d)	70
2.9	Analytical Data of Aryl Azides	70
2.10	Procedure for the Synthesis of Substituted Benzoic Acids from Corresponding Amides (6a-6d)	72
2.11	Analytical Data of Carboxylic Acids	72
2.12	Spectral Data for few Products	75
2.13	References	78

CHAPTER-3

An Efficient Metal-Free Method for the Denitrosation of Aryl *N*-Nitrosamines at Room Temperature

3.1	Introduction	84
3.2	Results and Discussion	86
3.2.1	Optimization for denitrosation under different reaction conditions	86
3.2.2	Substrate scope	89
3.3	Applications of Current Methodology to Multi-step Synthesis	93
3.3.1	Palladium catalyzed C-H activation followed by denitrosation	93
3.3.2	Rhodium catalyzed C-H activation followed by denitrosation	94

3.3.3	Nitrosative dealkylation of <i>tert</i> -amines followed by denitrosation	95
3.4	Nitroso as Protecting Group	95
3.5	Plausible Mechanism	96
3.6	Conclusion	98
3.7	Experimental Section	98
3.7.1	General experimental procedure for the denitrosation of <i>N</i> -nitrosamines	99
3.7.2	Denitrosation of <i>N</i> -methyl <i>N</i> -nitrosaniline using Triethylsilane with hydroiodic acid (HI), hydrobromic acid (HBr) and hydrochloric acid (HCl).	99
3.7.3	Experimental procedure for the synthesis of <i>O</i> -allyl <i>N</i> -benzyl (4-hydroxyaniline) (6h) <i>via</i> nitrosation and denitrosation	99
3.8	Analytical Data for Products	100
3.9	Spectral Data for few Products	123
3.10	References	125

CHAPTER-4

A Regioselective Ring Nitration of *N*-Alkyl Anilines Using *Tert*-Butyl Nitrite Under Mild Condition

4.1	Introduction	129
4.2	Results and Discussions	131
4.2.1	Optimization for <i>N</i> -nitrosation nitration under different reaction conditions	131
4.3	Substrate Scope	134
4.3.1	<i>N</i> -Nitrosation nitration of <i>N</i> -alkyl anilines	134
4.3.2	Synthesis of <i>N</i> -alkyl nitroanilines <i>via</i> denitrosation	138
4.3.3	Synthesis of <i>N</i> -substituted <i>o</i> -phenylenediamines	142
4.4	Control Experiments and Plausible Mechanism	145
4.5	Conclusion	148
4.6	Experimental Section	148
4.6.1	General procedure for the synthesis of <i>N</i> -alkyl <i>N</i> -nitroso nitroanilines	148
4.6.2	General procedure for the denitrosation of <i>N</i> -alkyl <i>N</i> -nitroso nitroanilines	149
4.6.3	General procedure for the denitrosation followed by reduction of nitro group in <i>N</i> -alkyl <i>N</i> -nitroso nitroanilines	149
4.7	Analytical Data of Products	150
4.8	Spectral Data for Few Products	212

4.9	References	215
-----	------------	-----

CHAPTER-5

A Metal Free Reduction of Aryl-*N*-Nitrosamines to the Corresponding Hydrazines Using a Sustainable Reductant Thiourea Dioxide

5.1	Introduction	216
5.2	Results and Discussions	221
	5.2.1 Optimization for reduction of <i>N</i> -nitrosamines	223
	5.2.2 Substrate scope	225
	5.2.3 Comparative study of current protocol with the previous approach	227
5.3	One-Pot Synthesis of Aryl- <i>N</i> -hydrazines	229
5.4	Plausible Mechanism	231
5.5	Conclusion	232
5.6	Experimental Section	232
	5.6.1 Experimental procedure for the reduction of <i>N</i> -nitrosamines	233
5.7	Analytical Data of Products	227
5.8	Spectral Data for few Products	246
5.9	References	247

CHAPTER-6

Summary and Conclusions

6.1	Summary and Conclusions	250
	List of Research Publications	255