Volume 41:
Nitro, Nitroso, Azo, Azoxy, and Diazonium Compounds, Azides, Triazenes, and Tetrazenes

Preface ........................................................................ V

Volume Editor’s Preface ........................................ VII

Table of Contents ................................................... XI

Introduction
K. Banert .................................................................. 1

41.1 Product Class 1: Nitroalkanes
R. A. Aitken and K. M. Aitken ............................................. 9

41.2 Product Class 2: Nitrosoalkanes and Nitroso Acetals (N,N-Dialkoxyamines)
H.-U. Reissig, B. Dugović, and R. Zimmer .................................. 259

41.3 Product Class 3: N-Nitroamines
U. Jahn .................................................................... 371

41.4 Product Class 4: N-Nitrosoamines
M. M. K. Boysen ........................................................... 437

41.5 Product Class 5: Aliphatic Azoxy Compounds (Aliphatic Diazene Oxides)
M. M. K. Boysen ........................................................... 449

41.6 Product Class 6: Aliphatic Azo Compounds
S. Kempa, L. Wallach, and K. Rück-Braun .................................. 459

41.7 Product Class 7: Diazonium Compounds
S. Kubik ................................................................... 507

41.8 Product Class 8: Azidoalkanes
S. Bräse, B. Lesch, and V. Zimmermann ................................. 543

41.9 Product Class 9: Alkyltriazenes
N. Jung and S. Bräse ..................................................... 613

41.10 Product Class 10: Alkyltetrazenes
N. Jung and S. Bräse ..................................................... 641

41.11 Product Class 11: N,N-Dihaloamines
S. J. Collier and W. Xiang .................................................. 651

Keyword Index ........................................................... 681

Author Index .............................................................. 721

Abbreviations ............................................................. 765
# Table of Contents

## Introduction

K. Banert

### Introduction

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

## 41.1 Product Class 1: Nitroalkanes

R. A. Aitken and K. M. Aitken

### 41.1 Product Class 1: Nitroalkanes

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9</td>
</tr>
</tbody>
</table>

#### 41.1.1 Synthesis by Substitution

<table>
<thead>
<tr>
<th>Variation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>14</td>
</tr>
</tbody>
</table>

#### 41.1.2 Method 2: Substitution of Hydrogen Using Metal Nitrates

<table>
<thead>
<tr>
<th>Variation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
</tr>
</tbody>
</table>

#### 41.1.3 Method 3: Substitution of Hydrogen Using Sulfuric Acid and Ammonium Nitrate

<table>
<thead>
<tr>
<th>Variation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
</tr>
</tbody>
</table>

#### 41.1.4 Method 4: Substitution of Hydrogen Using Nitrogen Dioxide

<table>
<thead>
<tr>
<th>Variation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>17</td>
</tr>
</tbody>
</table>

#### 41.1.5 Method 5: Substitution of Hydrogen Using Sodium Nitrite and Silver(I) Nitrate

<table>
<thead>
<tr>
<th>Variation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
</tr>
</tbody>
</table>

#### 41.1.6 Method 6: Substitution of Hydrogen Using Alkyl Nitrates

<table>
<thead>
<tr>
<th>Variation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
</tr>
</tbody>
</table>

#### 41.1.7 Method 7: Substitution of Hydrogen Using Alkyl Nitrates with a Base

<table>
<thead>
<tr>
<th>Variation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
</tr>
</tbody>
</table>

#### 41.1.8 Method 8: Substitution of Hydrogen Using 2,4,6-Trichloro-N-nitroaniline

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>20</td>
</tr>
</tbody>
</table>

#### 41.1.9 Method 9: Substitution of Lithium

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>20</td>
</tr>
</tbody>
</table>

#### 41.1.10 Method 10: Substitution of Potassium

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

#### 41.1.11 Method 11: Substitution of Magnesium

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>20</td>
</tr>
</tbody>
</table>

#### 41.1.12 Method 12: Substitution of Mercury

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>21</td>
</tr>
</tbody>
</table>

#### 41.1.13 Method 13: Substitution of a Carboxy Group

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>21</td>
</tr>
</tbody>
</table>
41.1.1.14 Method 14: Substitution of a Cyano Group ........................................ 22
41.1.1.15 Method 15: Substitution of Chlorine Using Sodium Nitrite ................. 22
41.1.1.15.1 Variation 1: Without Additional Reagents .................................. 23
41.1.1.15.2 Variation 2: With Urea .................................................. 23
41.1.1.15.3 Variation 3: With Benzene-1,3,5-triol ................................... 24
41.1.1.16 Method 16: Substitution of Chlorine Using Potassium Nitrite ............... 24
41.1.1.16.1 Variation 1: In the Presence of a Base ................................... 24
41.1.1.16.2 Variation 2: With Crown Ethers .......................................... 25
41.1.1.17 Method 17: Substitution of Chlorine Using Silver(I) Nitrite ................. 25
41.1.1.17.1 Variation 1: Without Additional Reagents ................................ 25
41.1.1.17.2 Variation 2: With Urea .................................................. 26
41.1.1.18 Method 18: Substitution of Chlorine Using Mercury(I) Nitrite .............. 27
41.1.1.19 Method 19: Substitution of Chlorine Using Polymer-Supported Nitrite .... 27
41.1.1.20 Method 20: Substitution of Bromine Using Sodium Nitrite ................... 27
41.1.1.20.1 Variation 1: Without Additional Reagents ................................ 27
41.1.1.20.2 Variation 2: With Benzene-1,2-diol ...................................... 29
41.1.1.20.3 Variation 3: With Benzene-1,3,5-triol ................................... 29
41.1.1.20.4 Variation 4: With Urea .................................................. 31
41.1.1.20.5 Variation 5: With Urea and Benzene-1,3,5-triol .......................... 32
41.1.1.20.6 Variation 6: With a Phase-Transfer Catalyst ................................ 34
41.1.1.20.7 Variation 7: With an Ionic Liquid ......................................... 34
41.1.1.21 Method 21: Substitution of Bromine Using Potassium Nitrite ............... 34
41.1.1.22 Method 22: Substitution of Bromine Using Silver(I) Nitrite ................. 35
41.1.1.23 Method 23: Substitution of Bromine Using Ammonium Nitrites .......... 38
41.1.1.24 Method 24: Substitution of Bromine Using Polymer-Supported Nitrite .... 39
41.1.1.25 Method 25: Substitution of Iodine Using Sodium Nitrite .................... 39
41.1.1.25.1 Variation 1: Without Additional Reagents ................................ 40
41.1.1.25.2 Variation 2: With Benzene-1,3,5-triol ................................... 41
41.1.1.25.3 Variation 3: With Urea .................................................. 41
41.1.1.25.4 Variation 4: With Urea and Benzene-1,3,5-triol .......................... 42
41.1.1.26 Method 26: Substitution of Iodine Using Silver(I) Nitrite .................. 43
41.1.1.27 Method 27: Substitution of Iodine Using Ammonium Nitrites .............. 46
41.1.1.28 Method 28: Substitution of Iodine Using Polymer-Supported Nitrite ....... 46
41.1.1.29 Method 29: Substitution of Sulfates ........................................ 46
41.1.1.30 Method 30: Substitution of Sulfonates ...................................... 47
41.1.1.31 Method 31: Substitution of Oxonium Tetrafluoroborates .................... 48
41.1.1.32 Method 32: Substitution of Nitrogen in Azo Compounds .................... 48
41.1.1.33 Method 33: Oxidation of a Primary Amino Group Using Caro’s Acid .... 49
41.1.1.34 Method 34: Oxidation of a Primary Amino Group Using Hypofluorous Acid ................................................................. 49
41.1.1.35 Method 35: Oxidation of a Primary Amino Group Using Organic Peroxides ................................................................. 50
41.1.1.36 Method 36: Oxidation of a Primary Amino Group Using tert-Butyl Hydroperoxide and Chromium Silicalite ................................. 52
<table>
<thead>
<tr>
<th>Method</th>
<th>Variation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.1.2.3</td>
<td>Variation 3</td>
<td>Using tert-Butyl Hydroperoxide and Zirconium(IV) tert-Butoxide</td>
</tr>
<tr>
<td>41.1.2.3</td>
<td>Variation 4</td>
<td>Using Oxaziridinium Salts</td>
</tr>
<tr>
<td>41.1.2.4</td>
<td>Method 4</td>
<td>Oxidation of a Primary Amino Group Using Organic Peroxy Acids</td>
</tr>
<tr>
<td>41.1.2.4.1</td>
<td>Variation 1</td>
<td>Using Peracetic Acid</td>
</tr>
<tr>
<td>41.1.2.4.2</td>
<td>Variation 2</td>
<td>Using 3-Chloroperoxybenzoic Acid</td>
</tr>
<tr>
<td>41.1.2.5</td>
<td>Method 5</td>
<td>Oxidation of a Primary Amino Group Using Ozone</td>
</tr>
<tr>
<td>41.1.2.6</td>
<td>Method 6</td>
<td>Oxidation of an Azido Group Using Hypofluorous Acid</td>
</tr>
<tr>
<td>41.1.2.7</td>
<td>Method 7</td>
<td>Oxidation of an Azido Group Using Ozone and a Phosphine</td>
</tr>
<tr>
<td>41.1.2.8</td>
<td>Method 8</td>
<td>Oxidation of a Hydroxyamino Group Using Nitric Acid</td>
</tr>
<tr>
<td>41.1.2.8.1</td>
<td>Variation 1</td>
<td>Without Additional Reagents</td>
</tr>
<tr>
<td>41.1.2.8.2</td>
<td>Variation 2</td>
<td>With Ammonium Nitrate</td>
</tr>
<tr>
<td>41.1.2.9</td>
<td>Method 9</td>
<td>Oxidation of a Hydroxyamino Group Using Potassium Permanganate in Sulfuric Acid</td>
</tr>
<tr>
<td>41.1.2.10</td>
<td>Method 10</td>
<td>Oxidation of a Nitroso Group Using Nitric Acid</td>
</tr>
<tr>
<td>41.1.2.10.1</td>
<td>Variation 1</td>
<td>With Ammonium Nitrate</td>
</tr>
<tr>
<td>41.1.2.10.2</td>
<td>Variation 2</td>
<td>With Acetic Acid</td>
</tr>
<tr>
<td>41.1.2.11</td>
<td>Method 11</td>
<td>Oxidation of a Nitroso Group Using Hydrogen Peroxide</td>
</tr>
<tr>
<td>41.1.2.11.1</td>
<td>Variation 1</td>
<td>Without Additional Reagents</td>
</tr>
<tr>
<td>41.1.2.11.2</td>
<td>Variation 2</td>
<td>With Sulfuric Acid</td>
</tr>
<tr>
<td>41.1.2.12</td>
<td>Method 12</td>
<td>Oxidation of a Nitroso Group Using Manganese(VII)</td>
</tr>
<tr>
<td>41.1.2.12.1</td>
<td>Variation 1</td>
<td>Using Potassium Permanganate in Acetone</td>
</tr>
<tr>
<td>41.1.2.12.2</td>
<td>Variation 2</td>
<td>Using Manganese(VII) Oxide</td>
</tr>
<tr>
<td>41.1.2.13</td>
<td>Method 13</td>
<td>Oxidation of a Nitroso Group Using Chromium(VI)</td>
</tr>
<tr>
<td>41.1.2.13.1</td>
<td>Variation 1</td>
<td>Using Chromium(VI) Oxide Alone</td>
</tr>
<tr>
<td>41.1.2.13.2</td>
<td>Variation 2</td>
<td>Using Chromium(VI) Oxide and Acetic Acid</td>
</tr>
<tr>
<td>41.1.2.13.3</td>
<td>Variation 3</td>
<td>Using Chromium(VI) Oxide with Acetic and Sulfuric Acids</td>
</tr>
<tr>
<td>41.1.2.14</td>
<td>Method 14</td>
<td>Oxidation of a Nitroso Group Using Lead(IV) Oxide</td>
</tr>
<tr>
<td>41.1.2.15</td>
<td>Method 15</td>
<td>Oxidation of a Nitroso Group Using Oxidizing Gases</td>
</tr>
<tr>
<td>41.1.2.15.1</td>
<td>Variation 1</td>
<td>Using Air</td>
</tr>
<tr>
<td>41.1.2.15.2</td>
<td>Variation 2</td>
<td>Using Oxygen</td>
</tr>
<tr>
<td>41.1.2.15.3</td>
<td>Variation 3</td>
<td>Using Nitrogen Dioxide/Dinitrogen Tetroxide</td>
</tr>
<tr>
<td>41.1.2.16</td>
<td>Method 16</td>
<td>Oxidation of a Nitroso Group Using Organic Peroxy Acids</td>
</tr>
<tr>
<td>41.1.2.16.1</td>
<td>Variation 1</td>
<td>Using Trifluoroperoxyacetic Acid</td>
</tr>
<tr>
<td>41.1.2.16.2</td>
<td>Variation 2</td>
<td>Using 3-Chloroperoxybenzoic Acid</td>
</tr>
<tr>
<td>41.1.2.17</td>
<td>Method 17</td>
<td>Photochemical Oxidation of a Nitroso Group</td>
</tr>
<tr>
<td>41.1.2.18</td>
<td>Method 18</td>
<td>Oxidation of a Nitroso Group Using Iodosylbenzene</td>
</tr>
<tr>
<td>41.1.2.19</td>
<td>Method 19</td>
<td>Oxidation of an Oxime Group Using Nitric Acid</td>
</tr>
<tr>
<td>41.1.2.19.1</td>
<td>Variation 1</td>
<td>Without Other Reagents</td>
</tr>
<tr>
<td>41.1.2.19.2</td>
<td>Variation 2</td>
<td>With Sulfuric Acid</td>
</tr>
<tr>
<td>41.1.2.20</td>
<td>Method 20</td>
<td>Oxidation of an Oxime Group Using Peroxysulfates</td>
</tr>
<tr>
<td>41.1.2.20.1</td>
<td>Variation 1</td>
<td>Using Caro’s Acid</td>
</tr>
<tr>
<td>41.1.2.20.2</td>
<td>Variation 2</td>
<td>Using Oxone</td>
</tr>
<tr>
<td>Method Number</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>41.1.2.21</td>
<td>Oxidation of an Oxime Group Using Hydrogen Peroxide with Urea and Methyltrioxorhenium(VII) Catalyst</td>
<td></td>
</tr>
<tr>
<td>41.1.2.22</td>
<td>Oxidation of an Oxime Group Using Lead(IV) Acetate</td>
<td></td>
</tr>
<tr>
<td>41.1.2.23</td>
<td>Oxidation of an Oxime Group with Potassium Permanganate</td>
<td></td>
</tr>
<tr>
<td>41.1.2.24</td>
<td>Oxidation of an Oxime Group with Sodium Perborate</td>
<td></td>
</tr>
<tr>
<td>41.1.2.25</td>
<td>Oxidation of an Oxime Group Using Organic Peroxy Acids</td>
<td></td>
</tr>
<tr>
<td>41.1.2.25.1</td>
<td>Variation 1: Using Trifluoroper oxyacetic Acid</td>
<td></td>
</tr>
<tr>
<td>41.1.2.25.2</td>
<td>Variation 2: Using 3-Chloroper oxybenzoic Acid</td>
<td></td>
</tr>
<tr>
<td>41.1.2.26</td>
<td>Oxidation of an Oxime Group Using Dinitrogen Tetroxide</td>
<td></td>
</tr>
<tr>
<td>41.1.2.27</td>
<td>Enzymatic Oxidation of an Oxime Group</td>
<td></td>
</tr>
<tr>
<td>41.1.3.1</td>
<td>Oxidative Nitrosation of an Oxime Group</td>
<td></td>
</tr>
<tr>
<td>41.1.3.2</td>
<td>Oxidative Nitration of an Oxime Using Nitric Acid</td>
<td></td>
</tr>
<tr>
<td>41.1.3.2.1</td>
<td>Variation 1: Without Additional Reagents</td>
<td></td>
</tr>
<tr>
<td>41.1.3.2.2</td>
<td>Variation 2: Followed by Hydrogen Peroxide</td>
<td></td>
</tr>
<tr>
<td>41.1.3.2.3</td>
<td>Variation 3: With Acetic Acid, Followed by Hydrogen Peroxide</td>
<td></td>
</tr>
<tr>
<td>41.1.3.3</td>
<td>Oxidative Nitration of an Oxime Using Nitrogen Oxides</td>
<td></td>
</tr>
<tr>
<td>41.1.3.3.1</td>
<td>Variation 1: Using Nitrogen Dioxide/Dinitrogen Tetroxide</td>
<td></td>
</tr>
<tr>
<td>41.1.3.3.2</td>
<td>Variation 2: Using Nitrogen Dioxide and Magnesium Sulfate</td>
<td></td>
</tr>
<tr>
<td>41.1.3.3.3</td>
<td>Variation 3: Using Dinitrogen Pentoxide</td>
<td></td>
</tr>
<tr>
<td>41.1.3.4</td>
<td>Oxidative Chlorination of an Oxime Using Chlorine</td>
<td></td>
</tr>
<tr>
<td>41.1.3.4.1</td>
<td>Variation 1: Using Chlorine Followed by Ozone</td>
<td></td>
</tr>
<tr>
<td>41.1.3.4.2</td>
<td>Variation 2: Using Chlorine with Hydrochloric, Nitric, and Acetic Acids</td>
<td></td>
</tr>
<tr>
<td>41.1.3.5</td>
<td>Oxidative Chlorination of an Oxime Using Sodium Hypochlorite</td>
<td></td>
</tr>
<tr>
<td>41.1.3.6</td>
<td>Oxidative Chlorination of an Oxime Using Sodium Chloride, Oxone, and Alumina</td>
<td></td>
</tr>
<tr>
<td>41.1.3.7</td>
<td>Oxidative Chlorination of an Oxime Using Hydrochloric Acid and Hydrogen Peroxide</td>
<td></td>
</tr>
<tr>
<td>41.1.3.8</td>
<td>Oxidative Bromination of an Oxime Using Sodium Hypobromite Followed by Nitric Acid</td>
<td></td>
</tr>
<tr>
<td>41.1.3.9</td>
<td>Oxidative Bromination of an Oxime Using N-Bromoacetamide</td>
<td></td>
</tr>
<tr>
<td>41.1.3.10</td>
<td>Oxidative Bromination of an Oxime Using N-Bromosuccinimide and Potassium Carbonate</td>
<td></td>
</tr>
<tr>
<td>41.1.3.11</td>
<td>Oxidative Bromination of an Oxime Using Sodium Bromide, Oxone, and Alumina</td>
<td></td>
</tr>
<tr>
<td>41.1.3.12</td>
<td>Oxidative Acetoxylation of an Oxime Using Lead(IV) Acetate, Hydrogen Peroxide, and Sodium Nitrite</td>
<td></td>
</tr>
<tr>
<td>41.1.3.13</td>
<td>Addition of Nitrous Acid to an Alkene</td>
<td></td>
</tr>
<tr>
<td>41.1.3.13.1</td>
<td>Variation 1: Using Sodium Nitrite and Acetic Acid</td>
<td></td>
</tr>
<tr>
<td>41.1.3.13.2</td>
<td>Variation 2: Using Sodium Nitrite and Hydrochloric Acid</td>
<td></td>
</tr>
<tr>
<td>41.1.3.14</td>
<td>Addition of Tetranitromethane to an Alkene</td>
<td></td>
</tr>
</tbody>
</table>
41.1.3.15 Method 15: Nitrofluorination of an Alkene ........................................ 84
41.1.3.15.1 Variation 1: Using Nitric and Hydrofluoric Acids .......................... 84
41.1.3.15.2 Variation 2: Using Nitril Fluoride ........................................... 85
41.1.3.15.3 Variation 3: Using Nitronium Tetrafluoroborate and Pyridinium Fluoride ........................................ 85
41.1.3.16 Method 16: Nitrochlorination of an Alkene ................................... 86
41.1.3.16.1 Variation 1: Using Nitrosyl Chloride ....................................... 86
41.1.3.16.2 Variation 2: Using Nitrosyl Chloride, Nitrogen Dioxide, and Oxygen ........................................ 87
41.1.3.16.3 Variation 3: Using Nitril Chloride ........................................... 88
41.1.3.16.4 Variation 4: Using Nitrogen Dioxide and Boron Trifluoride .......... 89
41.1.3.16.5 Variation 5: Using Nitrogen Dioxide and Chlorine ....................... 89
41.1.3.16.6 Variation 6: Using Nitrogen Dioxide, Phosphorus Trichloride, and Oxygen ........................................ 90
41.1.3.17 Method 17: Nitrobromination of an Alkene .................................. 90
41.1.3.17.1 Variation 1: Using Sodium Nitrite, Mercury(II) Chloride, and Bromine ... 90
41.1.3.17.2 Variation 2: Using Nitrosyl Bromide ....................................... 91
41.1.3.17.3 Variation 3: Using Nitrogen Dioxide and Bromine ...................... 92
41.1.3.17.4 Variation 4: Using Nitrogen Dioxide, Phosphorus Tribromide, and Oxygen ........................................ 92
41.1.3.18 Method 18: Nitroiodination of an Alkene ..................................... 92
41.1.3.18.1 Variation 1: Using Silver(I) Nitrite and Iodine ............................ 92
41.1.3.18.2 Variation 2: Using Nitrogen Dioxide and Iodine ......................... 93
41.1.3.19 Method 19: Nitroacetamidation of an Alkene ................................ 94
41.1.3.20 Method 20: Nitronitrosation of an Alkene (Synthesis of \( \gamma \)-Nitrosites) ... 94
41.1.3.20.1 Variation 1: Using Sodium Nitrite and Sulfuric Acid .................... 95
41.1.3.20.2 Variation 2: Using Sodium Nitrite and Hydrochloric Acid ............ 96
41.1.3.20.3 Variation 3: Using Sodium Nitrite and Acetic Acid ..................... 96
41.1.3.20.4 Variation 4: Using Sodium Nitrite and Phosphoric Acid .............. 97
41.1.3.20.5 Variation 5: Using Nitric Oxide with Catalysts .......................... 97
41.1.3.20.6 Variation 6: Using Nitric Oxide with Air ................................ 98
41.1.3.21 Method 21: 1,2-Dinitration of an Alkene ..................................... 99
41.1.3.21.1 Variation 1: Using Pentyl Nitrite and Acetic Acid ...................... 99
41.1.3.21.2 Variation 2: Using Nitrogen Dioxide ...................................... 99
41.1.3.21.3 Variation 3: Using Nitrogen Dioxide and Oxygen ....................... 101
41.1.3.22 Method 22: Nitrohydroxylation of an Alkene ................................ 101
41.1.3.22.1 Variation 1: Using Nitric Acid ............................................. 101
41.1.3.22.2 Variation 2: Using Nitric and Sulfuric Acids ............................ 102
41.1.3.22.3 Variation 3: Using Sodium Nitrate and Ammonium Cerium(IV) Nitrate ........................................ 102
41.1.3.22.4 Variation 4: Using Dinitrogen Trioxide ................................... 103
41.1.3.22.5 Variation 5: Using Nitrogen Dioxide ...................................... 103
41.1.3.22.6 Variation 6: Using Organic Nitrating Agents ............................ 104
41.1.3.23 Method 23: Nitromethoxylation of an Alkene Using Tetranitromethane and Methanol ........................................ 105
41.1.3.24 Method 24: Addition of a Nitro Group and a Nitrate Group to an Alkene ........................................ 105
### 1.3.24 Method 24: Nitroacetoxylation of an Alkene

#### 1.3.24.1 Variation 1: Using Nitric Acid

105

#### 1.3.24.2 Variation 2: Using Nitrogen Dioxide and Oxygen

105

#### 1.3.24.3 Variation 3: Using Dinitrogen Pentoxide

106

### 1.3.25 Method 25: Nitroacetoxylation of an Alkene

#### 1.3.25.1 Variation 1: Using Acetyl Nitrate

108

#### 1.3.25.2 Variation 2: Using Nitric and Sulfuric Acids Followed by Acetic Anhydride

109

### 1.3.26 Method 26: Addition of a Nitro Group and a Perchlorate Group to an Alkene

109

### 1.3.27 Method 27: Addition of a Nitro Group and an Ethyl Sulfate Group to an Alkene

110

### 1.3.28 Method 28: Conversion of Alkenes into \(-\)Nitro Ketones

#### 1.3.28.1 Variation 1: Using Nitrogen Dioxide and Oxygen in Dimethyl Sulfoxide

110

#### 1.3.28.2 Variation 2: Using Chlorotrimethylsilane, Silver(I) Nitrate, and Chromium(VI) Oxide

111

#### 1.3.28.3 Variation 3: Using Chlorotrimethylsilane, Silver(I) Nitrate, and Dimethyl Sulfoxide

112

### 1.3.29 Method 29: Nitration of Silyl Enol Ethers

#### 1.3.29.1 Variation 1: Using Tetranitromethane

112

#### 1.3.29.2 Variation 2: Using Nitronium Ethyl Sulfate

113

### 1.3.30 Method 30: Destructive Nitration

113

### 1.4 Synthesis by Rearrangement or Disproportionation

#### 1.4.1 Method 1: Rearrangement of Alkyl Nitrates

115

#### 1.4.2 Method 2: Disproportionation Reactions

116

### 1.5 Synthesis with Retention of the Nitro Group

#### 1.5.1 Method 1: Alkylation of Nitroalkanes with Alkyl Halides

117

#### 1.5.1.1 Variation 1: With Fluoroalkanes

117

#### 1.5.1.2 Variation 2: With Chloroalkanes

117

#### 1.5.1.3 Variation 3: With Bromoalkanes

119

#### 1.5.1.4 Variation 4: With Iodoalkanes

121

#### 1.5.2 Method 2: Alkylation of Nitroalkanes with Alkylammonium Salts

122

#### 1.5.3 Method 3: Alkylation of Nitroalkanes with Alkyl(phenyl)iodonium Reagents

122

#### 1.5.4 Method 4: Alkylation of Nitroalkanes with Alkyl Arenesulfonates

123

#### 1.5.5 Method 5: Alkylation of Nitroalkanes with Alkyl Aryl Sulfones

124

#### 1.5.6 Method 6: Alkylation of Nitroalkanes with Hydrates or Hemiacetals of Aldehydes

125

#### 1.5.7 Method 7: Alkylation of Nitroalkanes with Alkyl Azides

126

#### 1.5.8 Method 8: Alkylation of Nitroalkanes with an Alkyl Difluoromethyl Nitrite

126

#### 1.5.9 Method 9: Vinylation of Nitroalkanes

126

#### 1.5.10 Method 10: Arylation of Nitroalkanes

127

#### 1.5.11 Method 11: Allylation of Nitroalkanes

129

#### 1.5.11.1 Variation 1: Nucleophilic Substitution

129

#### 1.5.11.2 Variation 2: Palladium-Catalyzed Allylation

131
41.1.5.12 Method 12: Reaction of Nitroalkyl Anions with Aldehydes and Ketones (Henry Reaction) ................................... 133
41.1.5.13 Method 13: Aza-Henry Reaction ......................................... 137
41.1.5.14 Method 14: Reaction of Nitroalkyl Anions with Carboxylic and Carbonic Acid Derivatives ................................... 139
41.1.5.14.1 Variation 1: With Acid Halides ........................................... 139
41.1.5.14.2 Variation 2: With Esters ................................................. 140
41.1.5.14.3 Variation 3: With Anhydrides ............................................ 140
41.1.5.14.4 Variation 4: With Carbonates ............................................ 141
41.1.5.14.5 Variation 5: With Carbamoyl Chlorides .................................. 141
41.1.5.14.6 Variation 6: With Isatoic Anhydride ...................................... 142
41.1.5.14.7 Variation 7: With Benzotriazole Derivatives .............................. 142
41.1.5.15 Method 15: Reaction of Nitroalkyl Anions with Reactive Alkenes Not Conjugated to a Carbonyl Group ..................... 143
41.1.5.16 Method 16: Reaction of Nitroalkyl Anions with Alkylmercury Compounds ......................................................... 144
41.1.5.17 Method 17: Substitution of Chlorine in α-Chloronitroalkanes by a Carbanion Prepared from a Ketone ............................. 144
41.1.5.18 Method 18: Substitution of Chlorine in α-Chloronitroalkanes by a Carbanion Prepared from a Nitroalkane ..................... 145
41.1.5.19 Method 19: Substitution of Chlorine in α-Chloronitroalkanes by a Carbanion Prepared from a Malonate ......................... 146
41.1.5.20 Method 20: Substitution of Chlorine in α-Chloronitroalkanes by a Carbanion Prepared from a 3-Oxo Ester ....................... 147
41.1.5.21 Method 21: Substitution of Chlorine in α-Chloronitroalkanes by a Carbanion Prepared from a 1,3-Diketone ....................... 148
41.1.5.22 Method 22: Substitution of Chlorine in α-Chloronitroalkanes by a Carbanion Prepared from a Nitrile ........................... 149
41.1.5.23 Method 23: Substitution of Chlorine in α-Chloronitroalkanes by a Carbanion Prepared from an (Alkoxycarbonyl)methyl Aryl Sulfone ..................................................... 149
41.1.5.24 Method 24: Substitution of Chlorine in α-Chloronitroalkanes by an Alkynyllithium Reagent ........................................... 149
41.1.5.25 Method 25: Substitution of Chlorine in α-Chloronitroalkanes by an Organotin(IV) Reagent ............................................. 150
41.1.5.26 Method 26: Substitution of Bromine in α-Bromonitroalkanes by a Carbanion Prepared from a Nitroalkane ...................... 150
41.1.5.27 Method 27: Substitution of Bromine in α-Bromonitroalkanes by a Carbanion Prepared from a Malonate ......................... 151
41.1.5.28 Method 28: Substitution of Bromine in α-Bromonitroalkanes by a Carbanion Prepared from a Nitrile ........................... 151
41.1.5.29 Method 29: Substitution of Bromine in α-Bromonitroalkanes by a Carbanion Prepared from a 3-Oxo Nitrile ...................... 152
41.1.5.30 Method 30: Substitution of Bromine in α-Bromonitroalkanes by a Carbanion Prepared from a 2-Cyano Ester ...................... 152
41.1.5.31 Method 31: Substitution of Bromine in α-Bromonitroalkanes by a Carbanion Prepared from an α-Cyanoalkyl Sulfone ........ 153
<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.1.5.32</td>
<td>Method 32</td>
<td>Substitution of Bromine in α-Bromonitroalkanes by a Carbanion Prepared from a Malononitrile</td>
</tr>
<tr>
<td>41.1.5.33</td>
<td>Method 33</td>
<td>Substitution of Bromine in α-Bromonitroalkanes by an Organotin(IV) Reagent</td>
</tr>
<tr>
<td>41.1.5.34</td>
<td>Method 34</td>
<td>Substitution of Iodine in α-Iodonitroalkanes by a Carbanion Prepared from a Nitroalkane</td>
</tr>
<tr>
<td>41.1.5.35</td>
<td>Method 35</td>
<td>Substitution of an Arylsulfonyl Group or Arylsulfanyl Group in Nitroalkanes by Carbon Nucleophiles</td>
</tr>
<tr>
<td>41.1.5.36</td>
<td>Method 36</td>
<td>Substitution of a Nitro Group in Geminal Dinitroalkanes by Carbon Nucleophiles</td>
</tr>
<tr>
<td>41.1.5.37</td>
<td>Method 37</td>
<td>Dimerization of Nitroalkanes</td>
</tr>
<tr>
<td>41.1.5.37.1</td>
<td>Variation 1</td>
<td>Starting from Nitroalkanes</td>
</tr>
<tr>
<td>41.1.5.37.2</td>
<td>Variation 2</td>
<td>Starting from Halonitroalkanes</td>
</tr>
<tr>
<td>41.1.5.38</td>
<td>Method 38</td>
<td>Decarboxylation of 2-Nitro Acids</td>
</tr>
<tr>
<td>41.1.5.39</td>
<td>Method 39</td>
<td>Dehalogenation of α-Halonitroalkanes</td>
</tr>
<tr>
<td>41.1.5.39.1</td>
<td>Variation 1</td>
<td>Using Potassium Hydroxide</td>
</tr>
<tr>
<td>41.1.5.39.2</td>
<td>Variation 2</td>
<td>Using Sodium Borohydride</td>
</tr>
<tr>
<td>41.1.5.39.3</td>
<td>Variation 3</td>
<td>Using Catalytic Hydrogenation</td>
</tr>
<tr>
<td>41.1.5.39.4</td>
<td>Variation 4</td>
<td>Using Tributyltin Hydride</td>
</tr>
<tr>
<td>41.1.5.40</td>
<td>Method 40</td>
<td>Desulfonilation of Nitro Sulfones</td>
</tr>
<tr>
<td>41.1.5.41</td>
<td>Method 41</td>
<td>Catalytic Reduction of Nitroalkenes</td>
</tr>
<tr>
<td>41.1.5.42</td>
<td>Method 42</td>
<td>Borohydride Reduction of Nitroalkenes</td>
</tr>
<tr>
<td>41.1.5.42.1</td>
<td>Variation 1</td>
<td>Using Sodium Borohydride</td>
</tr>
<tr>
<td>41.1.5.42.2</td>
<td>Variation 2</td>
<td>Using Lithium Borohydride</td>
</tr>
<tr>
<td>41.1.5.42.3</td>
<td>Variation 3</td>
<td>Using Zinc Borohydride</td>
</tr>
<tr>
<td>41.1.5.42.4</td>
<td>Variation 4</td>
<td>Using Sodium Trimethoxyborohydride</td>
</tr>
<tr>
<td>41.1.5.43</td>
<td>Method 43</td>
<td>Reduction of Nitroalkenes with Lithium Aluminum Hydride</td>
</tr>
<tr>
<td>41.1.5.44</td>
<td>Method 44</td>
<td>Enantioselective Reduction of Nitroalkenes with Silanes</td>
</tr>
<tr>
<td>41.1.5.45</td>
<td>Method 45</td>
<td>Reduction of Nitroalkenes Using Biological and Biomimetic Reducing Agents</td>
</tr>
<tr>
<td>41.1.5.46</td>
<td>Method 46</td>
<td>Hydrocyanation of a Nitroalkene Using Hydrogen Cyanide</td>
</tr>
<tr>
<td>41.1.5.47</td>
<td>Method 47</td>
<td>Hydrocyanation of a Nitroalkene Using Potassium Cyanide</td>
</tr>
<tr>
<td>41.1.5.48</td>
<td>Method 48</td>
<td>Addition to a Nitroalkene by Electrophilic Aromatic Substitution</td>
</tr>
<tr>
<td>41.1.5.49</td>
<td>Method 49</td>
<td>Addition to a Nitroalkene Using a Carbanion Prepared from an Aldehyde</td>
</tr>
<tr>
<td>41.1.5.50</td>
<td>Method 50</td>
<td>Addition to a Nitroalkene Using a Carbanion Prepared from a Ketone</td>
</tr>
<tr>
<td>41.1.5.51</td>
<td>Method 51</td>
<td>Addition to a Nitroalkene Using a Carbanion Prepared from an Ester</td>
</tr>
<tr>
<td>41.1.5.52</td>
<td>Method 52</td>
<td>Addition to a Nitroalkene Using a Carbanion Prepared from a Nitrile</td>
</tr>
<tr>
<td>Method</td>
<td>Addition to a Nitroalkene Using a Carbanion</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>Prepared from an Amide ........................</td>
<td>182</td>
</tr>
<tr>
<td>54</td>
<td>Prepared from a 1,3-Diester .................</td>
<td>184</td>
</tr>
<tr>
<td>55</td>
<td>Prepared from a 1,3-Diketone ................</td>
<td>189</td>
</tr>
<tr>
<td>56</td>
<td>Prepared from a 3-Oxo Ester ................</td>
<td>191</td>
</tr>
<tr>
<td>57</td>
<td>Prepared from a 2-Cyano Ester ...............</td>
<td>194</td>
</tr>
<tr>
<td>58</td>
<td>Prepared from a Dinitrile ....................</td>
<td>195</td>
</tr>
<tr>
<td>59</td>
<td>Prepared from a Thioester ...................</td>
<td>195</td>
</tr>
<tr>
<td>60</td>
<td>Prepared from a (2,2,6,6-Tetramethylpiperidin-1-yloxycarbonyl)alkane</td>
<td>196</td>
</tr>
<tr>
<td>61</td>
<td>Prepared from a 1,3-Oxazine .................</td>
<td>196</td>
</tr>
<tr>
<td>62</td>
<td>Prepared from a Silyl Enol Ether ............</td>
<td>197</td>
</tr>
<tr>
<td>63</td>
<td>Prepared from an Isocyanide ................</td>
<td>205</td>
</tr>
<tr>
<td>64</td>
<td>Prepared from a Nitroalkane ................</td>
<td>206</td>
</tr>
<tr>
<td>65</td>
<td>Prepared from a 2-Nitro Ester ...............</td>
<td>207</td>
</tr>
<tr>
<td>66</td>
<td>Prepared from an (\alpha)-Cyano-(\alpha)-nitro Ester</td>
<td>208</td>
</tr>
<tr>
<td>67</td>
<td>Prepared from Organophosphorus Reagents ....</td>
<td>208</td>
</tr>
<tr>
<td>68</td>
<td>Prepared from Organolithium Reagent .........</td>
<td>210</td>
</tr>
<tr>
<td>69</td>
<td>Prepared from Organomagnesium Reagents ....</td>
<td>211</td>
</tr>
<tr>
<td>70</td>
<td>Prepared from Alkylmagnesium Chlorides .....</td>
<td>211</td>
</tr>
<tr>
<td>71</td>
<td>Prepared from Alkylmagnesium Bromides ......</td>
<td>212</td>
</tr>
<tr>
<td>72</td>
<td>Prepared from Alkylmagnesium Iodides ......</td>
<td>213</td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>Addition to a Nitroalkene Using an Alkylsamarium(II) Bromide</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>Addition to a Nitroalkene Using an Alkylmanganese(II) Chloride</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>Addition to a Nitroalkene Using an Alkylcopper Reagent</td>
<td></td>
</tr>
<tr>
<td>74.1</td>
<td>Variation 1: Using Alkylcoppers</td>
<td></td>
</tr>
<tr>
<td>74.2</td>
<td>Variation 2: Using Halozinc Alkylcyanocuprates</td>
<td></td>
</tr>
<tr>
<td>74.3</td>
<td>Variation 3: Using Alkylzinc Alkylcyanocuprates</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>Addition to a Nitroalkene Using an Organozinc Reagent</td>
<td></td>
</tr>
<tr>
<td>75.1</td>
<td>Variation 1: Using Alkylzinc Chlorides</td>
<td></td>
</tr>
<tr>
<td>75.2</td>
<td>Variation 2: Using Alkylzinc Bromides</td>
<td></td>
</tr>
<tr>
<td>75.3</td>
<td>Variation 3: Using Dialkylzincs</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>Addition to a Nitroalkene Using an Arylboronic Acid</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>Addition to a Nitroalkene Using an Alkylaluminum Reagent</td>
<td></td>
</tr>
<tr>
<td>77.1</td>
<td>Variation 1: Using Trialkylaluminums</td>
<td></td>
</tr>
<tr>
<td>77.2</td>
<td>Variation 2: Using Tetraalkylaluminates</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>Addition to a Nitroalkene Using a Lithium Tetraalkylgallate</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>Addition to a Nitroalkene Using Triethoxy(phenyl)silane</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>Addition to a Nitroalkene Using a Tetraalkylstannane</td>
<td></td>
</tr>
<tr>
<td>81</td>
<td>Addition to a Nitroalkene Using Dialkyl Phosphites</td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>[2 + 2]-Cycloaddition Reactions of Nitroalkenes</td>
<td></td>
</tr>
<tr>
<td>82.1</td>
<td>Variation 1: With Another Nitroalkene</td>
<td></td>
</tr>
<tr>
<td>82.2</td>
<td>Variation 2: With Enamines</td>
<td></td>
</tr>
<tr>
<td>82.3</td>
<td>Variation 3: With Tetramethoxyethene</td>
<td></td>
</tr>
<tr>
<td>83</td>
<td>[3 + 2]-Cycloaddition Reactions of Nitroalkenes</td>
<td></td>
</tr>
<tr>
<td>83.1</td>
<td>Variation 1: With Diazocompounds</td>
<td></td>
</tr>
<tr>
<td>83.2</td>
<td>Variation 2: With Methylene cyclopropanes</td>
<td></td>
</tr>
<tr>
<td>83.3</td>
<td>Variation 3: With Azides</td>
<td></td>
</tr>
<tr>
<td>83.4</td>
<td>Variation 4: With Azomethine Ylides</td>
<td></td>
</tr>
<tr>
<td>83.5</td>
<td>Variation 5: With Enamino Ketones</td>
<td></td>
</tr>
<tr>
<td>83.6</td>
<td>Variation 6: With Nitrones</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>[2 + 4]-Cycloaddition Reactions of Nitroalkenes with Dienes</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>Rearrangements in the Synthesis of Nitroalkanes from Other Nitro Compounds</td>
<td></td>
</tr>
<tr>
<td>85.1</td>
<td>Variation 1: Baylis–Hillman Reaction</td>
<td></td>
</tr>
<tr>
<td>85.2</td>
<td>Variation 2: Disproportionation</td>
<td></td>
</tr>
<tr>
<td>85.3</td>
<td>Variation 3: Thio-Claisen Rearrangement</td>
<td></td>
</tr>
<tr>
<td>85.4</td>
<td>Variation 4: Cope Rearrangement</td>
<td></td>
</tr>
</tbody>
</table>
41.2 Product Class 2: Nitrosoalkanes and Nitroso Acetals (N,N-Dialkoxyamines)  
H.-U. Reissig, B. Dugović, and R. Zimmer

41.2.1 Synthesis of Product Class 2  .................................................. 259

41.2.1.1 Method 1: Substitution Reactions  ........................................ 259

41.2.1.1.1 Variation 1: Substitution of a Hydrogen Atom in Nonactivated 
Compounds  ........................................................................ 260

41.2.1.1.2 Variation 2: Substitution of a Hydrogen Atom in Halogenated 
Compounds  ........................................................................ 260

41.2.1.1.3 Variation 3: Substitution of a Hydrogen Atom in Acceptor-Substituted 
Compounds  ........................................................................ 261

41.2.1.1.4 Variation 4: Substitution of Other Functional Groups  ............ 263

41.2.1.1.5 Variation 5: Substitution of Metals  ....................................... 264

41.2.1.2 Method 2: Addition Reactions  ........................................... 265

41.2.1.2.1 Variation 1: Addition to Alkenes  ....................................... 265

41.2.1.2.2 Variation 2: Addition to Electron-Rich Aromatic Compounds  .... 269

41.2.1.3 Method 3: Elimination Reactions and Pyrolysis  ..................... 269

41.2.1.4 Method 4: Oxidation Reactions  .......................................... 272

41.2.1.4.1 Variation 1: Oxidation of Amines  ....................................... 272

41.2.1.4.2 Variation 2: Oxidation of Hydroxylamines  ......................... 275

41.2.1.4.3 Variation 3: Oxidation of Cyclic Nitrogen Compounds  .......... 276

41.2.1.5 Method 5: Reduction of Nitroalkanes  .................................. 280

41.2.1.6 Method 6: Photochemical Reactions  ................................... 280

41.2.1.7 Method 7: Rearrangements  .................................................. 284

41.2.1.8 Method 8: Conversions of Oximes  ....................................... 285

41.2.1.9 Method 9: Derivatization of Stable Nitrosoalkanes  ................ 296

41.2.1.10 Method 10: Synthesis of Metal-Coordinated Nitrosoalkanes .... 299

41.2.1.11 Method 11: Synthesis of Nitroso Acetals  .......................... 302

41.2.2 Applications of Product Class 2 in Organic Synthesis  ............... 308

41.2.2.1 Method 1: Oxidation to Nitroalkanes  .................................. 308

41.2.2.2 Method 2: Reduction to Amines  ......................................... 311

41.2.2.3 Method 3: Formation of Oximes and Derivatives  .................. 316

41.2.2.3.1 Variation 1: Formation of Oximes  .................................... 316

41.2.2.3.2 Variation 2: Formation of Oxime Ethers and Phosphates ......... 323

41.2.2.3.3 Variation 3: Formation of Hydroxamic Acid Derivatives .......... 325

41.2.2.4 Method 4: Synthesis of Compounds with an N=X Functionality  
(X = C, N, P)  ........................................................................ 327

41.2.2.4.1 Variation 1: Synthesis of Nitrones  ..................................... 327

41.2.2.4.2 Variation 2: Synthesis of Azoxy Compounds  ...................... 327

41.2.2.4.3 Variation 3: Synthesis of Other N=X Compounds  
(Imines and Azo Compounds)  ................................................. 329

41.2.2.4.4 Variation 4: Synthesis of N=P Compounds  ......................... 330

41.2.2.5 Method 5: Conversion into Nitrosoalkenes  ........................... 331
<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.2.6</td>
<td>Method 6:</td>
<td>Synthesis of Heterocycles</td>
<td>332</td>
</tr>
<tr>
<td>41.2.6.1</td>
<td>Variation 1:</td>
<td>Synthesis of Four-Membered Heterocycles</td>
<td>332</td>
</tr>
<tr>
<td>41.2.6.2</td>
<td>Variation 2:</td>
<td>Synthesis of Five-Membered Heterocycles</td>
<td>334</td>
</tr>
<tr>
<td>41.2.6.3</td>
<td>Variation 3:</td>
<td>Synthesis of Six-Membered Heterocycles</td>
<td>338</td>
</tr>
<tr>
<td>41.2.7</td>
<td>Method 7:</td>
<td>Synthesis of α-Carbonyl Hydroxylamines and N-Allyl Hydroxylamines</td>
<td>347</td>
</tr>
<tr>
<td>41.2.8</td>
<td>Method 8:</td>
<td>Reactions of Nitroso Acetals</td>
<td>352</td>
</tr>
<tr>
<td>41.3</td>
<td>Product Class 3:</td>
<td>N-Nitroamines</td>
<td>371</td>
</tr>
<tr>
<td>41.3.1</td>
<td>Product Subclass 1:</td>
<td>N-Alkyl-N-nitroamines</td>
<td>373</td>
</tr>
<tr>
<td>41.3.1.1</td>
<td>Synthesis of Product Subclass 1</td>
<td></td>
<td>373</td>
</tr>
<tr>
<td>41.3.1.2</td>
<td>Method 1:</td>
<td>Nitration of Amines with Cyanohydrin Nitrates</td>
<td>373</td>
</tr>
<tr>
<td>41.3.1.3</td>
<td>Method 2:</td>
<td>Nitration of Lithium Amides</td>
<td>374</td>
</tr>
<tr>
<td>41.3.1.4</td>
<td>Method 3:</td>
<td>Decacylation of N-Acyl-N-nitroamines and Related Reactions</td>
<td>374</td>
</tr>
<tr>
<td>41.3.1.5</td>
<td>Variation 1:</td>
<td>Of N-Nitrocarbamates</td>
<td>374</td>
</tr>
<tr>
<td>41.3.1.6</td>
<td>Variation 2:</td>
<td>Of N-Nitroureas</td>
<td>377</td>
</tr>
<tr>
<td>41.3.1.7</td>
<td>Variation 3:</td>
<td>Of N-Nitroguanidines</td>
<td>379</td>
</tr>
<tr>
<td>41.3.1.8</td>
<td>Variation 4:</td>
<td>Of N-Nitroamides</td>
<td>381</td>
</tr>
<tr>
<td>41.3.1.9</td>
<td>Variation 5:</td>
<td>Of N-Nitrosulfonamides</td>
<td>382</td>
</tr>
<tr>
<td>41.3.1.10</td>
<td>Method 4:</td>
<td>Substitution of N,N-Dichloroamines</td>
<td>383</td>
</tr>
<tr>
<td>41.3.1.11</td>
<td>Method 5:</td>
<td>Reduction of N-Nitroimines</td>
<td>384</td>
</tr>
<tr>
<td>41.3.1.12</td>
<td>Method 6:</td>
<td>Cleavage of Alkyl Groups in N,N-Dialkyl-N-nitroamines</td>
<td>386</td>
</tr>
<tr>
<td>41.3.2</td>
<td>Product Subclass 2:</td>
<td>N-Aryl-N-nitroamines</td>
<td>387</td>
</tr>
<tr>
<td>41.3.2.1</td>
<td>Synthesis of Product Subclass 2</td>
<td></td>
<td>388</td>
</tr>
<tr>
<td>41.3.2.2</td>
<td>Method 1:</td>
<td>Nitration of Anilines</td>
<td>388</td>
</tr>
<tr>
<td>41.3.2.3</td>
<td>Method 2:</td>
<td>Nitration of Metal Anilides</td>
<td>395</td>
</tr>
<tr>
<td>41.3.2.4</td>
<td>Method 3:</td>
<td>Decacylation of N-Acyl-N-nitroanilines</td>
<td>395</td>
</tr>
<tr>
<td>41.3.2.5</td>
<td>Method 4:</td>
<td>Oxidation of (E)-Diazenolates</td>
<td>396</td>
</tr>
<tr>
<td>41.3.3</td>
<td>Product Subclass 3:</td>
<td>N-Nitro-N-vinylamines</td>
<td>397</td>
</tr>
<tr>
<td>41.3.3.1</td>
<td>Synthesis of Product Subclass 3</td>
<td></td>
<td>397</td>
</tr>
<tr>
<td>41.3.3.2</td>
<td>Method 1:</td>
<td>Isomerization of N-Nitroimines</td>
<td>397</td>
</tr>
<tr>
<td>41.3.4</td>
<td>Product Subclass 4:</td>
<td>N,N-Dialkyl-N-nitroamines</td>
<td>399</td>
</tr>
<tr>
<td>41.3.4.1</td>
<td>Synthesis of Product Subclass 4</td>
<td></td>
<td>399</td>
</tr>
<tr>
<td>41.3.4.2</td>
<td>Method 1:</td>
<td>Nitration of Amines</td>
<td>399</td>
</tr>
<tr>
<td>41.3.4.3</td>
<td>Variation 1:</td>
<td>Using Nitric Acid</td>
<td>399</td>
</tr>
<tr>
<td>41.3.4.4</td>
<td>Variation 2:</td>
<td>Using Dinitrogen Pentoxide or Dinitrogen Tetroxide</td>
<td>403</td>
</tr>
<tr>
<td>41.3.4.5</td>
<td>Variation 3:</td>
<td>Using Cyanohydrin Nitrates</td>
<td>404</td>
</tr>
<tr>
<td>41.3.4.6</td>
<td>Variation 4:</td>
<td>Using Mesitylcarbonyl Nitrate</td>
<td>405</td>
</tr>
<tr>
<td>41.3.4.7</td>
<td>Variation 5:</td>
<td>Using Nitronium Salts</td>
<td>405</td>
</tr>
</tbody>
</table>
41.3.4.1.1.6 Variation 6: Using N-Methyl-N,N-dinitroamine ................................. 406
41.3.4.1.2 Method 2: Nitrolysis of Amides .................................................. 406
41.3.4.1.2.1 Variation 1: Using Nitric Acid ................................................ 406
41.3.4.1.2.2 Variation 2: Using Dinitrogen Pentoxide ...................................... 408
41.3.4.1.2.3 Variation 3: Using Nitronium Salts ............................................. 408
41.3.4.1.3 Method 3: Nitration of Sulfamates ............................................. 409
41.3.4.1.4 Method 4: Substitution of tert-Butylamines .................................. 409
41.3.4.1.5 Method 5: Nitroso Group Exchange by Nitration ................................ 410
41.3.4.1.6 Method 6: Alkylation of N-Alkyl-N-nitroamines ............................. 411
41.3.4.1.6.1 Variation 1: Using Alkyl, Allyl, and Benzyl Halides, Dimethyl Sulfate, Activated Alcohols, or Activated Amines ................................. 411
41.3.4.1.6.2 Variation 2: Using Diazoalkanes ............................................. 415
41.3.4.1.7 Method 7: Radical Cyclizations of N-Alkyl-N-nitroamines .............. 416
41.3.5 Product Subclass 5: N-Alkyl-N-aryl-N-nitroamines .............................. 417
41.3.5.1 Synthesis of Product Subclass 5 ..................................................... 417
41.3.5.1.1 Method 1: Nitration of N-Alkylanilines ...................................... 417
41.3.5.1.2 Method 2: Nitration of N,N-Dialkylanilines .................................. 422

41.4 Product Class 4: N-Nitrosoamines

41.4.1 Synthesis of Product Class 4 .............................................................. 438
41.4.1.1 Formation of the N—N Bond .......................................................... 438
41.4.1.1.1 Method 1: Nitrosation with Sodium Nitrite and Acids .................... 438
41.4.1.1.1.1 Variation 1: Nitrosation with Sodium Nitrite and Aqueous Acids ................................. 438
41.4.1.1.1.2 Variation 2: Nitrosation with Sodium Nitrite and Solid Acids ............ 439
41.4.1.1.2 Method 2: Nitrosation with Nitrogen Oxides ................................. 439
41.4.1.1.3 Method 3: Nitrosation with Nitrosyl Chloride ................................. 440
41.4.1.1.4 Method 4: Nitrosation with Nitrosonium Tetrafluoroborate .............. 441
41.4.1.1.5 Method 5: Nitrosation with Alkyl Nitrites .................................... 442
41.4.1.1.6 Method 6: Dealkylating Nitrosation of Tertiary Amines .................... 443
41.4.1.2 Formation of C—C Bonds .............................................................. 443
41.4.1.2.1 Method 1: α-Alkylation of N-Nitrosoamines .................................. 443
41.4.1.2.2 Method 2: Alkylation of Diazlenolates ........................................ 445
41.4.1.3 Formation and Cleavage of N—O Bonds ........................................... 446
41.4.1.3.1 Method 1: Reduction of N-Nitroamines ....................................... 446
41.4.1.3.2 Method 2: Oxidation of 1,1-Disubstituted Hydrazines ..................... 446
41.5  
**Product Class 5: Aliphatic Azoxy Compounds (Aliphatic Diazene Oxides)**
M. M. K. Boysen

41.5.1  
Synthesis of Product Class 5  

41.5.1.1  
Formation or Cleavage of N—O Bonds  

41.5.1.2  
Method 2: Oxidation of Hydrazones

41.5.1.3  
Method 3: Oxidation of Hydrazines

41.5.1.4  
Method 4: Reduction of Dimeric Nitroso Compounds  

41.5.1.5  
Formation of the N=N Bond

41.5.1.6  
Method 1: Condensation of Hydroxylamines with Dimeric Nitroso Compounds

41.5.1.7  
Method 2: Condensation of N,N-Dihaloamines with Nitroso Compounds

41.5.1.8  
Method 3: Oxidation of Hydroxylamines

41.5.1.9  
Formation of the C—N Bond

41.5.1.10  
Method 1: Alkylation of Diazonolates

41.6  
**Product Class 6: Aliphatic Azo Compounds**
S. Kempa, L. Wallach, and K. Rück-Braun

41.6.1  
Synthesis by Formation of the N=N Bond

41.6.1.1  
Method 1: Oxidative Coupling of Primary Amines

41.6.1.2  
Method 2: Condensation of Nitrosoalkanes with Alkylamines

41.6.1.3  
Method 3: Rearrangement of N,N'-Dialkylsulfamides

41.6.1.4  
Variation 1: Rearrangement of N,N'-Dialkylureas

41.6.2  
Synthesis from Compounds Containing an N—N Bond

41.6.2.1  
Method 1: Oxidation of 1,2-Dialkylhydrazines

41.6.2.2  
Variation 1: From Corresponding Ketazines

41.6.2.3  
Method 2: Oxidation with Peracetic Acid

41.6.2.4  
Method 3: Oxidation with (Diacetoxyiodo)benzene

41.6.2.5  
Method 4: Oxidation of Ketazines with Lead(IV) Acetate

41.6.2.6  
Method 5: Alkylation of Alkylhydrazones

41.6.2.7  
Method 6: Isomerization of Alkylhydrazones

41.6.2.8  
Method 7: Hydrogenation of Ketazines

41.6.2.9  
Method 8: Chlorination of Ketazines
41.6.9 Method 9: Ring Opening of Heterocycles ............................... 497
41.6.10 Method 10: [2,3]-Sigmatropic Rearrangement of
1-Alkyl-1-allyldiazenes and 1-Alkyl-1-propargyldiazenes 500
41.6.11 Method 11: Reactions of 2-Diazo 1,3-Diketones with CH-Acidic
Compounds 501
41.6.12 Synthesis by Other Methods 502

41.7 Product Class 7: Diazonium Compounds
S. Kubik

41.7.1 Product Subclass 1: Alkanediazonium Compounds 507
41.7.1.1 Synthesis of Product Subclass 1 509
41.7.1.1.1 Method 1: Synthesis from Primary Amines 509
41.7.1.1.1.1 Variation 1: With Nitrous Acid 509
41.7.1.1.1.2 Variation 2: With Disodium Pentacyanonitrosylferrate(III) 510
41.7.1.1.1.3 Variation 3: With Alkyl Nitrites 510
41.7.1.1.1.4 Variation 4: With Nitrosyl Chloride 511
41.7.1.1.1.5 Variation 5: With Dinitrogen Tetroxide 511
41.7.1.1.2 Method 2: Synthesis from Triazenes 511
41.7.1.1.3 Method 3: Synthesis from N-Nitrosoamides 512
41.7.1.1.3.1 Variation 1: By Thermolysis 512
41.7.1.1.3.2 Variation 2: By Alkali Cleavage 513
41.7.1.1.4 Method 4: Synthesis from Diazoalkanes 514
41.7.1.1.5 Method 5: Miscellaneous Methods 514

41.7.2 Product Subclass 2: Alkenediazonium Compounds 514
41.7.2.1 Synthesis of Product Subclass 2 517
41.7.2.1.1 Method 1: Synthesis from Diazoalkanes 517
41.7.2.1.2 Method 2: Synthesis from 2-Diazocarbonyl Compounds 517
41.7.2.1.2.1 Variation 1: By O-Alkylation 518
41.7.2.1.2.2 Variation 2: By O-Sulfonylation or O-Benzoylation 520
41.7.2.1.3 Method 3: Synthesis from Hydrazones 521
41.7.2.1.3.1 Variation 1: From Aldehyde Hydrazones 522
41.7.2.1.3.2 Variation 2: From Ketone Hydrazones 524
41.7.2.1.4 Method 4: Synthesis from Alk-1-enyl Derivatives 525
41.7.2.1.4.1 Variation 1: From Enamines 525
41.7.2.1.4.2 Variation 2: From Alk-1-enyl Isocyanates 527
41.7.2.1.4.3 Variation 3: From Alk-1-enyltriazenes 528
41.7.2.1.4.4 Variation 4: From 1-(Tosylazo)alk-1-enes 529
41.7.2.1.5 Method 5: Synthesis from N-Nitrosooxazolidin-2-ones 529
41.7.2.1.6 Method 6: Synthesis from Other Alkenediazonium Compounds 531
41.7.2.2 Applications of Product Subclass 2 in Organic Synthesis 534
41.7.2.2.1 Method 1: Synthesis of Pyrazoles 534
41.7.2.2.2 Method 2: Synthesis of 1H-1,2,3-Triazoles 535
### Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.7.2.3</td>
<td>Method 3: Synthesis of 6H-1,3,4-Oxadiazines and 1,3,4-Oxadiazoles</td>
<td>536</td>
</tr>
<tr>
<td>41.7.2.4</td>
<td>Method 4: Synthesis of 2-Diazoimines</td>
<td>536</td>
</tr>
</tbody>
</table>

---

#### 41.8 Product Class 8: Azidoalkanes
S. Bräse, B. Lesch, and V. Zimmermann

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.8</td>
<td>Method 1: Synthesis from Benzyl Ethers or Related Compounds by Radical Substitution (C–H Activation)</td>
<td>543</td>
</tr>
<tr>
<td>41.8.1</td>
<td>Method 2: Synthesis from Carboxylic Acids by Azidative Decarboxylation</td>
<td>544</td>
</tr>
<tr>
<td>41.8.1.3</td>
<td>Method 3: Synthesis from Alkyl Halides by Radical Substitution</td>
<td>545</td>
</tr>
<tr>
<td>41.8.1.4</td>
<td>Method 4: Synthesis by Nucleophilic Substitution of Alkyl Halides</td>
<td>545</td>
</tr>
<tr>
<td>41.8.1.4.1</td>
<td>Variation 1: Classical Synthesis</td>
<td>545</td>
</tr>
<tr>
<td>41.8.1.4.2</td>
<td>Variation 2: Asymmetric Synthesis</td>
<td>548</td>
</tr>
<tr>
<td>41.8.1.4.3</td>
<td>Variation 3: 1,3-Substitution in Allyl Halides</td>
<td>550</td>
</tr>
<tr>
<td>41.8.1.5</td>
<td>Method 5: Synthesis by Nucleophilic Substitution of Alkyl Esters and Related Compounds</td>
<td>551</td>
</tr>
<tr>
<td>41.8.1.5.1</td>
<td>Variation 1: Classical Synthesis</td>
<td>551</td>
</tr>
<tr>
<td>41.8.1.5.2</td>
<td>Variation 2: Asymmetric Synthesis</td>
<td>554</td>
</tr>
<tr>
<td>41.8.1.6</td>
<td>Method 6: Synthesis by Nucleophilic Substitution of Alkanols and Related Compounds</td>
<td>556</td>
</tr>
<tr>
<td>41.8.1.6.1</td>
<td>Variation 1: Classical Synthesis</td>
<td>556</td>
</tr>
<tr>
<td>41.8.1.6.2</td>
<td>Variation 2: Asymmetric Synthesis</td>
<td>560</td>
</tr>
<tr>
<td>41.8.1.7</td>
<td>Method 7: Synthesis from Acetals</td>
<td>566</td>
</tr>
<tr>
<td>41.8.1.8</td>
<td>Method 8: Synthesis by Ring Opening of Epoxides, Aziridines, and Related Compounds</td>
<td>567</td>
</tr>
<tr>
<td>41.8.1.8.1</td>
<td>Variation 1: Classical Synthesis</td>
<td>567</td>
</tr>
<tr>
<td>41.8.1.8.2</td>
<td>Variation 2: Asymmetric Synthesis</td>
<td>577</td>
</tr>
<tr>
<td>41.8.1.9</td>
<td>Method 9: Electrophilic Azidation</td>
<td>578</td>
</tr>
<tr>
<td>41.8.1.10</td>
<td>Method 10: Synthesis by Addition to C=C Bonds</td>
<td>580</td>
</tr>
<tr>
<td>41.8.1.10.1</td>
<td>Variation 1: Nucleophilic Hydroazidation of C=C Bonds</td>
<td>580</td>
</tr>
<tr>
<td>41.8.1.10.2</td>
<td>Variation 2: Electrophilic Hydroazidation of C=C Bonds</td>
<td>581</td>
</tr>
<tr>
<td>41.8.1.10.3</td>
<td>Variation 3: Radical Hydroazidation of C=C Bonds</td>
<td>584</td>
</tr>
<tr>
<td>41.8.1.10.4</td>
<td>Variation 4: Carboazidation of C=C Bonds</td>
<td>585</td>
</tr>
<tr>
<td>41.8.1.10.5</td>
<td>Variation 5: Haloazidation of C=C Bonds</td>
<td>585</td>
</tr>
<tr>
<td>41.8.1.10.6</td>
<td>Variation 6: Azidoselanylazidation of C=C Bonds</td>
<td>590</td>
</tr>
<tr>
<td>41.8.1.11</td>
<td>Method 11: Synthesis by Addition to C=X Bonds</td>
<td>590</td>
</tr>
<tr>
<td>41.8.1.12</td>
<td>Method 12: Synthesis from Amines by Nitrogen Transfer</td>
<td>590</td>
</tr>
<tr>
<td>41.8.1.13</td>
<td>Method 13: Synthesis with Retention of Azide Functionality</td>
<td>591</td>
</tr>
<tr>
<td>41.8.2</td>
<td>Applications of Product Class 8 in Organic Synthesis</td>
<td>594</td>
</tr>
<tr>
<td>41.8.2.1</td>
<td>Method 1: Reactions with All-Carbon Functional Groups</td>
<td>594</td>
</tr>
<tr>
<td>41.8.2.1.1</td>
<td>Variation 1: [3 + 2]-Cycloaddition Reactions</td>
<td>594</td>
</tr>
<tr>
<td>Section</td>
<td>Method</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>41.8.2.2</td>
<td>Method 2:</td>
<td>Hydrogenation and Reactions with Heteroatom-Containing Groups</td>
</tr>
<tr>
<td>41.8.2.2.1</td>
<td>Variation 1:</td>
<td>Reduction to Amines</td>
</tr>
<tr>
<td>41.8.2.2.2</td>
<td>Variation 2:</td>
<td>Schmidt and Boyer Reactions</td>
</tr>
<tr>
<td>41.8.2.2.3</td>
<td>Variation 3:</td>
<td>Staudinger Reductions</td>
</tr>
<tr>
<td>41.8.2.2.4</td>
<td>Variation 4:</td>
<td>Staudinger Ligations</td>
</tr>
<tr>
<td>41.8.2.2.5</td>
<td>Variation 5:</td>
<td>Aza-Wittig Reactions</td>
</tr>
<tr>
<td>41.8.2.2.6</td>
<td>Variation 6:</td>
<td>Miscellaneous Reactions</td>
</tr>
<tr>
<td>41.9</td>
<td>Product Class 9:</td>
<td>Alkyltriazenes</td>
</tr>
<tr>
<td>41.9.1</td>
<td>Synthesis of Product Class 9</td>
<td></td>
</tr>
<tr>
<td>41.9.1.1</td>
<td>Method 1:</td>
<td>Alkylation of Alkyl Azides</td>
</tr>
<tr>
<td>41.9.1.1.1</td>
<td>Variation 1:</td>
<td>By Grignard Reagents</td>
</tr>
<tr>
<td>41.9.1.1.2</td>
<td>Variation 2:</td>
<td>By Lithium Reagents</td>
</tr>
<tr>
<td>41.9.1.1.3</td>
<td>Method 2:</td>
<td>Alkylation or Acylation of Aryl- or Alkyltriazenes</td>
</tr>
<tr>
<td>41.9.1.1.2.1</td>
<td>Variation 1:</td>
<td>Alkylation</td>
</tr>
<tr>
<td>41.9.1.1.2.2</td>
<td>Variation 2:</td>
<td>Acylation</td>
</tr>
<tr>
<td>41.9.1.1.3</td>
<td>Method 3:</td>
<td>Reaction of Arenediazonium Salts with Primary Amines</td>
</tr>
<tr>
<td>41.9.1.2</td>
<td>Method 4:</td>
<td>Reaction of Diazonium Salts with Secondary Amines</td>
</tr>
<tr>
<td>41.9.1.2.1.1</td>
<td>Variation 1:</td>
<td>Diazotization of Arylamines and Reaction with Secondary Amines</td>
</tr>
<tr>
<td>41.9.1.2.2</td>
<td>Variation 2:</td>
<td>Preparation of Bistriazenes of Secondary Amines</td>
</tr>
<tr>
<td>41.9.1.2.4</td>
<td>Variation 4:</td>
<td>Preparation of Imidazolytriazenes</td>
</tr>
<tr>
<td>41.9.1.2.5</td>
<td>Variation 5:</td>
<td>Preparation of Indol-3-yltriazenes</td>
</tr>
<tr>
<td>41.9.1.2.6</td>
<td>Variation 6:</td>
<td>Preparation of Pyrrol-3-yltriazenes</td>
</tr>
<tr>
<td>41.9.1.2.7</td>
<td>Variation 7:</td>
<td>Preparation of Pyridyltriazenes</td>
</tr>
<tr>
<td>41.9.1.2.8</td>
<td>Variation 8:</td>
<td>Preparation of Pyrazolyltriazenes/Indazolyltriazenes</td>
</tr>
<tr>
<td>41.9.1.2.9</td>
<td>Variation 9:</td>
<td>Preparation of Acyl(alkyl)triazenes</td>
</tr>
<tr>
<td>41.9.1.3</td>
<td>Method 5:</td>
<td>Synthesis from N'‑Alkyl‑N‑aryl‑N‑nitrosoureas</td>
</tr>
<tr>
<td>41.9.1.3.1</td>
<td>Variation 1:</td>
<td>With Primary Amines/Secondary Amines</td>
</tr>
<tr>
<td>41.9.1.3.2</td>
<td>Variation 2:</td>
<td>By Decomposition</td>
</tr>
<tr>
<td>41.9.1.4</td>
<td>Method 6:</td>
<td>Synthesis from Nitroso‑Containing Compounds with Alkylhydrazines</td>
</tr>
<tr>
<td>41.9.1.5</td>
<td>Method 7:</td>
<td>Reaction of Arenediazonium Salts with Primary Amines and Formaldehde</td>
</tr>
<tr>
<td>41.9.1.6</td>
<td>Method 8:</td>
<td>Reaction of Arenediazonium Salts with Diamines and Formaldehde</td>
</tr>
<tr>
<td>41.9.1.7</td>
<td>Method 9:</td>
<td>Synthesis by Ring Opening of Cyclic Compounds</td>
</tr>
<tr>
<td>41.9.1.8</td>
<td>Variation 1:</td>
<td>Ring Opening of Triaziridines</td>
</tr>
<tr>
<td>41.9.1.9</td>
<td>Variation 2:</td>
<td>Ring Opening to 3-Alkyl-1-aryltriazenes</td>
</tr>
<tr>
<td>41.9.1.9.3</td>
<td>Variation 3:</td>
<td>Ring Opening of Spiro cyclic Triazoles</td>
</tr>
</tbody>
</table>
41.9.4 Variation 4: Ring Opening of Benzotriazoles ............................. 634
41.9.2 Applications of Product Class 9 in Organic Synthesis .................... 635

41.10 Product Class 10: Alkyltetrazenes
N. Jung and S. Bräse

41.10 Product Class 10: Alkyltetrazenes ........................................ 641
41.10.1 Product Subclass 1: Tetraz-1-enes .................................. 641
41.10.1.1 Synthesis of Product Subclass 1 ........................................ 641
41.10.1.1.1 Method 1: Reaction of 1,1-Dialkylhydrazines with Diazonium Chlorides ........................................ 641
41.10.2 Product Subclass 2: Tetraz-2-enes .................................. 642
41.10.2.1 Synthesis of Product Subclass 2 ........................................ 642
41.10.2.1.1 Method 1: Symmetrical Oxidative Dimerization of Hydrazines ............................... 642
41.10.2.1.2 Method 2: Tetrazenes from \( N \)-Nitrosoamines .................. 645
41.10.2.1.3 Method 3: Dimerization of Diazenes Generated from Amines .... 645
41.10.2.1.4 Method 4: Dimerization of Diazenes Generated from Hydrazones .... 646
41.10.2.1.5 Method 5: Synthesis of Unsymmetrical Tetrazenes ................. 646
41.10.2.1.6 Method 6: Synthesis of Tetrazenes from Cyclic Precursors ......... 647
41.10.2.1.7 Method 7: Synthesis of Vinyltetrazenes ............................... 648

41.11 Product Class 11: \( N,N \)-Dihaloamines
S. J. Collier and W. Xiang

41.11 Product Class 11: \( N,N \)-Dihaloamines ........................................ 651
41.11.1 Product Subclass 1: \( N,N \)-Difluoroamines ............................. 651
41.11.1.1 Synthesis of Product Subclass 1 ........................................ 653
41.11.1.1.1 Method 1: Direct Fluorination of Amines and Related Reactions ...... 653
41.11.1.1.2 Method 2: Difluoroamination of Carbon Skeletons ..................... 655
41.11.1.1.2.1 Variation 1: With Tetrafluorohydrazine .......................... 655
41.11.1.1.1.2 Variation 2: With Difluoroamine and Related Reagents .......... 659
41.11.1.1.1.3 Method 3: Other Methods ............................................. 662
41.11.1.2 Product Subclass 2: \( N,N \)-Dichloroamines ............................ 663
41.11.1.2.1 Synthesis of Product Subclass 2 ........................................ 665
41.11.1.2.1.1 Method 1: Direct Chlorination of Amines ............................ 665
41.11.1.2.1.2 Method 2: Chlorination of Nitriles and Related Reactions .......... 666
41.11.1.2.1.3 Method 3: Dichloroamination of Carbon Skeletons .................. 668
41.11.1.2.1.4 Method 4: Other Methods ............................................. 669
41.11.1.3 Product Subclass 3: \( N,N \)-Dibromoamines ............................... 669
41.11.1.3.1 Synthesis of Product Subclass 3 ........................................ 670
41.11.1.3.1.1 Method 1: Direct Bromination of Amines ............................ 670