Volume 24: Three Carbon—Heteroatom Bonds: Ketene Acetals and Yne—X Compounds

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

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

Table of Contents .................................................. XV

Introduction
A. de Meijere ............................................................. 1

24.1 Product Class 1: 1,1-Bis(heteroatom-functionalized) Allenes

24.1.1 Product Subclass 1: 1,1-Dihaloallenes
R. R. Kostikov ............................................................. 17

24.1.2 Product Subclass 2: 1-Halo-1-(organooxy)allenes
R. Zimmer .................................................................. 37

24.1.3 Product Subclass 3: 1-Halo-1-(organochalcogeno)allenes and 1-Halo-1-(organochalcogeno)butatrienes
R. Zimmer .................................................................. 39

24.1.4 Product Subclass 4: 1-Nitrogen-Functionalized 1-Haloallenes
R. Zimmer .................................................................. 43

24.1.5 Product Subclass 5: 1-Phosphorus-Functionalized 1-Haloallenes
R. Zimmer .................................................................. 45

24.1.6 Product Subclass 6: 1,1-Bis(organooxy)allenes, 1,1-Bis(organooxy)butatrienes, 1-(Organooxy)-1-siloxyallenes, and 1-(Organooxy)allen-1-olates
R. Zimmer .................................................................. 49

24.1.7 Product Subclass 7: 1-(Organochalcogeno)-1-(organooxy)allenes
R. Zimmer .................................................................. 55

24.1.8 Product Subclass 8: 1-Nitrogen-Functionalized 1-(Organooxy)allenes and Allen-1-olates
R. Zimmer .................................................................. 57

24.1.9 Product Subclass 9: 1-Phosphorus-Functionalized 1-(Organooxy)allenes and 1-Siloxyallenes
R. Zimmer .................................................................. 61
24.1.10 Product Subclass 10: 1,1-Bis(organochalcogeno)allenes and 1,1-Bis(organochalcogeno)butatrienes
R. Zimmer ............................................................... 63

24.1.11 Product Subclass 11: 1-Nitrogen-Functionalized 1-(Organochalcogeno)allenes
R. Zimmer ............................................................... 69

24.1.12 Product Subclass 12: 1-Phosphorus-Functionalized 1-(Organochalcogeno)allenes
R. Zimmer ............................................................... 73

24.1.13 Product Subclass 13: 1,1-Bis(nitrogen-functionalized) Allenes and Butatrienes
R. Zimmer ............................................................... 75

24.1.14 Product Subclass 14: 1-Nitrogen-Functionalized 1-Phosphorus-Functionalized Allenes
R. Zimmer ............................................................... 79

24.1.15 Product Subclass 15: 1,1-Bis(phosphorus-functionalized) Allenes
M. Stankević and K. M. Pietrusiewicz ....................................... 81

24.2 Product Class 2: 1,1-Bis(heteroatom-functionalized) Alk-1-enes

24.2.1 Product Subclass 1: 1,1-Dihaloalk-1-enes
R. R. Kostikov ............................................................. 85

24.2.2 Product Subclass 2: 1-Halo-1-(organooxy)alk-1-enes
A. P. Molchanov and R. R. Kostikov ......................................... 129

24.2.3 Product Subclass 3: 1-Halo-1-(organochalcogeno)alk-1-enes
A. F. Khlebnikov and R. R. Kostikov ......................................... 167

24.2.4 Product Subclass 4: 1-Nitrogen-Functionalized 1-Haloalk-1-enes
J. G. Schantl .............................................................. 223

24.2.5 Product Subclass 5: 1-Phosphorus-Functionalized 1-Haloalk-1-enes
M. Stankević and K. M. Pietrusiewicz ....................................... 285

24.2.6 Product Subclass 6: 1,1-Bis(organooxy)alk-1-enes
C. Schneider .............................................................. 293

24.2.7 Product Subclass 7: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes
W. Dölling ............................................................... 323

24.2.8 Product Subclass 8: 1-(Organooxy)-1-(organoselanyl)- and 1-(Organooxy)-1-(organotellanyl)alk-1-enes
W. Dölling ............................................................... 331
<table>
<thead>
<tr>
<th>Product Subclass</th>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Product Subclass 9: 1-Nitrogen-Functionalized 1-(Organooxy)alk-1-enes (Ketene O,N-Acetals)</td>
<td>W. Kantlehner</td>
<td>337</td>
</tr>
<tr>
<td>10</td>
<td>Product Subclass 10: 1-Phosphorus-Functionalized 1-(Organooxy)alk-1-enes</td>
<td>H. Heydt</td>
<td>441</td>
</tr>
<tr>
<td>11</td>
<td>Product Subclass 11: 1,1-Bis(organosulfanyl)alk-1-enes (Ketene S,S-Acetals)</td>
<td>W. Dölling</td>
<td>461</td>
</tr>
<tr>
<td>12</td>
<td>Product Subclass 12: 1-(Organoselanyl)-1-(organosulfanyl)alk-1-enes and 1-(Organosulfanyl)-1-(organotellanyl)alk-1-enes</td>
<td>M. Yoshimatsu</td>
<td>517</td>
</tr>
<tr>
<td>14</td>
<td>Product Subclass 14: 1-Phosphorus-Functionalized 1-(Organosulfanyl)alk-1-enes</td>
<td>J. Romanński, G. Mlostoń, and K. M. Pietrusiewicz</td>
<td>541</td>
</tr>
<tr>
<td>15</td>
<td>Product Subclass 15: 1,1-Bis(organoselanyl)alk-1-enes and Derivatives</td>
<td>M. Yoshimatsu</td>
<td>547</td>
</tr>
<tr>
<td>16</td>
<td>Product Subclass 16: 1,1-Bis(organotellanyl)alk-1-enes and Derivatives</td>
<td>M. Yoshimatsu</td>
<td>563</td>
</tr>
<tr>
<td>17</td>
<td>Product Subclass 17: 1,1-Bis(nitrogen-functionalized) Alk-1-enes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.1</td>
<td>Alk-1-ene-1,1-diamines</td>
<td>W. Kantlehner</td>
<td>571</td>
</tr>
<tr>
<td>17.2</td>
<td>Alk-1-ene-1,1-diamines with Retention of the Functional Group</td>
<td>P. A. Keller and J. Morgan</td>
<td>707</td>
</tr>
<tr>
<td>17.3</td>
<td>1,1-Bisazo-, 1,1-Diazido-, and 1,1-Dinitroalk-1-enes</td>
<td>K. Banert</td>
<td>747</td>
</tr>
<tr>
<td>18</td>
<td>Product Subclass 18: 1-Nitrogen-Functionalized 1-Phosphorus-Functionalized Alk-1-enes</td>
<td>M. Stankević and K. M. Pietrusiewicz</td>
<td>767</td>
</tr>
<tr>
<td>19</td>
<td>Product Subclass 19: 1,1-Bis(phosphorus-functionalized) Alk-1-enes</td>
<td>M. Stankević and K. M. Pietrusiewicz</td>
<td>775</td>
</tr>
<tr>
<td>Chapter</td>
<td>Product Class</td>
<td>Description</td>
<td>Authors</td>
</tr>
<tr>
<td>---------</td>
<td>--------------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>24.3</td>
<td>3: Bis(heteroatom-functionalized) Acetylenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.3.1</td>
<td>1: Dihaloacetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.3.2</td>
<td>2: 1-Heteroatom-Functionalized 2-Haloacetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.3.3</td>
<td>3: Bis(organooxy)acetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.3.4</td>
<td>4: 1-(Organochalcogeno)-2-(organooxy)acetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.3.5</td>
<td>5: 1-Nitrogen-Functionalized 2-(Organooxy)acetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.3.6</td>
<td>6: 1-Phosphorus-Functionalized 2-(Organooxy)acetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.3.7</td>
<td>7: Bis(organochalcogeno)acetylenes</td>
<td>T. Murai</td>
<td></td>
</tr>
<tr>
<td>24.3.8</td>
<td>8: 1-Nitrogen-Functionalized 2-(Organochalcogeno)acetylenes</td>
<td>T. Murai</td>
<td></td>
</tr>
<tr>
<td>24.3.9</td>
<td>9: 2-Phosphorus-Functionalized 1-(Organochalcogeno)acetylenes</td>
<td>T. Murai</td>
<td></td>
</tr>
<tr>
<td>24.3.10</td>
<td>10: Bis(nitrogen-functionalized) Acetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.3.11</td>
<td>11: 1-Nitrogen-Functionalized 2-Phosphorus-Functionalized Acetylenes and Bis(phosphorus-functionalized) Acetylenes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.4</td>
<td>4: 1-Heteroatom-Functionalized Alk-1-ynes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.4.1</td>
<td>1: 1-Haloalk-1-ynes and Alk-1-yn-1-ols</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
<tr>
<td>24.4.2</td>
<td>2: 1-(Organooxy)alk-1-ynes and 1-(Heterooxy)alk-1-ynes</td>
<td>B. Witulski and C. Alayrac</td>
<td></td>
</tr>
</tbody>
</table>
24.4.3 Product Subclass 3: 1-(Organosulfanyl)-, 1-(Organoselanyl)-, and 1-(Organotellanyl)alk-1-ynes
V. A. Potapov and B. A. Trofimov .......................................... 957

24.4.4 Product Subclass 4: 1-Nitrogen-Functionalized Alk-1-ynes

24.4.4.1 Alk-1-yn-1-amines
B. Witulski and C. Alayrac ................................................ 1007

24.4.4.2 N-Acyl- and N-Sulfonylalk-1-yn-1-amines
B. Witulski and C. Alayrac ................................................ 1031

24.4.4.3 Alk-1-ynyl diazonium Salts, 1-Azido alk-1-ynes, and 1-Nitroalk-1-ynes
K. Banert ................................................................ 1059

24.4.5 Product Subclass 5: 1-Phosphorus-Functionalized Alk-1-ynes
K. M. Pietrusiewicz and M. Stankević ...................................... 1073

Keyword Index  ............................................................... 1087
Author Index ................................................................ 1145
Abbreviations ............................................................... 1189
Table of Contents

Introduction
A. de Meijere

Introduction ............................................................................................................. 1

24.1 Product Class 1: 1,1-Bis(heteroatom-functionalized) Allenes

24.1.1 Product Subclass 1: 1,1-Dihaloallenes
R. R. Kostikov

24.1.1 Product Subclass 1: 1,1-Dihaloallenes ......................................................... 17
24.1.1.1 Synthesis of Product Subclass 1 ............................................................... 17
24.1.1.1 Method 1: Synthesis from Allenes and Acetylenes by Substitution Reactions ........................................ 18
24.1.1.1.1 Variation 1: Substitution of the Stannyl Group ................................... 18
24.1.1.1.2 Variation 2: From Acetylenes by Substitution Reactions .................. 18
24.1.1.1.3 Variation 3: Via (gem-Difluoroalleny1)indium Derivatives .............. 20
24.1.1.1.2 Method 2: Dehydrohalogenation of Dihalopropanes or Halopropenes ........................................... 20
24.1.1.1.1 Variation 1: Direct Dehydrohalogenation ........................................... 20
24.1.1.1.2 Variation 2: Dehydrochlorination through gem-Lithio,Halo-Substituted Carbenoid or Carbene Intermediates .................................................................................. 23
24.1.1.1.3 Method 3: Synthesis by the Shapiro Reaction ....................................... 24
24.1.1.1.4 Method 4: Dehalogenation of Fluoropropenes .................................... 24
24.1.1.1.3 Variation 1: Direct Dehalogenation of Fluoropropenes ..................... 24
24.1.1.1.2 Variation 2: Defluorosilylation of Silyl-Substituted Fluoropropenes ...... 25
24.1.1.1.5 Method 5: Isomerization of Acetylenes, Cyclopropenes, or Methylene Cyclopropanes ......................................................................................................................... 25
24.1.1.2 Applications of Product Subclass 1 in Organic Synthesis ....................... 26
24.1.1.2.1 Method 1: Addition of Nucleophilic and Electrophilic Reagents ............ 27
24.1.1.2.1.1 Variation 1: 1,2-Addition to 1,1-Difluoroallenes .............................. 27
24.1.1.2.1.2 Variation 2: Nucleophilic Addition to 1,1-Dichloroallenes .............. 28
24.1.1.2.1.3 Variation 3: Electrophilic Addition of Acyl Chlorides .................... 28
24.1.1.2.1.4 Variation 4: Oxygenolytic Solvolysis of Polyiodoallenes ................ 28
24.1.1.2.2 Method 2: [2 + 2] Cycloaddition ......................................................... 29
24.1.1.2.2.1 Variation 1: Dimerization .............................................................. 29
24.1.1.2.2.2 Variation 2: Allene–Alkene [2 + 2] Cycloaddition ............................ 30
24.1.1.2.2.3 Variation 3: Allene–Alkyne [2 + 2] Cycloaddition .......................... 31
24.1.1.2.2.4 Method 3: [2 + 3]-Dipolar Cycloaddition ....................................... 31
24.1.1.2.2.5 Method 4: [2 + 4] Cycloaddition ..................................................... 32
24.1.1.2.2.6 Method 5: Metal Complexes ......................................................... 33
<table>
<thead>
<tr>
<th>Subclass</th>
<th>Product Description</th>
<th>Method(s)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.1.2</td>
<td>Product Subclass 2: 1-Halo-1-(organooxy)allenes</td>
<td>Synthesis of Product Subclass 2</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 1: Halogenation of 1-Alkoxyallenes</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 1: 1-Halo-1-(organochalcogeno)allenes by the Isomerization of 3-Halo-3-(organochalcogeno)alk-1-ynes with Base</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 2: 1-Halo-1-(organochalcogeno)allenes by the Reaction of 1-Haloalk-1-yn-3-ols with Sulfur Compounds, and Subsequent Rearrangement</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 3: 1-Halo-1-(organochalcogeno)butatrienes by Dehydrochlorination of 1,2-Dichloro-1-(organochalcogeno)buta-1,3-dienes</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 1: Halogenation of an Allene-1,1,3-triamine</td>
<td>43</td>
</tr>
<tr>
<td>24.1.5</td>
<td>Product Subclass 5: 1-Phosphorus-Functionalized 1-Haloallenes</td>
<td>Synthesis of Product Subclass 5</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 1: Reaction of 1-Haloalk-1-yn-3-ols with Phosphorus Compounds, and Subsequent Rearrangement</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Applications of Product Subclass 5 in Organic Synthesis</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 1: Palladium-Catalyzed Cross Coupling</td>
<td>46</td>
</tr>
</tbody>
</table>
24.1.6 Product Subclass 6: 1,1-Bis(organooxy)allenes, 1,1-Bis(organooxy)-butatrienes, 1-(Organooxy)-1-siloxyallenes, and 1-(Organooxy)-allen-1-olates
R. Zimmer

24.1.6 Synthesis of Product Subclass 6

24.1.6.1 Synthesis of 1,1-Bis(organooxy)allenes and 1,1-Bis(organooxy)butatrienes

24.1.6.1.1 Method 1: 1,1-Bis(organooxy)allenes and 1,1-Bis(organooxy)butatrienes by Deprotonation–Alkylation of 1,1-Bis(organooxy)alk-2ynes

24.1.6.1.2 Method 2: 1,1-Bis(organooxy)allenes by Ring Opening of Highly Functionalized Cyclopropanes

24.1.6.1.3 Method 3: 1,1-Bis(organooxy)allenes by Wittig Alkenation

24.1.6.2 Synthesis of 1-(Organooxy)-1-siloxyallenes

24.1.6.2.1 Method 1: Cuprate Addition and Silylation of Alkyl Propynoates

24.1.6.3 Synthesis of 1-(Organooxy)allen-1-olates

24.1.6.3.1 Method 1: Deprotonation of Dialkyl Malonates

24.1.6.3.2 Method 2: Synthesis from Alkyl Propynoates

24.1.6.4 Applications of Product Subclass 6 in Organic Synthesis

24.1.6.4.1 Method 1: [2 + 2]-Cycloaddition Reactions of 1,1-Bis(organooxy)allenes

24.1.6.4.2 Method 2: Synthesis of 2H-Pyran-2,4(3H)-diones and Furan-2,5-diones from Tetraalkoxyallenes

24.1.7 Product Subclass 7: 1-(Organochalcogeno)-1-(organooxy)allenes
R. Zimmer

24.1.7 Synthesis of Product Subclass 7

24.1.7.1 Method 1: Deprotonation–Addition Reaction of 1-(Organooxy)allenes

24.1.7.2 Method 2: Wittig Alkenation

24.1.8 Product Subclass 8: 1-Nitrogen-Functionalized 1-(Organooxy)allenes and Allen-1-olates
R. Zimmer

24.1.8 Synthesis of Product Subclass 8

24.1.8.1 Method 1: 1-(Organooxy)allen-1-amines by Alkylation–Deprotonation of Malonamides
24.1.8.1.2 Method 2: 1-(Organooxy)-1-(1H-1,2,4-triazol-1-yl)allenes by Deprotonation–Alkylation of 3-(Organooxy)-3-(1H-1,2,4-triazol-1-yl)prop-1-ynes ........................................ 57

24.1.8.1.3 Method 3: Generation of 1-Nitrogen-Functionalized Allen-1-olates from α-Hydrazono N-Monosubstituted Amides by the Shapiro Reaction ........................................ 58

24.1.9 Product Subclass 9: 1-Phosphorus-Functionalized 1-(Organooxy)allenes and 1-Siloxyallenes
R. Zimmer

24.1.9 Method 1: 1-Phosphorus-Functionalized 1-(Organooxy)allenes by the Addition of Phosphorus Compounds to 1-Alkoxyalk-1-yynes ....................................................... 61

24.1.9.1 Method 2: 1-Phosphorus-Functionalized 1-Siloxyallenes by the Reaction of Carbon Suboxide with Silylated Phosphites .......................................................... 61

24.1.10 Product Subclass 10: 1,1-Bis(organochalcogeno)allenes and 1,1-Bis(organochalcogeno)butatrienes
R. Zimmer

24.1.10 Method 1: Deprotonation–Addition Sequence ................................................................. 63

24.1.10.1 Method 2: Alkylation–Elimination Starting from a Vinylphosphonium Salt ......................................................... 64

24.1.10.2 Method 3: Isomerization of 2-Ethynyl-1,3-dithianes ......................................................... 64

24.1.10.2.1 Method 4: Reaction of 1-(Organosulfanyl)alk-1-yn-3-ols with Sulfenyl Halides and Subsequent Rearrangement ................................................................. 65

24.1.10.2 Synthesis of 1,1-Bis(organochalcogeno)butatrienes ............................................................ 65

24.1.10.2.1 Method 1: Nucleophilic Substitution ............................................................................. 65

24.1.10.2.1 Method 2: Reaction of 1,4-Dilithiobuta-1,3-diyne with Electrophiles ........................... 66

24.1.10.2.3 Method 3: Wittig Alkenation of Diarylketenes ................................................................ 66

24.1.10.2.4 Method 4: Elimination–Isomerization Starting from 4-Alkoxy-1,1-bis(organosulfanyl)alk-2-yynes ................................................................. 67
Product Subclass 11: 1-Nitrogen-Functionalized 1-(Organochalcogeno)allenes
R. Zimmer

Synthesis of Product Subclass 11

Method 1: Deprotonation–Addition Reaction of 1-Nitrogen-Functionalized Allenes

Method 2: Deprotonation of Amidinium Salts

Method 3: Alkylation of 2-Ethynylbenzothiazolium Salts

Method 4: Isomerization of 1-Azido-1-(phenylsulfanyl)prop-2-yn-1-amine

Product Subclass 12: 1-Phosphorus-Functionalized 1-(Organochalcogeno)allenes
R. Zimmer

Synthesis of Product Subclass 12

Method 1: Deprotonation–Addition Reaction of 1-Phosphorus-Functionalized Allenes

Product Subclass 13: 1,1-Bis(nitrogen-functionalized) Allenes and Butatrienes
R. Zimmer

Synthesis of Product Subclass 13

Method 1: 1,1-Bis(nitrogen-functionalized) Allenes by Deprotonation of Amidinium Salts

Method 2: 1,1-Bis(nitrogen-functionalized) Allenes by Dehydrobromination of 2-Bromopropenes

Method 3: 1,1-Bis(nitrogen-functionalized) Allenes by the Reaction of 3,6-Dihydropyrimidinium-4-olates with N,N-Diethylprop-1-yn-1-amine

Method 4: 1,1-Bis(nitrogen-functionalized) Butatrienes by the Condensation Reaction of 1,1-Dichloroethenes with N,N,N',N'-Tetramethylethene-1,1-diamine
24.1.14  
Product Subclass 14: 1-Nitrogen-Functionalized 1-Phosphorus-Functionalized Allenes  
R. Zimmer

24.1.14  
Product Subclass 14: 1-Nitrogen-Functionalized 1-Phosphorus-Functionalized Allenes ........................................ 79

24.1.14.1  
Synthesis of Product Subclass 14 ........................................ 79

24.1.14.1.1  
Method 1: Reaction of an Iminium Iodide with Triphenylphosphine .... 79

24.1.15  
Product Subclass 15: 1,1-Bis(phosphorus-functionalized) Allenes  
M. Stankević and K. M. Pietrusiewicz

24.1.15  
Product Subclass 15: 1,1-Bis(phosphorus-functionalized) Allenes .......... 81

24.1.15.1  
Synthesis of Product Subclass 15 ........................................ 81

24.1.15.1.1  
Method 1: Synthesis from Phosphorus-Functionalized Alkynes .......... 81

24.1.15.1.2  
Method 2: Synthesis from Other Phosphorus-Functionalized Allenes ....... 82

24.2  
Product Class 2: 1,1-Bis(heteroatom-functionalized) Alk-1-enes

24.2.1  
Product Subclass 1: 1,1-Dihaloalk-1-enes  
R. R. Kostikov

24.2.1  
Product Subclass 1: 1,1-Dihaloalk-1-enes .................................. 85

24.2.1.1  
Synthesis of Product Subclass 1 ........................................... 85

24.2.1.1.1  
Method 1: Vinylic Substitution of Halogens, Metals, or Other Groups .... 85

24.2.1.1.1.1  
Variation 1: Substitution of a Silyl Group or a Metal in 1-Metal-Substituted 1-Haloalk-1-enes ...................... 86

24.2.1.1.2  
Variation 2: From 1-Substituted Alk-1-ynes ................................ 87

24.2.1.1.2  
Method 2: 2-Aryl- and 2-Hetaryl-Substituted 1,1-Dihaloalk-1-enes from Hydrazones of Aromatic Aldehydes and Ketones .......... 88

24.2.1.1.3  
Method 3: Dehydrohalogenation of Oligohaloalkanes and Halovinyl Intermediates ................................... 89

24.2.1.1.3.1  
Variation 1: Dehydrohalogenation of Oligohaloalkanes .................... 89

24.2.1.1.3.2  
Variation 2: From Vinyllithium Reagents .................................. 90

24.2.1.1.3.3  
Variation 3: From Halovinylzinc or Halovinylmagnesium Reagents ...... 91

24.2.1.1.4  
Method 4: From 2,2,2-Trihaloethanols and Derivatives ..................... 93

24.2.1.1.5  
Method 5: Dehalogenation of Oligohaloalkanes ........................................ 94

24.2.1.1.6  
Method 6: Wittig-Type Reaction ............................................. 95

24.2.1.1.7  
Method 7: Synthesis from Ketones and Lithium Carbenoids ................ 99

24.2.1.1.8  
Method 8: Electrophilic Addition to 1-Haloalk-1-ynes ....................... 100

24.2.1.1.8.1  
Variation 1: Halogen Addition to 1-Haloalk-1-ynes ....................... 100

24.2.1.1.8.2  
Variation 2: Dimerization of 1-Aryl-2-iodoacetylenes ..................... 102

24.2.1.1.9  
Method 9: Synthesis by Rearrangement ...................................... 102
24.2.1.9.1 Variation 1: Friedel–Crafts Reactions  ................................... 102
24.2.1.9.2 Variation 2: From 1-Haloalk-1-yn-3-ols ................................. 103
24.2.1.10 Applications of Product Subclass 1 in Organic Synthesis  ............ 104
24.2.1.10.1 Method 1: Substitution of Halogen for Hydrogen ...................... 104
24.2.1.10.2 Method 2: Substitution of Halogen for Nitrogen, Phosphorus, and Other Elements ....................................... 105
24.2.1.10.3 Method 3: Synthesis of Substituted Allyl Alcohols with Vinyllithium Derivatives ................................... 107
24.2.1.10.4 Method 4: Styrene Synthesis with Perfluoroalk-1-enylzinc Derivatives 107
24.2.1.10.5 Method 5: Synthesis of 1,3-Dienes  .................................... 109
24.2.1.10.6 Method 6: Synthesis of Acrylates ..................................... 111
24.2.1.10.7 Method 7: Alkylolation and Acylation .................................... 111
24.2.1.10.8 Method 8: Synthesis of Stilbenes by Suzuki Coupling ............... 112
24.2.1.10.9 Method 9: Synthesis of Enynes by Sonogashira Coupling ............ 112
24.2.1.10.10 Method 10: Intramolecular Cyclization for Fused Carbocycles and Heterocycles .............................................. 113
24.2.1.10.11 Method 11: Synthesis of Alkynes ...................................... 116
24.2.1.10.11.1 Variation 1: Synthesis of 1-Haloalk-1-ynes .............................. 116
24.2.1.10.11.2 Variation 2: Synthesis of 1,3-Diynes .................................... 117
24.2.1.10.12 Method 12: Synthesis of Oligohaloalkanes by Addition to Oligohaloalk-1-enes  ....................................... 117
24.2.1.10.13 Method 13: Addition of Alcohols ........................................ 118
24.2.1.10.14 Method 14: Synthesis of Esters ........................................ 120
24.2.1.10.14.1 Variation 1: Synthesis of Esters by Reaction with Alkoxides 120
24.2.1.10.14.2 Variation 2: Synthesis of Esters by Mukaiyama-Type Condensation of Acetals  ........................................ 120
24.2.1.10.15 Method 15: [2 + 1], [2 + 2], [2 + 3], and [2 + 4] Cycloadditions 121

24.2.2 Product Subclass 2: 1-Halo-1-(organooxy)alk-1-enes
A. P. Molchanov and R. R. Kostikov

24.2.2.1 Synthesis of Product Subclass 2 ........................................... 129
24.2.2.1.1 Method 1: Substitution of Hydrogen for Halogen ...................... 129
24.2.2.1.2 Method 2: Substitution of Halogen for Oxygen ........................ 129
24.2.2.1.2.1 Variation 1: From 1,1-Dihaloalk-1-enes with a Hydrogen Atom in the α-Position  ........................................ 130
24.2.2.1.2.2 Variation 2: From 1,1,2-Trihaloalk-1-enes without a Hydrogen Atom in the α-Position  ........................................ 131
24.2.2.1.3 Method 3: Elimination of Hydrogen Halides or Halogens .......... 132
24.2.2.1.4 Method 4: Decarboxylation or Elimination of Carbonyl Difluoride 134
24.2.2.1.5 Method 5: Addition of Oxygen Nucleophiles to 1-Haloalk-1-ynes 136
24.2.2.1.6 Method 6: Addition of Hydrogen Halides to 1-Alkoxyalk-1-ynes 136
24.2.2.1.7 Method 7: Addition of Phosgene to 1-Alkoxyalk-1-ynes .......... 137
24.2.2.1.8 Method 8: Addition of Halogens to 1-(Organoxy)alk-1-ynes 138
<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.2.1.9</td>
<td>Method 9</td>
<td>Addition of Heteroelement Halides to 1-(Organooxy)alk-1-ynes</td>
</tr>
<tr>
<td>24.2.1.9.1</td>
<td>Variation 1</td>
<td>Addition of Boron Halides</td>
</tr>
<tr>
<td>24.2.1.9.2</td>
<td>Variation 2</td>
<td>Addition of Carbon, Silicon, Germanium, and Tin Halides</td>
</tr>
<tr>
<td>24.2.1.9.3</td>
<td>Variation 3</td>
<td>Addition of Phosphorus Halides</td>
</tr>
<tr>
<td>24.2.1.9.4</td>
<td>Variation 4</td>
<td>Addition of Sulfur Halides</td>
</tr>
<tr>
<td>24.2.1.9.5</td>
<td>Variation 5</td>
<td>Addition of Mercury(II) Chloride</td>
</tr>
<tr>
<td>24.2.1.10</td>
<td>Method 10</td>
<td>Addition of Carbonyl Compounds to 1-Halo- or 1-Alkoxyalk-1-ynes</td>
</tr>
<tr>
<td>24.2.1.11</td>
<td>Method 11</td>
<td>O-Acylation of Acyl Halides or Aldehydes</td>
</tr>
<tr>
<td>24.2.2</td>
<td>Applications of Product Subclass 2 in Organic Synthesis</td>
<td></td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 1</td>
<td>Thermolysis</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 2</td>
<td>Substitution of Halogen</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 3</td>
<td>Elimination of Hydrogen Halides</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 4</td>
<td>Elimination of Halogens</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 5</td>
<td>Addition of Mineral Acids, Halogens, and Water</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 6</td>
<td>Addition of Alcohols, Phenols, and Amines</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 7</td>
<td>Addition of Carboxylic Acids and Their Derivatives</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 8</td>
<td>Radical Addition</td>
</tr>
<tr>
<td>24.2.2.2</td>
<td>Method 9</td>
<td>Addition of Alkyl Hypofluorites</td>
</tr>
<tr>
<td>24.2.2.10</td>
<td>Method 10</td>
<td>Addition of Sulfur-Containing Reagents</td>
</tr>
<tr>
<td>24.2.2.11</td>
<td>Method 11</td>
<td>Cycloadditions</td>
</tr>
<tr>
<td>24.2.2.11.1</td>
<td>Variation 1</td>
<td>[2 + 1] Cycloadditions</td>
</tr>
<tr>
<td>24.2.2.11.2</td>
<td>Variation 2</td>
<td>[2 + 2] Cycloadditions</td>
</tr>
<tr>
<td>24.2.2.11.3</td>
<td>Variation 3</td>
<td>Synthesis of Heterocyclic Compounds</td>
</tr>
<tr>
<td>24.2.2.12</td>
<td>Method 12</td>
<td>Rearrangements</td>
</tr>
</tbody>
</table>

**Product Subclass 3: 1-Halo-1-(organochalcogeno)alk-1-enes**

A. F. Khlebnikov and R. R. Kostikov

<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.2.3.1</td>
<td>Synthesis of Product Subclass 3</td>
<td></td>
</tr>
<tr>
<td>24.2.3.1.1</td>
<td>Method 1</td>
<td>Substitution of Metal for Halogen</td>
</tr>
<tr>
<td>24.2.3.1.2</td>
<td>Method 2</td>
<td>Substitution of Halogen for Chalcogen</td>
</tr>
<tr>
<td>24.2.3.1.3</td>
<td>Method 3</td>
<td>Substitution of Oxygen for Halogen</td>
</tr>
<tr>
<td>24.2.3.1.4</td>
<td>Method 4</td>
<td>Elimination of Hydrogen Halides or Halogens</td>
</tr>
<tr>
<td>24.2.3.1.5</td>
<td>Method 5</td>
<td>Wittig-Type Reactions</td>
</tr>
<tr>
<td>24.2.3.1.6</td>
<td>Method 6</td>
<td>Miscellaneous Eliminations</td>
</tr>
<tr>
<td>24.2.3.1.7</td>
<td>Method 7</td>
<td>Addition of Hydrogen Halides to Alk-1-ynes</td>
</tr>
<tr>
<td>24.2.3.1.8</td>
<td>Method 8</td>
<td>Addition of Halogens to Alk-1-ynes</td>
</tr>
<tr>
<td>24.2.3.1.9</td>
<td>Method 9</td>
<td>Addition of Heteroelement Halides to Alk-1-ynes</td>
</tr>
<tr>
<td>24.2.3.1.10</td>
<td>Method 10</td>
<td>Miscellaneous Additions to Alk-1-ynes</td>
</tr>
<tr>
<td>24.2.3.1.11</td>
<td>Methods 11</td>
<td>Miscellaneous Reactions</td>
</tr>
<tr>
<td>24.2.3.2</td>
<td>Applications of Product Subclass 3 in Organic Synthesis</td>
<td></td>
</tr>
<tr>
<td>24.2.3.2.1</td>
<td>Method 1</td>
<td>Substitution of Halogen by Hydrogen, Deuterium, or a Metal</td>
</tr>
<tr>
<td>24.2.3.2.2</td>
<td>Method 2</td>
<td>Substitution of a Halogen for a Carbon Group</td>
</tr>
</tbody>
</table>
### 24.2.3.2.3 Method 3: Substitution of a Halogen for a Heteroatom Group ........................................... 204
### 24.2.3.2.4 Method 4: Substitution of a Sulfonyl Group ................................................................. 207
### 24.2.3.2.5 Method 5: Elimination Reactions .................................................................................. 208
### 24.2.3.2.6 Method 6: Addition Reactions ....................................................................................... 210
### 24.2.3.2.7 Method 7: Cyclizations ................................................................................................. 213
### 24.2.3.2.8 Methods 8: Miscellaneous Reactions ........................................................................... 217

## 24.2.4 Product Subclass 4: 1-Nitrogen-Functionalized 1-Haloalk-1-enes

**J. G. Schantl**

### 24.2.4 Product Subclass 4: 1-Nitrogen-Functionalized 1-Haloalk-1-enes ................................. 223

#### 24.2.4.1 Synthesis of Product Subclass 4 ................................................................. 223

##### 24.2.4.1.1 1-Haloalk-1-en-1-amines ............................................................................... 223

- **Method 1:** 1,2-Dehydrohalogenation of 1,2-Dihaloalkan-1-amines .............................. 223
- **Variation 1:** 1,2-Dehydrobromination of Oligohalogenated \( N,N \)-Bis(trifluoromethyl)ethanamines ................................................. 223
- **Variation 2:** 1,2-Dehydrochlorination of 1-(1,2,2,2-Tetrachloroethyl)-pyridinium Chloride ......................................................... 224

- **Method 2:** 1,2-Dehalogenation ..................................................................................... 224

- **Method 3:** Monosubstitution of 1,1-Dihaloalk-1-enes by Nitrogen Nucleophiles ............... 225
  - **Variation 1:** Nucleophilic Substitution of Vinylic Fluorine by Amide Anions .......... 225
  - **Variation 2:** Nucleophilic Substitution of Vinylic Bromine or Chlorine by Amines .... 226
  - **Variation 3:** Nucleophilic Substitution of 2,2-Dichlorovinyl Ketones ..................... 226
  - **Variation 4:** Nucleophilic Monosubstitution of Vinylic Chlorine by Amines ............. 227
  - **Variation 5:** Nucleophilic Monosubstitution of Vinylic Chlorine by Heterocyclic Amides ................................................................. 229
  - **Variation 8:** Nucleophilic Monosubstitution of a Vinylic Chlorine by Nucleic Acid Bases and Related Heterocycles .......................... 230
  - **Variation 9:** Nucleophilic Monosubstitution of a Vinylic Chlorine by Lithium Diisopropylamide .......................................................... 231
  - **Method 4:** Nucleophilic Addition of a Nitrogen Functionality to 1-Haloalk-1-ynes .... 231
  - **Variation 1:** Addition of Nitrogen Nucleophiles to 1-Haloalk-1-ynes .................. 231
  - **Variation 2:** Nucleophilic Addition of Dimethyl Hydrazine-1,2-dicarboxylate to Dichloroacetylene .................................................. 232
  - **Variation 3:** Nucleophilic Addition of Amines to Dichloroacetylene ...................... 232
  - **Variation 5:** Addition of Hydrogen Halides or Halide Anions to Ynamines or N,N-Ynecarboxamides ......................................................... 232
  - **Variation 1:** Addition of Hydrogen Halides to \( N,N \)-Dimethylalk-1-yn-1-amines .... 232
  - **Variation 2:** Addition of Hydrogen Halides to 1-Acyl-\( N,N \)-dialkylalk-1-en-3-yn-4-amines .............................................................. 233
24.2.4.1.1.5.3 Variation 3: Hydrohalogenation of N-Alk-1-ynylcarboxamides with Magnesium Halides ........................................ 233
24.2.4.1.1.5.4 Variation 4: Addition of N,N-Diethyl-2-(trimethylstannyl)acetylen-1-amine to 2-(Chloromethylene)malononitrile ........................... 235
24.2.4.1.1.6 Method 6: Treatment of Carboxamides with Phosphoryl Chloride ........................................ 235
24.2.4.1.1.7 Method 7: Transformation of Imidoyl Chlorides or of Amides via Imidoyl Chlorides ........................................ 236
24.2.4.1.1.7.1 Variation 1: Conversion of N,N-Disubstituted Amides ................... 236
24.2.4.1.1.7.2 Variation 2: Isomerization of Imidoyl Chlorides .......................... 238
24.2.4.1.1.7.3 Variation 3: Conversion of Imidoyl Chlorides with Trialkyl Phosphites (Aza-Perkow Reaction) .................................... 238
24.2.4.1.1.7.4 Variation 4: Nucleophilic Substitution of N-(Dichloromethylene)-N,N-dimethyliminium Chloride by an In Situ Generated Allyl Anion Intermediate ........................... 239
24.2.4.1.1.7.5 Variation 5: Nucleophilic Substitution of N-(Dichloromethylene)-N,N-dimethyliminium Chloride by an In Situ Generated Enamine Intermediate ........................................ 239
24.2.4.1.1.8 Method 8: Synthesis from Nitriles (via Ketenimine Intermediates) ........ 240
24.2.4.1.1.8.1 Variation 1: Addition of Hydrogen Halides to Dicyanoacetates ........ 240
24.2.4.1.1.8.2 Variation 2: Addition of Hydrogen Halides to Tri- and Tetracyanomethanes ........................................ 241
24.2.4.1.1.8.3 Variation 3: Addition of Hydrogen Halides to 2-(1-Hydroxyalkylidene)-malononitriles ........................................ 241
24.2.4.1.1.8.4 Variation 4: Addition of Hydrogen Chloride to 2-Sulfonyl-Substituted Malononitriles ........................................ 242
24.2.4.1.1.8.5 Variation 5: Addition of Hydrogen Halides to 2-[2-(Dicyanomethylene)-hydrazino]malononitrile .......................... 242
24.2.4.1.1.8.6 Variation 6: Addition of Hydrogen Chloride to Ethane-1,1,2,2-tetracarbonitrile ........................................ 242
24.2.4.1.1.8.7 Variation 7: Addition of Liquid Hydrogen Bromide to Malononitrile .... 243
24.2.4.1.1.8.8 Variation 8: Reaction of Hydrogen Chloride with Nitriles Containing an α-Hydrogen To Form [2 + 2] Adducts ..................... 243
24.2.4.1.1.8.9 Variation 9: Phosphorus Halide Addition to Oligocyanomethanes ........ 245
24.2.4.1.1.8.10 Variation 10: Addition of Sulfur Chlorides to Oligocyanomethanes .... 245
24.2.4.1.1.9 Method 9: Conversion of Ketenimines ........................................ 246
24.2.4.1.1.9.1 Variation 1: Thermal Rearrangement of Vinyl Azides to Ketenimine Intermediates ........................................ 246
24.2.4.1.1.9.2 Variation 2: Addition of Chlorine to a Ketenimine .......................... 246
24.2.4.1.1.10 Methods 10: Miscellaneous Reactions ........................................ 247
24.2.4.1.1.10.1 Variation 1: Iodinolysis of In Situ Generated Amino-Substituted Titanacyclopentadienes ........................................ 247
24.2.4.1.1.10.2 Variation 2: Rearrangement of a Heterocyclic Azide ..................... 248
24.2.4.1.1.10.3 Variation 3: Rearrangement of an Alkyl Azide in the Presence of an Alkyne .......................... 248
24.2.4.1.1.10.4 Variation 4: Pyrolysis of 1,2,3,4,4-Hexafluoro-N,N,N,N'-tetrakis-(trifluoromethyl)cyclobutane-1,2-diamine .......................... 248
24.2.4.1.1.11 Method 11: Transformation of 1-Nitrogen-Functionalized 1-Haloalk-1-enes into 1-Haloalk-1-en-1-amines and Derivatives ....... 249
24.2.4.1.1.11.1 Variation 1: Reactions Involving the Nitrogen Functionality of 1-Nitrogen-Functionalized 1-Haloalk-1-enes:
- Conversion into Amines ................................... 249

24.2.4.1.1.11.2 Variation 2: Derivatization Reactions at a Remote Site of the Nitrogen Moiety ...................................... 251

24.2.4.1.1.11.3 Variation 3: Halogen Exchange at C1 ................................... 251

24.2.4.1.1.11.4 Variation 4: Remote Reaction at C2 ................................... 252

24.2.4.2 1-Halo-1-iminoalk-1-enes (3-Halo-2-azabuta-1,3-dienes) ........................... (252

24.2.4.2.1 Method 1: 1,2-Dehydrohalogenation  ................................... 252

24.2.4.2.2 Method 2: 1,2-Dehalogenation ....................................... 253

24.2.4.2.3 Method 3: Nucleophilic Substitution of Vinylic Fluorine by Imines ........................... 253

24.2.4.2.4 Method 4: Treatment of Acylureas with Phosphorus Chlorides  ........ 254

24.2.4.2.4.1 Variation 1: Conversion of N-Acetylureas ............................... 254

24.2.4.2.4.2 Variation 2: Conversion of N-Acetylureas ............................... 254

24.2.4.2.5 Method 5: 1,4-Dehydrochlorination of N-Alkyl-Substituted
- Chloroimidoyl Chlorides ........................................ 255

24.2.4.2.6 Method 6: Addition of Ketenimines to Chloroiminium Chlorides  .......... 256

24.2.4.2.7 Method 7: Wittig-Type Condensation ....................................... 256

24.2.4.2.8 Method 8: Transformation of 1-Nitrogen-Functionalized
- 1-Haloalk-1-enes into 1-Halo-1-iminoalk-1-enes ........................... 256

24.2.4.2.8.1 Variation 1: Reactions Involving the Nitrogen Functionality of
1-Nitrogen-Functionalized 1-Haloalk-1-enes ........................... 256

24.2.4.2.8.2 Variation 2: Derivatization Reactions at Remote Sites at C2 and in
the Imine Moiety .......................................... 257

24.2.4.2.8.3 Variation 3: Remote Reactions at C2 ................................... 257

24.2.4.2.8.4 Variation 4: Reaction of Isothiocyanates with Triethyl Phosphite .......... 258

24.2.4.3 1-Halo-1-isocyanatoalk-1-enes ............................................ 258

24.2.4.3.1 Method 1: 1,2-Dehydrochlorination ................................... 258

24.2.4.3.2 Method 2: 1,2-Debromination ....................................... 258

24.2.4.3.3 Method 3: Synthesis from Carbamates ................................ 259

24.2.4.3.4 Method 4: Synthesis from Nitriles .................................... 259

24.2.4.3.5 Method 5: Synthesis by Curtius Reaction .............................. 259

24.2.4.3.6 Methods 6: Miscellaneous Reactions ................................... 260

24.2.4.4 1-Halo-1-isothiocyanatoalk-1-enes ........................................ 260

24.2.4.4.1 Method 1: \(\alpha\)-Halogenation of Alkyl Isothiocyanates ........................... 260

24.2.4.4.2 Method 2: Nucleophilic Substitution of Vinylic Fluorine by
Thiocyanate Anion ........................................ 261

24.2.4.5 1-Haloalk-1-enyl Isocyanides .............................................. 261

24.2.4.5.1 Method 1: 1,2-Dehydrohalogenation  ................................... 261

24.2.4.5.2 Method 2: 1,2-Dehalogenation ....................................... 261

24.2.4.5.2.1 Variation 1: 1,2-Dechlorination of (1,1,2,2-Tetrachloroalkyl isocyanide)-
and (1,2-Dichloro-1,1,2,2,2-pentahaloethyl isocyanide)-
chromium Complexes ........................................ 261

24.2.4.5.2.2 Variation 2: 1,2-Dechlorination of (1,2-Dichlorooligohaloethyl isocyanide)-
chromium Complexes ........................................ 262
24.2.4.5.3 Method 3: Horner–Wadsworth–Emmons Reaction .............................. 262
24.2.4.5.4 Method 4: Derivatization of 1-Haloalk-1-enyl Isocyanides with Retention of the Functional Group ......................................................... 263
24.2.4.5.4.1 Variation 1: Nucleophilic Substitution at C2 .............................. 263
24.2.4.5.4.2 Variation 2: Remote Reactions at the Nitrogen Moiety ................... 264
24.2.4.6 1-Haloalk-1-enyldiazenes (1-Halo-1-diazenylalk-1-enes) ..................... 264
24.2.4.6.1 Method 1: 1,4-Elimination of Hydrogen Halides from α-Halo hydrazonoyl Halides ................................................................. 264
24.2.4.6.1.1 Variation 1: 1,4-Dehydrofluorination of N-Phenylperfluoroalkane hydrazonoyl Fluorides ............................................................. 264
24.2.4.6.1.2 Variation 2: 1,4-Dehydrohalogenation of α-Chlorohydrazonoyl Chlorides ...... 265
24.2.4.6.2 Method 2: Reaction of β-Functionalized α-Halo hydrazonoyl Halides ........ 265
24.2.4.6.3 Method 3: 1,2-Dehydrohalogenation of 2-Alkyl-1-(1,2-dihaloalkyl)diazene 1-Oxides ................................................................. 266
24.2.4.6.4 Method 4: Azo Coupling onto Activated Halomethyl Groups ............ 266
24.2.4.6.4.1 Variation 1: Coupling of Diazonium Salts with Halomethyl-Substituted Heterarenium Salts ......................................................... 267
24.2.4.6.4.2 Variation 2: Azo Coupling of α-Chloro Ketones ......................... 267
24.2.4.6.5 Method 5: Nucleophilic Substitution of Vinyl Halides by Nitrogen Nucleophiles ................................................................. 267
24.2.4.6.6 Method 6: Nucleophilic Substitution of Chlorine in Carbonohydrazonic Dichlorides ................................................................. 268
24.2.4.7 1-Azido-1-haloalk-1-enes ................................................................... 268
24.2.4.7.1 Method 1: Nucleophilic Substitution of Vinylic Fluorine ................... 268
24.2.4.8 1-Halo-1-nitroalk-1-enes .................................................................... 269
24.2.4.8.1 Method 1: 1,2-Elimination of Hydrogen Halides .............................. 269
24.2.4.8.1.1 Variation 1: 1,2-Dehydrohalogenation of 1,2-Dihalo-1-nitroalkanes ...... 269
24.2.4.8.1.2 Variation 2: 1,2-Dehydrobromination of 1,2-Dibromo-1-nitroalkanes ..... 270
24.2.4.8.1.3 Variation 3: 1,2-Dehydrochlorination of 1,2-Dichloro-1-nitroalkanes ... 272
24.2.4.8.1.4 Variation 4: 1,2-Dehydrochlorination of 1,2,2-Trichloro-1-nitroethane ... 272
24.2.4.8.1.5 Variation 5: 1,2-Dehydration of 2-Bromo-2-nitroethanol .............. 273
24.2.4.8.1.6 Variation 6: 1,2-Elimination of Nitrous Acid from a 1-Fluoro-2,2-dinitroalkane ................................................................. 273
24.2.4.8.2 Method 2: Introduction of a Nitro Group ......................................... 274
24.2.4.8.2.1 Variation 1: By Displacement of Bromine ................................... 274
24.2.4.8.2.2 Variation 2: By Nitration ......................................................... 274
24.2.4.8.3 Method 3: Iodonitration of Silylacetylenes ...................................... 275
24.2.4.8.4 Method 4: C=C Bond Formation by Condensation of Halonitromethanes with Carbonyl Compounds ........................................ 275
24.2.4.8.4.1 Variation 1: Condensation of Bromonitromethane with Aromatic Aldehydes ................................................................. 275
24.2.4.8.4.2 Variation 2: Condensation of Halonitromethanes with Aromatic and Heteroaromatic Aldehydes ........................................ 276
24.2.4.8.4.3 Variation 3: Condensation of Bromonitromethane with an N-Alkylbenzaldehyde ................................................................. 277
24.2.4.8.4 Variation 4: Condensation of Bromonitromethane with Triethyl Orthoformate ........................................... 277
24.2.4.8.5 Method 5: Pyrolysis .................................................. 278
24.2.4.8.6 Method 6: Derivatization Reactions of 1-Halo-1-nitroalk-1-enes ........ 278
24.2.4.8.6.1 Variation 1: Nucleophilic Substitution at C2 ....................... 278
24.2.4.8.6.2 Variation 2: Nucleophilic Substitution at C4 of 1,1,4-Trichloro-2,4-dinitrobuta-1,3-diene ................. 279

24.2.5 Product Subclass 5: 1-Phosphorus-Functionalized 1-Haloalk-1-enes
M. Stankević and K. M. Pietrusiewicz

24.2.5

Product Subclass 5: 1-Phosphorus-Functionalized 1-Haloalk-1-enes ...... 285
24.2.5.1 Synthesis of Product Subclass 5 ........................................ 285
24.2.5.1.1 Method 1: Synthesis from 1,1-Dihaloalkenes ....................... 285
24.2.5.1.2 Method 2: Synthesis from Alkynes ................................ 286
24.2.5.1.3 Method 3: Synthesis from 1-Phosphorus-Functionalized 1-Haloalkanes and Carbonyl Compounds .......... 287
24.2.5.1.3.1 Variation 1: By the Horner–Wadsworth–Emmons Reaction .... 287
24.2.5.1.3.2 Variation 2: By Peterson Alkenation ............................ 288
24.2.5.1.3.3 Variation 3: By Condensation ..................................... 288
24.2.5.2 Applications of Product Subclass 5 in Organic Synthesis .......... 289

24.2.6

Product Subclass 6: 1,1-Bis(organooxy)alk-1-enes
C. Schneider

24.2.6

Product Subclass 6: 1,1-Bis(organooxy)alk-1-enes ........................ 293
24.2.6.1 Synthesis of Product Subclass 6 ........................................ 295
24.2.6.1.1 Method 1: Elimination from 2-Halo Acetals ....................... 295
24.2.6.1.1.1 Variation 1: Phase-Transfer-Catalyzed Elimination from 2-Halo Acetals .................................................. 296
24.2.6.1.1.2 Variation 2: Ultrasound-Accelerated Elimination from 2-Halo Acetals .................................................. 296
24.2.6.1.1.3 Variation 3: Elimination from 2-Bromo Peracetyl Glycosides .......... 296
24.2.6.1.1.4 Variation 4: Elimination from 2-Selanyl Acetals ................. 297
24.2.6.1.2 Method 2: Elimination from Ortho Esters .......................... 297
24.2.6.1.2.1 Variation 1: Acid-Catalyzed Elimination from In Situ Formed Ortho Esters ............................... 298
24.2.6.1.3 Method 3: O-Heteroacylation of Ester Enolates .................... 299
24.2.6.1.4 Method 4: O-Alkylation of Ester Enolates .......................... 300
24.2.6.1.5 Method 5: Alkenation of Carbonates with Transition Metal–Carbene Complexes ......................... 301
24.2.6.1.6 Method 6: Horner–Wittig Alkenation of Carbonyl Compounds ...... 302
24.2.6.1.7 Method 7: Nucleophilic Addition to Alkoxylkynes .................. 303
24.2.6.1.8 Method 8: Nucleophilic Addition to 1,1-Dihaloalk-1-enes ........... 303
24.2.6.1.9 Method 9: Decarboxylation of β-Lactones ............................ 304
24.2.6.2 Applications of Product Subclass 6 in Organic Synthesis .......... 305
24.2.6.2.1 Method 1: Alkylation and Arylation of Ketene O,O-Acetals .......... 305
24.2.6.2.1.1 Variation 1: Lewis Acid Catalyzed Arylation of Ketene O,O-Acetals ...... 306
24.2.6.2 Method 2: Acylation of Ketene O-O-Acetals .......................... 306
24.2.6.3 Method 3: Bromination of Ketene O-O-Acetals ...................... 307
24.2.6.4 Method 4: Silylation of Ketene O-O-Acetals ......................... 308
24.2.6.5 Method 5: Reaction of Ketene O-O-Acetals with Diazo Compounds 309
24.2.6.6 Method 6: Dihydroxylolation of Ketene O-O-Acetals ............... 310
24.2.6.7 Method 7: [2 + 2] Cycloadditions of Ketene O-O-Acetals with Carbonyl Compounds ............................................................ 311
24.2.6.7.1 Variation 1: Lewis Acid Catalyzed [2 + 2] Cycloadditions ......... 312
24.2.6.7.2 Variation 2: High-Pressure-Promoted [2 + 2] Cycloadditions with Carbonyl Compounds ............................................................. 313
24.2.6.8 Method 8: [2 + 2] Cycloadditions of Ketene O,O-Acetals with Electron-Deficient Alkenes ......................................................... 313
24.2.6.8.1 Variation 1: Thermal [2 + 2] Cycloadditions .......................... 314
24.2.6.8.2 Variation 2: Lewis Acid Catalyzed [2 + 2] Cycloadditions ......... 315
24.2.6.8.3 Variation 3: [2 + 2] Cycloadditions with 2-Halo-1,4-quinones .... 315
24.2.6.9 Method 9: [4 + 2] Cycloadditions of Ketene O,O-Acetals with Electron-Deficient Heterodienes ....................................................... 316
24.2.6.10 Method 10: [4 + 2] Cycloadditions of Ketene O,O-Acetals with Electron-Deficient Dienes ............................................................ 318
24.2.6.11 Method 11: 1,3-Dipolar Cycloadditions of Ketene O,O-Acetals ....... 319

24.2.7 Product Subclass 7: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes

W. Dölling

24.2.7.1 Synthesis of Product Subclass 7 ........................................... 323
24.2.7.1.1 Method 1: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes from Acylated Ketene Acetals ......................................................... 323
24.2.7.1.2 Method 2: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes by Addition of Sodium Alkanethiolates to Either Ethoxyacetylene or Phenoxyacetylene ................................................................. 324
24.2.7.1.3 Method 3: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes by Alkylation of O-Alkyl Thiocarboxylates ................................................. 324
24.2.7.1.4 Method 4: 2-Alkylidene-1,3-oxathiolanes from the Anions of Alkyl Thiocarboxylates and 4-Toluene-sulfonates ................................. 325
24.2.7.1.5 Method 5: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes from Carbonyl Compounds ................................................................. 326
24.2.7.1.5.1 Variation 1: From Aldehydes or Ketones by Horner–Emmons Reactions 326
24.2.7.1.5.2 Variation 2: From Ketones by the Peterson Reaction ............ 326
24.2.7.1.6 Method 6: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes by Treatment of Sulfanylacetylenes with 4-Toluene-sulfonic Acid ................. 328
24.2.7.1.7 Method 7: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes from Ketene Dithioacetals ................................................................. 328
24.2.7.1.8 Method 8: 1-(Organooxy)-1-(organosulfanyl)alk-1-enes by Other Routes 329
Product Subclass 8: 1-(Organooxy)-1-(organoselanyl)- and 1-(Organooxy)-1-(organotellanyl)alk-1-enes

W. Dölling

Synthesis of Product Subclass 8

Method 1: Synthesis from Selenoates or Telluroates

Variation 1: Se-Alkylation of O-Alkyl Selenoates

Variation 2: O-Silylation of Se-Phenyl or Se-Methyl 2-Methylpropane-selenoates and Te-Butyl Diphenylethanetelluroate

Variation 3: Reaction of Halogenated Esters and Carbamates

Method 2: Addition of 4-Toluenesulfonic Acid to 1-(Phenylselanyl)alk-1-ynes

Method 3: Synthesis from Oxygen Heterocycles

Product Subclass 9: 1-Nitrogen-Functionalized 1-(Organooxy)alk-1-enes (Ketene O,N-Acetals)

W. Kantlehner

Synthesis of Product Subclass 9

Method 1: Synthesis from Dimethyl 3-Oxopentanedioate and Ortho Amide Derivatives of Alkynecarboxylic Acids

Method 2: Synthesis from Oxazoles and Their Derivatives and Isocyanates

Method 3: Synthesis from β-Dicarbonyl Compounds and Isocyanates

Method 4: Synthesis from Aldehydes and Activated Isocyanates

Method 5: Synthesis from 2-Alkylxazoloxal salts

Method 6: Synthesis from Alkyl Carboximidates and Ethyl 2-Cyano-3-ethoxyacrylate

Method 7: Synthesis from Oxazoles and Their Derivatives by Self-Condensation

Method 8: Synthesis from 2-Alkylxazoles and Halogens

Method 9: Synthesis from 3-Iodo-4H-1-benzopyran-4-one and Piperidine

Method 10: Synthesis from 5-(Ethoxymethylene)-1,3-bis(2-methoxyphenyl)thiobarbituric Acid

Method 11: Synthesis from 4-Halo-β-oxo Esters and Isocyanates

Method 12: Synthesis from Carboxamides by Alkylation

Method 13: Synthesis from 3-Aminoalk-2-enenitriles and Alcohols or Phenols

Method 14: Synthesis from 5-(4-Chloro-5H-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione

Method 15: Synthesis from Oligohaloalkane Derivatives by Substitution and Concomitant Dehydrohalogenation
24.2.9.16 Method 16: Synthesis from 1,1-Dihaloalkenes and Related Compounds 346
24.2.9.17 Method 17: Synthesis from β-Bromoenamines 350
24.2.9.18 Method 18: Synthesis from Ketene O,O-Acetals 350
24.2.9.19 Method 19: Synthesis from α-Phosphoryl Thioamide Derivatives 353
24.2.9.20 Method 20: Synthesis from O,O-Dialkyl Dithiomalonates or Thiomalonic Acid O-Ester Nitriles and Amines 354
24.2.9.21 Method 21: Synthesis from Iminocarbonic O,S-Esters 357
24.2.9.22 Method 22: Synthesis from Benzoxazole-2-thiones 358
24.2.9.23 Method 23: Synthesis from Ketene S,S-Acetals 358
24.2.9.24 Method 24: Synthesis from Ketene S,N-Acetals 360
24.2.9.25 Method 25: Synthesis from Ketene N,N-Acetals 363
24.2.9.26 Method 26: Deprotonation of Alkoxy(alkyl)(dialkylamino)carbenium Salts (Iminium Salts) 364
24.2.9.27 Method 27: Elimination of Hydrogen Halides, Alcohols, or Sulfonic Acids from α-Halo or α-Oxy Aldehyde O,N-Acetals 370
24.2.9.28 Method 28: Elimination of Alcohols or Amines from Amide O,O-Acetals or Ester N,N-Acetals 372
24.2.9.29 Method 29: Addition to 3-Oxocarboxylic Acid Derivatives 375
24.2.9.30 Method 30: Addition of CH-Acidic Compounds to Dialkoxy(amino)-carbenium Salts, Dialkoxy(diamino)methanes, (Trialkoxy)-aminomethanes, and Alkoxy(alkylsulfanyl)aminocarbenium Salts 375
24.2.9.31 Method 31: Addition of CH-Acidic Compounds to Imidocarbonates 379
24.2.9.32 Method 32: Addition of CH-Acidic Compounds to Alkyl or Aryl Cyanates 380
24.2.9.33 Method 33: Synthesis from Carbonyl Compounds and Barbituric Acid Derivatives 382
24.2.9.34 Method 34: Synthesis from α,β-Unsaturated Carbonyl Compounds and Malononitrile or Alkyl Cyanoacetates 382
24.2.9.35 Method 35: Synthesis from Alkyl Methyleneacyanoacetates or Methylenemalononitriles and Hydroxyarenes, Hydroxysterarenes, or Enolizable Ketones 383
24.2.9.36 Method 36: Synthesis from Isocyanides by Multicomponent Reactions 390
24.2.9.37 Method 37: Synthesis from Furan-2,3-diones 391
24.2.9.38 Method 38: Synthesis from 2-(Alk-1-enyl)oxazole Derivatives by Cycloaddition Reactions 392
24.2.9.39 Method 39: Synthesis from Vinyliminophosphoranes 393
24.2.9.40 Method 40: Synthesis from Nitriles and Alcohols 393
24.2.9.41 Method 41: Synthesis from Ketenes 400
24.2.9.42 Method 42: Synthesis from Ketenimines 402
24.2.9.43 Method 43: Synthesis from 1-Alkoxyalk-1-ynes 403
24.2.9.44 Method 44: Synthesis from Alk-1-yn-1-amines 404
24.2.9.45 Method 45: Rearrangement of Cyclobuta-1,3-diene-2,4-diamines 407
24.2.9.46 Method 46: Synthesis from Oxazoles or Isoxazolium Salts 407
24.2.9.47 Method 47: Synthesis from 2,6-Dialkoxypyridines and Electron-Rich Alkenes 408
24.2.9.48 Method 48: Synthesis from 2-Amino-4,5-dihydrothiophene-3-carbonitriles and Dibenzyldiazomethane 408
24.2.9.49 Method 49: Synthesis from N-Hydroxyenamines 409
24.2.9.1.50 Method 50: Synthesis by Transformation with Retention of the Functional Group ................................................................................. 410
24.2.9.1.51 Method 51: Reaction in the Ene Moiety with Formation of New C–C Bonds .................................................................................. 410
24.2.9.1.51.1 Variation 1: Substitution of the β-Hydrogen Atom by 2,4,6-Trichloro-1,3,5-triazine, Ortho Esters, Methylene malonic Acid Derivatives, Trimethylsilyl Trifluoromethanesulfonate, and Dialkyl Imidodithiocarbonates .............................................. 411
24.2.9.1.51.2 Variation 2: Substitution of the β-Hydrogen Atom by Isocyanates and Isothiocyanates ................................................................. 412
24.2.9.1.51.3 Variation 3: Substitution of the β-Hydrogen Atom by Ketenes and Ketene Dimers ............................................................................. 414
24.2.9.1.51.4 Variation 4: Substitution of the β-Hydrogen Atom by α,β-Unsaturated Carboxylic Acid Derivatives ......................................................... 414
24.2.9.1.51.5 Variation 5: From Ortho Amide Derivatives as Precursors .................................................................................................................. 414
24.2.9.1.51.6 Variation 6: Substitution of the β-Hydrogen Atom by Alkynes ........................................................................................................ 415
24.2.9.1.51.7 Variation 7: From Carboxylic Acid Ortho Amide Derivatives and α,β-Unsaturated Carbonyl Compounds .................................................. 416
24.2.9.1.51.8 Variation 8: Substitution of the β-Hydrogen Atom by the N=N Bond of Dialkyl Azodicarboxylates ................................................................. 417
24.2.9.1.52 Method 52: Reactions at the Ene Moiety with Cleavage of C–C Bonds .............................................................................................. 417
24.2.9.1.53 Method 53: Reaction at the Acetal Moiety ........................................... 417
24.2.9.1.53.1 Variation 1: Exchange of Alkoxy Groups ................................................. 417
24.2.9.1.53.2 Variation 2: Exchange of Amino Groups .................................................. 418
24.2.9.1.53.3 Variation 3: Alteration of Substituents on the Oxygen or Nitrogen Atom ................................................................................................. 419
24.2.9.1.54 Method 54: Reactions in the Ene and Acetal Moieties ...................... 426
24.2.9.1.55 Method 55: Alteration of Substituents on Remote Functional Groups ........................................................................................................ 431

24.2.10 Product Subclass 10: 1-Phosphorus-Functionalized 1-(Organooxy)alk-1-enes
H. Heydt

24.2.10 Product Subclass 10: 1-Phosphorus-Functionalized 1-(Organooxy)alk-1-enes .................................................................................. 441
24.2.10.1 Synthesis of Product Subclass 10 .................................................................. 442
24.2.10.1.1 Method 1: Alkylation, Acylation, Phosphorylation, and Metalation of Enols or Enolates of Acylphosphoryl Compounds ................. 442
24.2.10.1.2 Method 2: Alkylation, Acylation, Silylation, Sulfonylation, and Phosphorylation of Anions of (1-Methoxyalk-2-enyl)-phosphonium Salts and Related Compounds ......................................................... 444
24.2.10.1.3 Method 3: Acylation of Dialkyl Phosphonates ............................................ 448
24.2.10.1.4 Method 4: Reaction of Esters of Phosphinous, Phosphonous, and Phosphorous Acids (Michaelis–Arbuzov and Related Reactions) ......................................................................................... 448
24.2.10.1.5 Method 5: Substitution of 1-Alkoxy-1-haloalk-1-enes with Phosphines under Palladium Catalysis ........................................................... 450
24.2.10.1.6 Method 6: Elimination of Hydrogen Halides from Phosphorylated 1,2-Difunctionalized Compounds ......................................................... 451
24.2.10.1.7 Method 7: Generation of (1-Alkoxyalk-1-enyl)phosphonates by the Horner–Emmons Reaction

24.2.10.1.8 Method 8: Generation of (1-Alkoxyalk-1-enyl)phosphonates by the Peterson Alkenation Reaction

24.2.10.1.9 Method 9: [4 + 2]-Cycloaddition Reactions of Phosphorylated Hetero-1,3-dienes with Enol Ethers

24.2.10.1.10 Method 10: Addition of Phosphines, Phosphinites, Phosphonites, and Phosphites to Ketenes

24.2.10.1.11 Method 11: Addition of Esters of Diphenylphosphinous Acid to Unsaturated Acyl Phosphonates

24.2.10.1.12 Method 12: Addition of Trialkyl Phosphites or 1,1,2,2-Tetraalkoxy-diphosphines to Alk-1-ynyl Ethers

24.2.10.2 Applications of Product Subclass 10 in Organic Synthesis

24.2.11 Product Subclass 11: 1,1-Bis(organosulfanyl)alk-1-enes (Ketene S,S-Acetals)

W. Dölling

24.2.11 Product Subclass 11: 1,1-Bis(organosulfanyl)alk-1-enes (Ketene S,S-Acetals)

24.2.11.1 Synthesis of Product Subclass 11

24.2.11.1.1 Method 1: Alkylation of Dithiocarboxylic Acids and Their Derivatives

24.2.11.1.1.1 Variation 1: From Dithiocarboxylic Acids

24.2.11.1.1.2 Variation 2: From Alkyl Dithiocarboxylates

24.2.11.1.1.3 Variation 3: From 1,1,1-Tris(alkylsulfanyl)ethanes

24.2.11.1.1.4 Variation 4: Reactions of Carboxylic Esters, Lactones, and Carboxylic Acids with Metal Thiolates

24.2.11.1.2 Method 2: Ketene S,S-Acetals from 1,1-Dihaloalkanes

24.2.11.1.3 Method 3: Ketene S,S-Acetals from 2-Substituted 1,1-Disulfanylated Ethanes

24.2.11.1.3.1 Variation 1: O-Acylation of 1-Aryl-2,2-bis(methylsulfanyl)ethanones

24.2.11.1.3.2 Variation 2: Dehydrochlorination of 2-Chloro-1,1-disulfanylethanes

24.2.11.1.3.3 Variation 3: Dehydration of 2,2-Bis(methylsulfanyl)ethanols

24.2.11.1.3.4 Variation 4: Elimination of a Thiol from 1,1,2-Tris(organosulfanyl)ethanes

24.2.11.1.3.5 Variation 5: Elimination of an Amine from 2-(Aminomethyl)-1,3-dithiane S,S-Dioxides

24.2.11.1.4 Method 4: Alkenation of Carbonyl Compounds

24.2.11.1.4.1 Variation 1: Using Bis(phenylsulfanyl)methylboronates

24.2.11.1.4.2 Variation 2: Wittig and Horner–Emmons Reactions

24.2.11.1.4.3 Variation 3: Peterson Reactions

24.2.11.1.5 Method 5: Synthesis from 1,3-Dithianes, Nitriles, and Amides

24.2.11.1.6 Method 6: Reactions of Carbon Disulfide with Carbaniions

24.2.11.1.6.1 Variation 1: From Aldehydes and Ketones

24.2.11.1.6.2 Variation 2: From Esters, Lactones, Amides, Nitriles, and Hydrazones

24.2.11.1.6.3 Variation 3: From Isocyanides or Nitroalkanes

24.2.11.1.6.4 Variation 4: From Sulfur-Stabilized Carbanions
24.2.11.6.5 Variation 5: From Phosphorus-Stabilized Carbanions ........................................ 497
24.2.11.6.6 Variation 6: From α-Aminated Carbanions or Nitrogen Ylides .......................... 498
24.2.11.6.7 Variation 7: From Heterocycles Containing Endocyclic Methylene Groups ....... 500
24.2.11.6.8 Variation 8: From Other Resonance-Stabilized Carbanions .............................. 501
24.2.11.6.9 Variation 9: From Nonstabilized Carbanions .................................................. 501
24.2.11.7 Method 7: Transformations of Other Ketene S,S-Acetals .................................. 503
24.2.11.8 Method 8: Synthesis from the Diesters of Trithiocarbonates .................................. 507
24.2.11.8.1 Variation 1: Reactions with Acetonitriles and Other CH-Acidic Compounds ....... 507
24.2.11.8.2 Variation 2: By Desulfurization ........................................................................... 508
24.2.11.8.3 Variation 3: By the Reactions of Carbenes or Ylides ........................................ 509
24.2.11.9 Method 9: Ring Opening and/or Rearrangement ................................................. 509
24.2.12 Applications of Product Subclass 11 in Organic Synthesis ................................ 510

24.2.12 Product Subclass 12: 1-(Organoselanyl)-1-(organosulfanyl)alk-1-enes and 1-(Organosulfanyl)-1-(organotellanyl)alk-1-enes
M. Yoshimatsu

24.2.12.1 Synthesis of Product Subclass 12 ................................................................. 517
24.2.12.1.1 Method 1: Alkylation of Alkaneselenothioate Esters ...................................... 517
24.2.12.1.1.1 Variation 1: By Alkylation of Lithium Enethiolates or Eneselenolates ....... 517
24.2.12.1.1.2 Variation 2: By Alkylation of Ammonium Eneselenolates of S-Alkyl Alkaneselenothioates ................................................................. 519
24.2.12.1.1.3 Variation 3: By Cadmium(II) Acetate Mediated Conversion of S-Alkyl Alkaneselenothioates ................................................................. 520
24.2.12.1.1.4 Variation 4: By Reaction of S-Alkyl Alkaneselenothioates with Trialkyl Phosphites ................................................................. 521
24.2.12.1.2 Method 2: Chalcogenation of α-Metalated 1-(Organochalcogeno)alkenes ........ 521
24.2.12.1.3 Method 3: Horner–Emmons Alkenation of Carbonyl Compounds .................. 524
24.2.12.1.4 Method 4: Alkylation with Thiols of Lithium Eneselenolates Generated from Alkynylselenolates ................................................................. 525
24.2.12.1.5 Method 5: Selenenylation of 1-(Organosulfonyl)alkynes .............................. 526
24.2.12.2 Applications of Product Subclass 12 in Organic Synthesis .............................. 526

24.2.13 Product Subclass 13: 1-Nitrogen-Functionalized 1-(Organosulfanyl)alk-1-enes
W. Dölling

24.2.13.1 Synthesis of Product Subclass 13 ................................................................. 529
24.2.13.1.1 Method 1: 1-(Organosulfanyl)alk-1-en-1-amines by the S-Alkylation of Thiocarboxamides ................................................................. 529
24.2.13.1.2 Method 2: Synthesis from 1-Halo-1-(organosulfanyl)alk-1-enes or Ketene S,S-Acetals .................................................. 530
24.2.13.1.2.1 Variation 1: Reaction of 1-Halo-1-(organosulfanyl)alk-1-enes with Amines 530
24.2.13.1.2.2 Variation 2: Reaction of Ketene S,S-Acetals with Amines and Related Compounds ................................. 531
24.2.13.1.2.3 Variation 3: Reaction of 1-Chloroethenamines with Sodium Alkanethiolates .................................................. 534
24.2.13.1.3 Method 3: Synthesis from Dithiocarboxylates or Dithiocarbonates ................................................................. 535
24.2.13.1.4 Method 4: Synthesis from Ynamines ................................................................. 536
24.2.13.1.5 Method 5: Synthesis from Isothiocyanates and S-Alkylation of the Adducts ..................................................... 536
24.2.13.2 Applications of Product Subclass 13 in Organic Synthesis .............................................................. 538

24.2.14 Product Subclass 14: 1-Phosphorus-Functionalized
1-(Organosulfanyl)alk-1-enes
J. Romanśki, G. Młostoń, and K. M. Pietrusiewicz

24.2.14 Product Subclass 14: 1-Phosphorus-Functionalized
1-(Organosulfanyl)alk-1-enes .................................................. 541
24.2.14.1 Synthesis of Product Subclass 14 ............................................ 541
24.2.14.1.1 Method 1: Synthesis from 1-Phosphorus-Functionalized 1-(Organosulfanyl)alkanes .................................................. 541
24.2.14.1.1.1 Variation 1: By Elimination of Hydrogen Chloride or Methanesulfenic or Methaneselenenic Acid ................................. 541
24.2.14.1.1.2 Variation 2: By the Pummerer Reaction ........................................ 542
24.2.14.1.1.3 Variation 3: By Condensation with Carbonyl Compounds and Derivatives .................................................. 543
24.2.14.2 Applications of Product Subclass 14 in Organic Synthesis .............................................................. 544

24.2.15 Product Subclass 15: 1,1-Bis(organoselanyl)alk-1-enes and Derivatives
M. Yoshimatsu

24.2.15 Product Subclass 15: 1,1-Bis(organoselanyl)alk-1-enes and Derivatives .............................................................. 547
24.2.15.1 Synthesis of Product Subclass 15 ............................................. 547
24.2.15.1.1 Method 1: Selenenylation of α-Metalated 1-(Organoselanyl)alkenes ................................................................. 547
24.2.15.1.2 Method 2: Nickel-Catalyzed Substitution of 1,1-Dibromoalkenes with Benzeneselenolates ................................................................. 549
24.2.15.1.3 Method 3: Alkenation of Carbonyl Compounds ................................................................. 549
24.2.15.1.3.1 Variation 1: Peterson Alkenation of Aldehydes with [Bis(organoselanyl)- (trimethylsilyl)methyl]lithium Reagents ................................................................. 549
24.2.15.1.3.2 Variation 2: Reaction of Lithiated 1,1-[Bis(organoselanyl)methyl]- phosphonates with Aldehydes and Ketones ................................................................. 550
24.2.15.1.4 Method 4: [β-Elimination from Selenoothro Esters with or without a 2-Hydroxy Group ................................................................. 551
24.2.15.1.5 Method 5: Reaction of Alkylidenecarbenes with Diselenides ................................................................. 553
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.2.15.1.6</td>
<td>Method 6: Reaction of C—H Acidic Methylene Compounds with Carbon Diselenide</td>
<td>553</td>
</tr>
<tr>
<td>24.2.15.1.7</td>
<td>Method 7: Reaction of Alkenes or Alkynes with Selenols, Selenolates, or Other Selenenylating Agents</td>
<td>555</td>
</tr>
<tr>
<td>24.2.15.2</td>
<td>Applications of Product Subclass 15 in Organic Synthesis</td>
<td>558</td>
</tr>
<tr>
<td>24.2.16</td>
<td><strong>Product Subclass 16: 1,1-Bis(organotellanyl)alk-1-enes and Derivatives</strong></td>
<td></td>
</tr>
<tr>
<td>24.2.16.1</td>
<td>Synthesis of Product Subclass 16</td>
<td>563</td>
</tr>
<tr>
<td>24.2.16.1.1</td>
<td>Method 1: Chalcogenation of α-Metalated 1-(Organochalcogeno)alk-1-enes</td>
<td>563</td>
</tr>
<tr>
<td>24.2.16.1.2</td>
<td>Method 2: Reaction of Aldehydes with Lithium [Bi(organotellanyl)methyl]phosphonates</td>
<td>564</td>
</tr>
<tr>
<td>24.2.16.1.3</td>
<td>Method 3: Syntheses of [1-(Organotellanyl)alkenyl]phosphonates and [1-(Organotellanyl)alkenyl]stannanes</td>
<td>565</td>
</tr>
<tr>
<td>24.2.16.2</td>
<td>Applications of Product Subclass 16 in Organic Synthesis</td>
<td>566</td>
</tr>
<tr>
<td>24.2.17</td>
<td><strong>Product Subclass 17: 1,1-Bis(nitrogen-functionalized) Alk-1-enes</strong></td>
<td></td>
</tr>
<tr>
<td>24.2.17.1</td>
<td>Alk-1-ene-1,1-diamines</td>
<td>571</td>
</tr>
<tr>
<td>24.2.17.1.1</td>
<td>Synthesis of Alk-1-ene-1,1-diamines</td>
<td>571</td>
</tr>
<tr>
<td>24.2.17.1.1.1</td>
<td>Method 1: Synthesis from Chloroformamidinium Salts and Alkyllithium Compounds</td>
<td>571</td>
</tr>
<tr>
<td>24.2.17.1.1.2</td>
<td>Method 2: Synthesis from But-2-yne-1,1,4,4,4-hexamines and Trimethylsilyl Cyanide</td>
<td>571</td>
</tr>
<tr>
<td>24.2.17.1.1.3</td>
<td>Method 3: Synthesis from Amines and Carbenes or Carbenoids</td>
<td>572</td>
</tr>
<tr>
<td>24.2.17.1.1.4</td>
<td>Method 4: Synthesis from Nitroketene N,N-Acetals and (Ethoxymethylene)malonic Acid Derivatives</td>
<td>572</td>
</tr>
<tr>
<td>24.2.17.1.1.5</td>
<td>Method 5: Synthesis from Diaziridinones and Malonic Acid Derivatives</td>
<td>573</td>
</tr>
<tr>
<td>24.2.17.1.1.6</td>
<td>Method 6: Synthesis from Alk-1-yn-1-amines</td>
<td>573</td>
</tr>
<tr>
<td>24.2.17.1.1.7</td>
<td>Method 7: Synthesis from N-Aryl-2-chloroacetamides and Malononitrile</td>
<td>575</td>
</tr>
<tr>
<td>24.2.17.1.1.8</td>
<td>Method 8: Synthesis from Alkylidenemalononitriles and Compounds Containing a CH-Acidic Group</td>
<td>576</td>
</tr>
<tr>
<td>24.2.17.1.1.9</td>
<td>Method 9: Synthesis from Alkylidene Malononitriles and Amines or Amine Derivatives</td>
<td>578</td>
</tr>
<tr>
<td>24.2.17.1.1.10</td>
<td>Method 10: Synthesis from Aziridines and Malonic Acid Derivatives</td>
<td>580</td>
</tr>
<tr>
<td>24.2.17.1.1.11</td>
<td>Method 11: Synthesis from 1,1,1-Trihaloalkanes</td>
<td>581</td>
</tr>
</tbody>
</table>
24.2.17.1.12 Method 12: Synthesis from a Triethylammonium Dichloromethane-sulfonate Derivative .............................................. 582
24.2.17.1.13 Method 13: Synthesis from Anhydrides, Esters, or Amides and Tetrakis(dimethylamino)titanium .............................................. 583
24.2.17.1.14 Method 14: Synthesis from Dithioesters and Amines .............................................. 587
24.2.17.1.15 Method 15: Synthesis from Dithioamides and Amines .............................................. 587
24.2.17.1.16 Method 16: Synthesis from 3H-1,2-Dithiole-3-thiones and Related Heterocycles .............................................. 589
24.2.17.1.17 Method 17: Synthesis from Benzodiazepines .............................................. 590
24.2.17.1.18 Method 18: Synthesis from (3-Oxo-3-phenylpropanoyl)malononitrile .............................................. 591
24.2.17.1.19 Method 19: Synthesis from Malononitrile and N,N'-Bis(2-aminoethyl)-ethane-1,2-diamine .............................................. 592
24.2.17.1.20 Method 20: Synthesis from Ketenes and Diaziridines .............................................. 592
24.2.17.1.21 Method 21: Synthesis from 1-Haloalk-1-ynes or Alk-1-yn-1-amines and Amines, Amides, or Betaines .............................................. 593
24.2.17.1.22 Method 22: Synthesis from 2,2-Dichloroalkanamines .............................................. 601
24.2.17.1.23 Method 23: Synthesis from Hetarenes .............................................. 602
24.2.17.1.24 Method 24: Synthesis from Chloroformamidinium Salts .............................................. 604
24.2.17.1.25 Method 25: Synthesis from 1,1-Dialkoxythioetheramines .............................................. 608
24.2.17.1.26 Method 26: Synthesis from Alkoxy-N,N',N'-tetraalkylformamidinium Salts .............................................. 609
24.2.17.1.27 Method 27: Synthesis from Isouronium Salts .............................................. 610
24.2.17.1.28 Method 28: Synthesis from Urea–Phosphoryl Chloride Adducts .............................................. 611
24.2.17.1.29 Method 29: Synthesis from Imidothiocarbamates .............................................. 612
24.2.17.1.30 Method 30: Synthesis from Isothiuronium Salts .............................................. 614
24.2.17.1.31 Method 31: Synthesis from Alkoxy-N,N,N',N'-tetraalkylformamidinium Salts or Tetrakis(dimethylamino)methane .............................................. 616
24.2.17.1.32 Method 32: Synthesis from Guanidinium Salts .............................................. 618
24.2.17.1.33 Method 33: Synthesis from Carboxylic acids .............................................. 619
24.2.17.1.34 Method 34: Synthesis from Cyanamides .............................................. 620
24.2.17.1.35 Method 35: Synthesis from 1-tert-Butoxy-N,N,N',N'-tetramethylmethanediamine or 1,1-Diethoxy-N,N-dimethylethanamine .............................................. 622
24.2.17.1.36 Method 36: Synthesis from Alkyne- and Allene-Substituted Ortho Amides .............................................. 623
24.2.17.1.37 Method 37: Synthesis from Amidines (With C–C Bond Formation) .............................................. 629
24.2.17.1.38 Method 38: Synthesis from 1,2,4-Triazolium Salts .............................................. 633
24.2.17.1.39 Method 39: Synthesis from Amidinium Salts and Amidines (Without C–C Bond Formation) .............................................. 634
24.2.17.1.40 Method 40: Synthesis from 2-Haloethane-1,1-diamines .............................................. 640
24.2.17.1.41 Method 41: Synthesis from Diaminopropanenitriles .............................................. 641
24.2.17.1.42 Method 42: Synthesis from 1,1-Dihaloalk-1-enes .............................................. 641
24.2.17.1.43 Method 43: Synthesis from 1-Haloalk-1-en-1-amines or 6-Chloropyrimidine Derivatives .............................................. 649
24.2.17.1.44 Method 44: Synthesis from 1-Chloro-1-sulfonylalk-1-enes .............................................. 655
24.2.17.1.45 Method 45: Synthesis from Ketene O,O-Acetals .............................................. 657
24.2.17.1.46 Method 46: Synthesis from Ketene O,N-Acetals .............................................. 659
24.2.17.1.47 Method 47: Synthesis from Ketene S,S-Acetals .............................................. 664
24.2.17.1.48 Method 48: Synthesis from Ketene S,N-Acetals .............................................. 673
24.2.17.1.49 Method 49: Synthesis from Ketenimines .............................................. 678
24.2.17.1.50 Method 50: Synthesis from 2-Bromoethenamines ........................................ 682
24.2.17.1.51 Method 51: Synthesis from Heterocyclic or Heteroaromatic Compounds 682
24.2.17.1.52 Method 52: Synthesis from 3,3,3-Trihaloprop-1-en-2-amines ...................... 683
24.2.17.1.53 Method 53: Synthesis from 2-Aminoacrylonitriles, 2-(Alkylsulfanyl)-acrylonitriles, or Alkylidenemalononitriles .............................................. 684
24.2.17.1.54 Method 54: Synthesis from Amino-Substituted Hetarenes or Dihydrohetarenes ................................................................. 686
24.2.17.1.55 Method 55: Synthesis Using Carbonic Acid Derivatives ............................. 688
24.2.17.1.56 Method 56: Synthesis from (Diethylamino)(diethyliminio)dithioacetate 693
24.2.17.1.57 Method 57: Synthesis from Imidazolium Salts via Nucleophilic Carbenes 694
24.2.17.1.58 Method 58: Synthesis from 2-Oxocyclododecane-1-carbonitrile ............. 694

24.2.17.2 
Alk-1-ene-1,1-diamines with Retention of the Functional Group
P. A. Keller and J. Morgan

24.2.17.2 Alk-1-ene-1,1-diamines with Retention of the Functional Group .............. 707
24.2.17.2.1 Synthesis with Formation of C—C Bonds ........................................... 707
24.2.17.2.1.1 Method 1: Reactions of Ketene $N,N$-Acetals with Carboxylic Acid Derivatives .............................................................. 707
24.2.17.2.1.2 Method 2: Reactions of Ketene $N,N$-Acetals with Activated Chloroalkenes, Enamines, or Nitro Compounds ........................................... 709
24.2.17.2.1.3 Method 3: Reactions of Ketene $N,N$-Acetals with Alkynes or Allenes ......... 711
24.2.17.2.1.4 Method 4: Reactions of Ketene $N,N$-Acetals with Activated Alkenes ............. 714
24.2.17.2.1.5 Method 5: Reactions of Ketene $N,N$-Acetals with Alkyl or Aryl Halides, Related Alkylating Reagents, or Aryldiazenes ........................................... 717
24.2.17.2.1.6 Method 6: Reactions of Ketene $N,N$-Acetals with Activated Methylene Compounds ........................................................................... 719
24.2.17.2.2 Synthesis without Formation of New C—C Bonds ...................................... 720
24.2.17.2.2.1 Method 1: Disulfide Reduction with Hydrogen ........................................ 720
24.2.17.2.2.2 Method 2: Reactions of Ketene $N,N$-Acetals with Halogens or Halogen Carriers ................................................................. 720
24.2.17.2.2.3 Method 3: Reactions of Ketene $N,N$-Acetals with Sulfur Electrophiles .......... 721
24.2.17.2.2.4 Method 4: Reactions of Ketene $N,N$-Acetals with Metal Halides, Other Metal Salts, or Metal Carbonyl Compounds ........................................... 722
24.2.17.2.3 Synthesis with Cleavage of C—C Bonds .................................................. 723
24.2.17.2.3.1 Method 1: Deacylation Reactions ....................................................... 723
24.2.17.2.4 Reactions at the Ketene $N,N$-Acetal Moiety ............................................ 725
24.2.17.2.4.1 Method 1: Reactions of Ketene $N,N$-Acetals with Carbonic Acid Derivatives ................................................................. 725
24.2.17.2.4.2 Method 2: Reactions of Ketene $N,N$-Acetals with Carboxylic Acid Derivatives ........................................................................ 726
24.2.17.2.4.3 Method 3: Reactions of Ketene $N,N$-Acetals with Alkynoic Acid Derivatives ................................................................. 729
24.2.17.2.4.4 Method 4: Reactions of Ketene $N,N$-Acetals with Ketones ...................... 729
24.2.17.2.4.5 Method 5: Reactions of Ketene $N,N$-Acetals with Alkylating and Arylating Reagents ........................................ 729
24.2.17.2.4.6 Method 6: Reactions of Ketene $N,N$-Acetals with Mineral Acids, Potassium Iodide, and Acidic Hydrolysis ............................... 730
24.2.17.2.4.7 Method 7: Reactions of Ketene $N,N$-Acetals with Aqueous Sodium Hydroxide or Alcoholic Alkoxides (Hydrolysis, Cyclizations, and N-Deacylation) ........................................ 732
24.2.17.2.4.8 Method 8: Reactions of Ketene $N,N$-Acetals with Sulfur and Phosphorus Electrophiles ........................................... 732
24.2.17.2.4.9 Method 9: Reactions of Ketene $N,N$-Acetals with Amines ............................................................................. 733
24.2.17.2.4.10 Method 10: Reactions of Ketene $N,N$-Acetals with Hydrogen ............................................................................ 734
24.2.17.2.5 Reactions at the Periphery of the System ................................................................................................................. 735
24.2.17.2.5.1 Method 1: Aminodechlorination Reactions ........................................ 735
24.2.17.2.5.2 Method 2: Reactions of Imidoyl Chloride Groups .......................... 736
24.2.17.2.5.3 Method 3: Hydrolysis of Remote Ester or Amide Groups ............... 737
24.2.17.2.5.4 Method 4: Addition of Chloro Compounds across a $\beta$-Cyan Group ........................................................................... 737
24.2.17.2.5.5 Method 5: Reactions of $\beta$-Cyan Groups with Hydrogen Sulfide .................................................................................. 738
24.2.17.2.5.6 Method 6: Transformations of $\beta$-Carbonyl Groups ........................ 739
24.2.17.2.5.7 Method 7: Transformations of $\beta$-Imidoyl Groups ........................................ 739
24.2.17.2.5.8 Method 8: Transformations of Remote Nitro or Amino Groups ....... 740
24.2.17.2.5.9 Method 9: Transformations of C$\equiv$O Bonds .................................. 741
24.2.17.2.5.10 Method 10: Transformations by Oxidation or Reduction ................ 741
24.2.17.2.5.11 Method 11: Alkylation Reactions ............................................... 742
24.2.17.2.6 Transformations of Hydrazino or N-Hydroxyamino Derivatives of Ketene $N,N$-Acetals .............................................................................................................. 743
24.2.17.2.6.1 Method 1: Reactions of Ketene $N,N$-Acetals with Isocyanates and Isothiocyanates ........................................ 743
24.2.17.2.6.2 Method 2: Reactions of Ketene $N,N$-Acetals with Carboxylic Acid Derivatives ................................................................. 743
24.2.17.2.6.3 Method 3: Reactions of Ketene $N,N$-Acetals with Aldehydes or Ketones ........................ ......................................................... 744
24.2.17.2.6.4 Method 4: Reactions of Ketene $N,N$-Acetals with Diazomethane ........ 744
24.2.17.2.6.5 Method 5: Reactions of Ketene $N,N$-Acetals with Sodium Nitrite/Hydrochloric Acid ........................................................... 744

24.2.17.3 1,1-Bisazo-, 1,1-Diazido-, and 1,1-Dinitroalk-1-enes

K. Banert

24.2.17.3 1,1-Bisazo-, 1,1-Diazido-, and 1,1-Dinitroalk-1-enes ......................... 747
24.2.17.3.1 Synthesis of 1,1-Bisazo-, 1,1-Diazido-, and 1,1-Dinitroalk-1-enes ...... 747
24.2.17.3.3.1 Method 1: 1,1-Bisazoalk-1-enes from Formazans ...................... 747
24.2.17.3.1.1 Variation 1: By Dehydrogenation ........................................ 747
24.2.17.3.1.2 Variation 2: By Base-Induced Deprotonation ................................ 748
24.2.17.3.1.3 Variation 3: By Dehydration ............................................... 748
24.2.17.3.1.2 Method 2: 1,1-Diazidoalk-1-enes from 3,3-Dichloroacrylonitriles .... 749
24.2.17.3.1.3 Method 3: 1,1-Dinitroalk-1-enes by Formation of the C$\equiv$C Bond from Two Carbon Components ....................................................... 750
24.2.17.3.1.3.1 Variation 1: Reactions between Di- or Trinitromethyl Reagents and Diazo Compounds ........................................ 750

24.2.17.3.1.3.2 Variation 2: Reactions between Tetra- or Dinitromethane and Other Reagents ........................................... 750

24.2.17.3.1.4 Method 4: 1,1-Dinitroalk-1-enes by Formation of the C=C Bond by Elimination ............................................... 752

24.2.17.3.1.5 Method 5: 1,1-Dinitroalk-1-enes by Introduction of the Nitro Groups at the C=C Bonds of Alkenes .......................... 753

24.2.17.3.1.6 Method 6: 1,1-Dinitroalk-1-enes from Methyl-Substituted Heterocycles .......................................................... 755

24.2.17.3.1.7 Method 7: 1,1-Dinitroalk-1-enes from Methyl-Substituted Heterocycles .......................................................... 757

24.2.17.3.1.7.1 Variation 1: By Substitution at the C=C Bond ........................................... 757

24.2.17.3.1.7.2 Variation 2: By Other Substitutions ........................................... 759

24.2.17.3.2 Applications of 1,1-Bisazo-, 1,1-Diazido-, and 1,1-Dinitroalk-1-enes in Organic Synthesis .......................... 760

24.2.18 Product Subclass 18: 1-Nitrogen-Functionalized 1-Phosphorus-Functionalized Alk-1-enes
M. Stankević and K. M. Pietrusiewicz

24.2.18 Product Subclass 18: 1-Nitrogen-Functionalized 1-Phosphorus-Functionalized Alk-1-enes ............................................. 767

24.2.18.1 Synthesis of Product Subclass 18 ............................................. 767

24.2.18.1.1 Method 1: Synthesis from Haloenamines and Haloimines ................. 767

24.2.18.1.2 Method 2: Synthesis from 1-Phosphorus-Functionalized Alkanamines 768

24.2.18.1.2.1 Variation 1: By Condensation with Carbonyl Compounds ................ 768

24.2.18.1.2.2 Variation 2: By the Horner–Wadsworth–Emmons Reaction .............. 769

24.2.18.1.2.3 Variation 3: By Elimination ............................................ 769

24.2.18.2 Applications of Products Subclass 18 in Organic Synthesis ................. 770

24.2.19 Product Subclass 19: 1,1-Bis(phosphorus-functionalized) Alk-1-enes
M. Stankević and K. M. Pietrusiewicz

24.2.19 Product Subclass 19: 1,1-Bis(phosphorus-functionalized) Alk-1-enes .............. 775

24.2.19.1 Synthesis of Product Subclass 19 ............................................. 775

24.2.19.1.1 Method 1: Substitution Reactions of 1,1-Dihaloalkenes .......................... 775

24.2.19.1.2 Method 2: Synthesis from Methylenephosphorus and Methylenephosphine sulfides ................................................. 777

24.2.19.1.3 Method 3: Synthesis from α-Acyl Ylides ........................................... 777

24.2.19.2 Applications of Product Subclass 19 in Organic Synthesis ................. 777
24.3 Product Class 3: Bis(heteroatom-functionalized) Acetylenes

24.3.1 Product Subclass 1: Dihaloacetylenes
B. Witulski and C. Alayrac

24.3.1.1 Synthesis of Product Subclass 1

24.3.1.1.1 Method 1: Vacuum Pyrolysis

24.3.1.1.2 Method 2: Electrical Discharge

24.3.1.1.3 Method 3: Photolysis

24.3.1.1.4 Method 4: Dehydrohalogenation and Dehalogenation Reactions

24.3.1.1.4.1 Variation 1: Dehydrohalogenation of 2-Fluoro-1,1-dihaloalkenes

24.3.1.1.4.2 Variation 2: Dehydrohalogenation of Trihaloalkanes

24.3.1.1.4.3 Variation 3: Dehalogenation of Tetrahaloalkanes

24.3.1.1.4.4 Variation 4: Dehydrochlorination of Trichloroethene

24.3.1.1.4.5 Method 5: Halogenation of Acetylene

24.3.1.1.4.6 Variation 1: Metalation and Chlorination of Acetylene

24.3.1.1.4.7 Variation 2: Metalation and Bromination of Acetylene

24.3.1.1.4.8 Variation 3: Iodination of Acetylene Using Iodine in Liquid Ammonia

24.3.1.1.4.9 Variation 4: Iodination of Acetylenes Using Bis(2,4,6-collidine)iodonium Hexafluorophosphate

24.3.1.2 Applications of Product Subclass 1 in Organic Synthesis

24.3.2 Product Subclass 2: 1-Heteroatom-Functionalized 2-Haloacetylenes
B. Witulski and C. Alayrac

24.3.2.1 Synthesis of Product Subclass 2

24.3.2.1.1 Method 1: Synthesis of 1-Halo-2-(triorganosilyl)acetylenes

24.3.2.1.1.1 Variation 1: Halogenation of Silylated Acetylenes

24.3.2.1.1.2 Variation 2: Halogenation of Metal Silylacetylides

24.3.2.1.1.3 Variation 3: Synthesis of 1-Fluoro-2-(triisopropylsilyl)acetylene from 1,1-Difluoroethene

24.3.2.1.1.4 Variation 4: Silylation of Metal Chloro- or Bromoacetylides

24.3.2.1.1.5 Variation 5: Iodination of Disilylated Acetylenes

24.3.2.1.2 Method 2: Synthesis of 1-Alkoxy-2-haloacetylenes

24.3.2.1.3 Method 3: Synthesis of 1-Halo-2-(organosulfonyl)- and 1-Halo-2-(organosulfanyl)acetylenes

24.3.2.1.3.1 Variation 1: Bromination of Sulfonylated Acetylenes with N-Bromosuccinimide

24.3.2.1.3.2 Variation 2: By the Hypobromite or Hypochlorite Methods

24.3.2.1.3.3 Variation 3: Halogenation of Lithium 2-Sulfonylacetylides

24.3.2.1.3.4 Variation 4: Alkylthiolation of Lithium Chloroacetylide
24.3.2.1.3.5 Variation 5: 1-(Alkylsulfanyl)-2-chloroacetylenes under Phase-Transfer Conditions ................................. 807
24.3.2.1.4 Method 4: Synthesis of 2-Haloacetylen-1-amines ............................. 808
24.3.2.1.4.1 Variation 1: By the Hypobromite Method .................................. 808
24.3.2.1.4.2 Variation 2: From 1,1-Dichloro-2-fluoroethene .......................... 808
24.3.2.1.4.3 Variation 3: From Chloroenamines ..................................... 809
24.3.2.1.5 Method 5: Synthesis of 1-Halo-2-(phosphoryl)acetylenes .............. 810
24.3.2.1.5.1 Variation 1: By the Hypochlorite Method ............................... 811
24.3.2.1.5.2 Variation 2: By the Ionin–Petrov Method ............................... 811
24.3.2.2 Applications of Product Subclass 2 in Organic Synthesis .................... 812
24.3.2.2.1 Method 1: Substitution Reactions toward Diheterosubstituted Acetylenes .................................................. 812
24.3.2.2.1.1 Variation 1: Heterosubstituted Ynamines ................................ 812
24.3.2.2.1.2 Variation 2: 1-Heteroatom-Functionalized 2-(Phosphoryl)acetylenes ..... 813
24.3.2.2.2 Method 2: Cross-Coupling Reactions in the Presence of Transition Metals 813
24.3.2.2.2.1 Variation 1: With Aryl- or Alkylcopper Reagents ........................ 813
24.3.2.2.2.2 Variation 2: With Alkenylcopper Reagents .............................. 814
24.3.2.2.2.3 Variation 3: 1-Bromo-2-silylacetylenes in Cadiot–Chodkiewicz Coupling Reactions ........................................ 814
24.3.2.2.2.4 Variation 4: Chemoselective Two-Carbon Homologation of Aldehydes ... 815
24.3.2.2.2.5 Variation 5: Catalytic ortho-Ethynylation of Phenols and Anilines with 1-Chloro-2-(triethylsilyl)acetylene ........................................... 816
24.3.2.2.3 Method 3: Cycloaddition Reactions ................................... 816

24.3.3 Product Subclass 3: Bis(organooxy)acetylenes
B. Witulski and C. Alayrac

24.3.3 Product Subclass 3: Bis(organooxy)acetylenes ........................... 821
24.3.3.1 Synthesis of Product Subclass 3 ........................................... 824
24.3.3.1.1 Method 1: Synthesis of Diphenoxyacetylene by Substitution Reactions 824
24.3.3.1.2 Method 2: Synthesis of Bis(organooxy)acetylenes by Elimination Reactions .................................................. 825
24.3.3.1.2.1 Variation 1: From Polymeric Glyoxal ................................ 825
24.3.3.1.2.2 Variation 2: Dialkoxyacetylenes from Bromoalkenes ................. 826
24.3.3.1.2.3 Variation 3: Di-tert-butoxyacetylene from trans-2,3-Dichloro-1,4-dioxane 828
24.3.3.1.3 Method 3: Photochemical Synthesis of Acetylenediol .................. 829
24.3.3.2 Applications of Product Subclass 3 in Organic Synthesis ............... 829
24.3.3.2.1 Method 1: Synthesis of Hexasubstituted Benzenes ........................ 829
24.3.3.2.2 Method 2: Synthesis of Deltic Acid .................................... 830
24.3.3.2.3 Method 3: Synthesis of Squaric and Semisquaric Acids ................ 830
24.3.3.2.4 Method 4: Synthesis of Hydrocroconic Acid and Croconate Dianion ... 831
### 24.3.4 Product Subclass 4: 1-(Organochalcogeno)-2-(organooxy)acetylenes
B. Witulski and C. Alayrac

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.3.4.1</td>
<td>Synthesis of Product Subclass 4</td>
<td>836</td>
</tr>
<tr>
<td>24.3.4.1.1</td>
<td>Method 1: Substitution Reactions of Lithium Alkoxyacetylides</td>
<td>836</td>
</tr>
<tr>
<td>24.3.4.1.2</td>
<td>Method 2: Substitution Reactions of 1-Alkoxy-2-stannylacetylenes</td>
<td>837</td>
</tr>
<tr>
<td>24.3.4.1.3</td>
<td>Method 3: Elimination Reactions of 1,1-Dichloro-2-(organosulfanyl)ethenes</td>
<td>837</td>
</tr>
<tr>
<td>24.3.4.1.4</td>
<td>Method 4: Elimination of Hydrogen Chloride from 1,2-Dichloro-2-(phenylselanyl)ethene</td>
<td>838</td>
</tr>
</tbody>
</table>

### 24.3.5 Product Subclass 5: 1-Nitrogen-Functionalized 2-(Organooxy)acetylenes
B. Witulski and C. Alayrac

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.3.5.1</td>
<td>Synthesis of Product Subclass 5</td>
<td>841</td>
</tr>
<tr>
<td>24.3.5.1.1</td>
<td>Method 1: Generation of 2-Aminoacetylen-1-ols</td>
<td>841</td>
</tr>
</tbody>
</table>

### 24.3.6 Product Subclass 6: 1-Phosphorus-Functionalized 2-(Organooxy)acetylenes
B. Witulski and C. Alayrac

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.3.6.1</td>
<td>Synthesis of Product Subclass 6</td>
<td>843</td>
</tr>
<tr>
<td>24.3.6.1.1</td>
<td>Method 1: Substitution Reactions of (Chloroethynyl)phosphonates</td>
<td>843</td>
</tr>
<tr>
<td>24.3.6.1.2</td>
<td>Method 2: Substitution Reactions of Lithium Alkoxyacetylides</td>
<td>844</td>
</tr>
<tr>
<td>24.3.6.1.3</td>
<td>Method 3: Reaction of Potassium Alkoxyacetylides with Tetrphenylphosphonium Chloride</td>
<td>845</td>
</tr>
<tr>
<td>24.3.6.1.4</td>
<td>Method 4: Sulfuration of 1-Alkoxy-2-phosphinoacetylenes</td>
<td>845</td>
</tr>
</tbody>
</table>

### 24.3.7 Product Subclass 7: Bis(organochalcogeno)acetylenes
T. Murai

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.3.7.1</td>
<td>Synthesis of Product Subclass 7</td>
<td>849</td>
</tr>
</tbody>
</table>
24.3.7.1 Bis(organosulfanyl)acetylenes ............................................. 849

24.3.7.1.1 Method 1: Reaction of Electrophilic Acetylenic Species with Organosulfanyl Compounds ............................................. 849

24.3.7.1.2 Method 2: Reaction of Metal Acetylenides with Organosulfanyl Compounds ............................................. 851

24.3.7.1.3 Method 3: Elimination from 1-Chloro-1,2-bis(organosulfanyl)ethenes ............................................. 853

24.3.7.1.4 Method 4: Oxidation of 1,2-Bis(organosulfanyl)acetylenes ............................................. 854

24.3.7.1.2 1-(Organoselanyl)-2-(organosulfanyl)acetylenes ............................................. 854

24.3.7.1.3 Method 1: Reaction of 1-Chloro-2-(organosulfanyl)acetylenes with Organoselenols ............................................. 854

24.3.7.1.4 1-(Organosulfanyl)-2-(organotellanyl)acetylenes ............................................. 855

24.3.7.1.5 Method 1: Reaction of Diorgano Ditellurides with 1,1-Dichloro-2-(organosulfanyl)ethenes ............................................. 855

24.3.7.1.6 Bis(organoselanyl)acetylenes ............................................. 855

24.3.7.1.7 Method 1: Reaction of Sodium Acetylide with Elemental Selenium and Alkyl Halides ............................................. 855

24.3.7.1.8 Method 2: Reaction of Lithium Acetylenides with Bis(selenocyanato)alkanes ............................................. 856

24.3.7.1.9 Method 3: Reaction of (Organoselanyl)acetylides with Areneselenenyl Halides ............................................. 856

24.3.7.1.10 Bis(organotellanyl)acetylenes ............................................. 856

24.3.7.1.11 Method 1: Reaction of Dimetal Acetylenides with Elemental Tellurium and Alkyl Halides or Organotellanyl Compounds ............................................. 857

24.3.7.1.12 Method 2: Reaction of Acetylene with Dialkyl Ditellurides ............................................. 857

24.3.8 Product Subclass 8: 1-Nitrogen-Functionalized 2-(Organochalcogeno)acetylenes

T. Murai

24.3.8 Product Subclass 8: 1-Nitrogen-Functionalized 2-(Organochalcogeno)acetylenes ............................................. 859

24.3.8.1 Synthesis of Product Subclass 8 ............................................. 859

24.3.8.1.1 N,N-Dialkyl-2-(organosulfanyl)acetylen-1-amines ............................................. 859

24.3.8.1.2 Method 1: Reaction of 1-Chloro-2-(organosulfanyl)acetylenes with Amines or Metal Amides ............................................. 859

24.3.8.1.3 Variation 1: Reaction of Phenyl(2-tosylethynyl)iodonium Trifluoromethanesulfonate with Metal Amides ............................................. 860

24.3.8.1.4 Method 2: Reaction of Metal 2-(Diorganoamino)acetylides with Sulfur and Alkyl Halides or Sulfur Electrophiles ............................................. 861

24.3.8.1.5 2-(Organoselanyl)acetylen-1-amines ............................................. 861

24.3.8.1.6 Method 1: Reaction of Phenyl 2,2,2-Trifluoroethyl Selenide with Lithium Dialkylamides ............................................. 861
24.3.9  
**Product Subclass 9: 2-Phosphorus-Functionalized 1-(Organochalcogeno)acetylenes**  
T. Murai

---

24.3.10  
**Product Subclass 10: Bis(nitrogen-functionalized) Acetylenes**  
B. Witulski and C. Alayrac

---

24.3.9  
**Product Subclass 9: 2-Phosphorus-Functionalized 1-(Organochalcogeno)acetylenes** ........................................ 863

24.3.9.1  
Synthesis of Product Subclass 9 ........................................... 863

24.3.9.1.1  
2-Phosphorus-Functionalized 1-(Organosulfanyl)acetylenes 863

24.3.9.1.1.1  
**Method 1:** Reaction of 1-Chloro-2-(organosulfanyl)acetylenes with Trivalent Phosphorus Compounds ....................................... 863

24.3.9.1.1.2  
**Method 2:** Reaction of 1-Chloro-2-phosphorylacetylenes with Thiols or Metal Thiolates ........................................ 864

24.3.10  
**Product Subclass 10: Bis(nitrogen-functionalized) Acetylenes** ............ 867

24.3.10.1  
Synthesis of Product Subclass 10 .......................................... 869

24.3.10.1.1  
**Method 1:** Synthesis from α-Diiminium Salts 869

24.3.10.1.2  
**Method 2:** Synthesis from 1-Bromoethene-1,2-diamines 869

24.3.10.1.3  
**Method 3:** Synthesis from Chloroketene N,N-Acetals 870

24.3.10.1.3.1  
Variation 1: From Isolated Chloroketene N,N-Acetals 870

24.3.10.1.3.2  
Variation 2: One-Pot Procedure from Trichloroethene 871

24.3.10.1.4  
**Method 4:** One-Pot Procedure from Trichloroethenamines 871

24.3.10.1.5  
**Method 5:** Flash Pyrolysis ........................................ 872

24.3.10.1.5.1  
Variation 1: From 2,3-Diaminocyclopropenones 872

24.3.10.1.5.2  
Variation 2: From 1,2,4-Triazine-3,5,6-triamines 873

24.3.10.1.6  
**Method 6:** Dimerization of Alkyl Isocyanides 873

24.3.10.1.7  
**Method 7:** 1,2-Diisocyanoacetylene by UV Photolysis 874

24.3.10.2  
Applications of Product Subclass 10 in Organic Synthesis ................... 875

24.3.10.2.1  
**Method 1:** Synthesis of N,N,N′,N′-Tetraethyl(dichalcogenooxalamides) 875

24.3.10.2.2  
**Method 2:** Synthesis of Bis(dialkylamino)cyclopropene Derivatives 875

24.3.10.2.2.1  
Variation 1: Bis(dialkylamino)cyclopropenethiones 875

24.3.10.2.2.2  
Variation 2: Bis(dialkylamino)cyclopropenimines 876

24.3.10.2.3  
**Method 3:** Synthesis of Bis(dialkylamino)cyclobutene Derivatives 876

24.3.10.2.3.1  
Variation 1: Tris- or Tetrakis(dimethylamino)cyclobutenes 876

24.3.10.2.3.2  
Variation 2: Spiro-Annulated Products ........................................ 877

24.3.10.2.4  
**Method 4:** Synthesis of Heterocyclic Compounds 878

24.3.10.2.4.1  
Variation 1: N,N,N′,N′-Tetramethylpyrazolediamines 878

24.3.10.2.4.2  
Variation 2: 2,6-Diazabicyclo[2.2.2]oct-7-ene-3,5-diones 878

24.3.10.2.4.3  
Variation 3: 2-Thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-6,7-diamines 879

24.3.10.2.4.4  
Variation 4: 1,3-Diphospha-Dewar Benzenes 879

24.3.10.2.5  
**Method 5:** Synthesis of Metal Complexes 880

24.3.10.2.5.1  
Variation 1: Tricarbonyliron Complexes of Cyclopentadienones 880
### Product Subclass 11: 1-Nitrogen-Functionalized 2-Phosphorus-Functionalized Acetylenes and Bis(phosphorus-functionalized) Acetylenes

B. Witulski and C. Alayrac

<table>
<thead>
<tr>
<th>Table of Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.3.11.1 Product Subclass 11: 1-Nitrogen-Functionalized 2-Phosphorus-Functionalized Acetylenes and Bis(phosphorus-functionalized) Acetylenes</td>
</tr>
</tbody>
</table>

#### 24.3.11.1 Synthesis of Product Subclass 11

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthesis of 1-Amino-2-(phosphoryl)acetylenes</td>
</tr>
<tr>
<td>2</td>
<td>Synthesis of 1-Amino-2-(thiophosphoryl)acetylenes</td>
</tr>
<tr>
<td>3</td>
<td>Synthesis of 1-Amino-2-(selenophosphoryl)acetylenes</td>
</tr>
<tr>
<td>4</td>
<td>Synthesis of 1-Amino-2-(phosphorimidoyl)acetylenes</td>
</tr>
<tr>
<td>5</td>
<td>Synthesis of (Aminoethynyl)triphenylphosphonium Salts</td>
</tr>
<tr>
<td>6</td>
<td>Synthesis of Bis(phosphorylated) Acetylenes</td>
</tr>
<tr>
<td>7</td>
<td>Synthesis of Bis(thiophosphoryl)acetylenes</td>
</tr>
<tr>
<td>8</td>
<td>Synthesis of Bis(diorganophosphoryl)acetylenes by Oxidation Reactions</td>
</tr>
<tr>
<td>9</td>
<td>Synthesis of Bis(diorganoselenophosphoryl)acetylenes</td>
</tr>
<tr>
<td>10</td>
<td>Synthesis of Bis(diorganophosphoryl)acetylenes by Substitution Reactions</td>
</tr>
<tr>
<td>11</td>
<td>Synthesis of Bis(diorganoselenophosphoryl)acetylenes</td>
</tr>
<tr>
<td>12</td>
<td>Synthesis of Bis(diorganophosphoryl)acetylenes by Substitution with Chlorine Atoms</td>
</tr>
<tr>
<td>13</td>
<td>Synthesis of Bis(diorganophosphoryl)acetylenes from Acetylene</td>
</tr>
<tr>
<td>14</td>
<td>Synthesis of Bis(diorganophosphoryl)acetylenes from Tetrachloroethene</td>
</tr>
</tbody>
</table>

---

Science of Synthesis Original Edition Volume 24 © Georg Thieme Verlag KG
24.4  Product Class 4: 1-Heteroatom-Functionalized Alk-1-ynes

24.4.1  Product Subclass 1: 1-Haloalk-1-ynes and Alk-1-yn-1-ols

B. Witulski and C. Alayrac

24.4.1.1  Synthesis of Product Subclass 1 ................................. 906

24.4.1.1.1  Method 1: Halogenation of Alk-1-ynes ................................. 906

24.4.1.1.1.1  Variation 1: By Reaction with N-Halosuccinimides ................................. 906

24.4.1.1.1.2  Variation 2: Bis(trimethylsilyl) Peroxide and Metal-Promoted Transfer of Halides ................................. 907

24.4.1.1.1.3  Variation 3: Straus Reaction ................................. 908

24.4.1.1.1.4  Variation 4: Bromination Reaction with Triphenylphosphine and Carbon Tetrabromide ................................. 909

24.4.1.1.1.5  Variation 5: Iodination with a Polymer-Supported Bis(aclyoxy)iodate(I) Reagent ................................. 910

24.4.1.1.1.6  Variation 6: Iodination with Bis(2,4,6-collidine)iodonium Hexafluorophosphate ................................. 911

24.4.1.1.1.7  Variation 7: Iodination with Molecular Iodine ................................. 911

24.4.1.1.2  Method 2: Halogenation of Metal Acetylides ................................. 912

24.4.1.1.2.1  Variation 1: Halogenation with Molecular Bromine or Iodine ................................. 912

24.4.1.1.2.2  Variation 2: Chlorination of Lithium Acetylides with N-Chlorosuccinimide ................................. 913

24.4.1.1.2.3  Variation 3: Iodination of Sodium Acetylides with Bis(pyridine)iodonium Tetrafluoroborate ................................. 914

24.4.1.1.3  Method 3: Halodecarboxylation of Propynoic Acids ................................. 915

24.4.1.1.3.1  Variation 1: With N-Halosuccinimides and Tributylammonium Trifluoroacetate ................................. 915

24.4.1.1.3.2  Variation 2: With Bis(2,4,6-collidine)iodonium or Bis(2,4,6-collidine)-bromonium Hexafluorophosphate ................................. 915

24.4.1.1.4  Method 4: Direct Transformation of Trimethylsilylalkynes into Haloalkynes ................................. 916

24.4.1.1.5  Method 5: Dehydrohalogenation of 1,1-Dihaloalkenes ................................. 916

24.4.1.1.5.1  Variation 1: Dehydrohalogenation under Phase-Transfer Conditions ................................. 917

24.4.1.1.5.2  Variation 2: Dehydrohalogenation in Organic Solvents ................................. 917

24.4.1.1.6  Method 6: Dehalogenation of Oligohaloalkanes with a Metal ................................. 918

24.4.1.1.7  Method 7: Functionalization of Metal Haloacetylides ................................. 919
24.4.1.8 Method 8: Synthesis of 1-Haloalk-1-ynes from Carbonyl Compounds ................................................................. 920
  24.4.1.8.1 Variation 1: Synthesis of 2-Aryl-1-bromoacetylenes from Hydrazones ...................................................... 920
  24.4.1.8.2 Variation 2: Synthesis of 1-Chloroalk-1-ynes from Dihydroisoxazolones .............................................. 920
  24.4.1.8.3 Variation 3: Synthesis of 1-Chloroalk-1-ynes from Esters ................................................................. 921
  24.4.1.8.4 Variation 4: One-Pot Conversion of Aldehydes into 1-Haloalk-1-ynes with Dihalomethylphosphonates ....... 921
  24.4.1.8.5 Variation 5: One-Pot Conversion of Aldehydes into 1-Haloalk-1-ynes with Dihalomethylenetriphenylphosphoranes ..................... 922
  24.4.1.9 Method 9: Base-Induced Rearrangement of (Z)-(2-Halovinyl)iodonium Salts ................................................. 923
  24.4.1.10 Method 10: Synthesis of 1-Fluoroalk-1-ynes by Electrical Discharge ...................................................... 924
  24.4.1.11 Method 11: Synthesis of 1-Haloalk-1-ynes by Vacuum Pyrolysis ............................................................. 925
  24.4.1.12 Method 12: Synthesis of 1-Fluoroalk-1-ynes by Photolysis ..................................................... 925
  24.4.1.13 Method 13: Photochemical Synthesis of Alk-1-yn-1-ols ............................................................... 926
  24.4.1.14 Applications of Product Subclass 1 in Organic Synthesis .......................................................... 927
  24.4.1.2 Method 1: Cadiot–Chodkiewicz Coupling .......................................................... 927
  24.4.1.2.2 Method 2: Cross Coupling of 1-Haloalk-1-ynes with Metalated Ethenes ............................................. 928
  24.4.1.2.3 Method 3: Cross-Coupling Reactions of 1-Haloalk-1-ynes with Alkylzinc–Copper Reagents ................. 928
  24.4.1.2.4 Method 4: Synthesis of Stereochemically Defined Vinylboronates by Hydroboration of 1-Haloalk-1-ynes ................................. 929

24.4.2 Product Subclass 2: 1-(Organoxy)alk-1-ynes and 1-(Heterooxy)alk-1-ynes
B. Witulski and C. Alayrac

24.4.2.1 Synthesis of Product Subclass 2 .......................................................... 933
  24.4.2.1.1 Method 1: Synthesis of Alk-1-ynyl Carbamates by Elimination ................................................................. 935
  24.4.2.1.2 Method 2: Synthesis of Alk-1-ynyl Carboxylates from Alk-1-ynyliodonium Salts ................................................................. 936
  24.4.2.1.3 Method 3: Synthesis of Alk-1-ynyl Ethers from 1-Alkoxo-2-haloacetylenes ................................................................. 937
  24.4.2.1.4 Method 4: Synthesis of Alk-1-ynyl Ethers by Dehydrohalogenation ................................................................. 938
  24.4.2.1.4.1 Variation 1: From Alkoxides and Trichloroethene .................................................................................. 938
  24.4.2.1.4.2 Variation 2: Dehydrohalogenation of 2-Halovinyl Ethers ................................................................. 939
  24.4.2.1.4.3 Variation 3: From Chloroacetaldehyde Dialkyl Acetals .............................................................................. 940
  24.4.2.1.4.4 Variation 4: From 2,2,2-Trifluoroethyl Ethers ................................................................................. 942
  24.4.2.1.4.5 Variation 5: From Acetates .............................................................................................................. 942
  24.4.2.1.5 Method 5: Synthesis of Alk-1-ynyl Sulfonates from Alk-1-ynyliodonium Salts ................................................................. 943
  24.4.2.1.6 Method 6: Synthesis of Dialkyl Alk-1-ynyl Phosphates ........................................................................... 944
  24.4.2.1.6.1 Variation 1: From Alk-1-ynyliodonium Salts .................................................................................. 944
  24.4.2.1.6.2 Variation 2: From Lithium Alk-1-ylnolates ................................................................................ 945
  24.4.2.1.7 Method 7: Synthesis of 1-Siloxyalk-1-ynes .......................................................................................... 946
  24.4.2.1.7.1 Variation 1: From Alk-1-ynyl 4-Toluensulfonates .............................................................................. 946
24.4.2.1.7.2 Variation 2: By Oxygenation of Acetylides ........................................... 946
24.4.2.1.7.3 Variation 3: From Ester-Derived Ynolates ........................................... 947
24.4.2.1.7.4 Variation 4: From (Z)-2-Halovinyl Silyl Ethers ....................................... 948
24.4.2.1.7.5 Variation 5: From Silylated α-Diazo Carbonyl Compounds ........................ 949
24.4.2.2 Applications of Product Subclass 2 in Organic Synthesis ............................. 950
24.4.2.2.1 Method 1: Synthesis of Stereochemically Defined Metalated Vinyl Ethers .......... 950
24.4.2.2.2 Method 2: Addition Reactions to Carbonyl Compounds .................................. 952
24.4.2.2.3 Method 3: Enyne Metathesis ........................................................................ 952
24.4.2.2.4 Method 4: Metal- or Acid-Promoted Cycloisomerization of 1-Siloxyalk-1-ynes .. 953
24.4.2.2.5 Method 5: Aromatic Annulation Reactions ................................................. 953

24.4.3 Product Subclass 3: 1-(Organosulfanyl)-, 1-(Organoselanyl)-, and 1-(Organotellanyl)alk-1-ynes
V. A. Potapov and B. A. Trofimov

24.4.3.1 Synthesis of (Organosulfanyl)-, (Organoselanyl)-, and (Organotellanyl)acetylenes ................................................................. 958
24.4.3.1.1 Method 1: Synthesis from Metal Acetylides and Chalcogen Electrophiles .......... 958
24.4.3.1.2 Method 2: Synthesis from Ethynylmagnesium Halides and Organochalcogeno Halides ......................................................... 960
24.4.3.1.3 Method 3: (Organotellanyl)acetylenes from Acetylene, Diorgano Ditellurides, and Iodomethane .................................................. 961
24.4.3.1.4 Method 4: Dehydrohalogenation Reactions ............................................... 962
24.4.3.1.5 Method 5: (Organosulfanyl)acetylenes from 1,2-Bis(organosulfanyl)-ethenes and 1-(Organooxy)-2-(organosulfanyl)ethenes .......... 963
24.4.3.2 Applications of (Organosulfanyl)-, (Organoselanyl)-, and (Organotellanyl)-acetylenes in Organic Synthesis ........................................... 964
24.4.3.2.1 Method 1: The Mannich Reaction ............................................................. 965
24.4.3.2.2 Method 2: Syntheses Based on the Reactions of Metal (Organosulfanyl)-acetylides ................................................................. 965
24.4.3.2.3 Method 3: Syntheses Based on the Addition and Cycloaddition Reactions of (Organochalcogeno)acetylenes ........................................ 966
24.4.3.2.4 Method 4: Oxidation of (Organosulfanyl)acetylenes to (Organosulfinyl)- and (Organosulfonyl)acetylenes .................................. 968
24.4.3.2.5 Method 5: Dialk-1-ynyl Sulfides by Dehydrohalogenation Reactions .......... 970
24.4.3.2.4 Methods 4: Additional Methods .............................................. 971

24.4.3.2.2 Applications of Dialk-1-ynyl Sulfides, Selenides, and Tellurides in Organic Synthesis .................................................. 972

24.4.3.2.2.1 Method 1: Synthesis of Heterocyclic Compounds from Dialk-1-ynyl Sulfides .................................................. 972

24.4.3.3 1-(Alkylsulfanyl)- and 1-(Arylsulfanyl)alk-1-ynes and Their Selenium and Tellurium Analogues ........................................... 973

24.4.3.3.1 Synthesis of 1-(Alkylsulfanyl)- and 1-(Arylsulfanyl)alk-1-ynes and Their Selenium and Tellurium Analogues ........................................... 973

24.4.3.3.1.1 Method 1: Synthesis from Metal Acetylides, Elemental Chalcogens, and Haloalkanes .............................................. 973

24.4.3.3.1.1.1 Variation 1: From Alkali Metal Acetylides in Liquid Ammonia .............................................. 974

24.4.3.3.1.1.2 Variation 2: From Lithium Acetylides in Organic Solvents .............................................. 974

24.4.3.3.1.1.3 Variation 3: Generation of Acetylides in Potassium Hydroxide/Nonhydroxylic Solvent Systems .............................................. 975

24.4.3.3.1.1.4 Variation 4: Generation of Acetylides under Phase-Transfer Conditions .............................................. 976

24.4.3.3.1.2 Method 2: Synthesis from Metal Acetylides and Electrophilic Chalcogen Species .............................................. 976

24.4.3.3.1.2.1 Variation 1: From Alkali Metal Acetylides in Liquid Ammonia .............................................. 977

24.4.3.3.1.2.2 Variation 2: From Alkali Metal Acetylides in Organic Solvents .............................................. 978

24.4.3.3.1.2.3 Variation 3: Generation of Acetylides under Phase-Transfer Conditions .............................................. 978

24.4.3.3.1.3 Method 3: Synthesis from Alk-1-ynes, Chalcogen Electrophiles, and Copper(I) Salts .............................................. 979

24.4.3.3.1.4 Method 4: Synthesis from Alk-1-ynyliodonium Salts and Chalcogen Nucleophiles .............................................. 980

24.4.3.3.1.5 Method 5: 1-(Phenylselenyl)alk-1-ynes from Alk-1-ynes, Diphenyl Diselenide, and (Diacetoxyiodo)benzene .............................................. 981

24.4.3.3.1.6 Method 6: 1-(Arylchalco geno)alk-1-ynes from Dialk-1-ynylmercurials and Diaryl Dichalcogenides .............................................. 982

24.4.3.3.1.7 Method 7: Synthesis from 1-Haloalk-1-ynes .............................................. 982

24.4.3.3.1.7.1 Variation 1: From 1-Bromoalk-1-ynes and Diorganod Dichalcogenides in the Presence of Copper(I) Iodide .............................................. 982

24.4.3.3.1.7.2 Variation 2: From 1-Haloalk-1-ynes and Chalcogen Nucleophiles .............................................. 983

24.4.3.3.1.8 Method 8: 1-(Organosulfanyl)- and 1-(Organoselenanyl)alk-1-ynes from 1,2,3-Thia- and 1,2,3-Selenadiazoles .............................................. 984

24.4.3.3.1.9 Method 9: 1-(Alkylsulfanyl)- and 1-(Arylsulfanyl)alk-1-ynes by Elimination Reactions .............................................. 985

24.4.3.3.1.9.1 Variation 1: 1,2-Elimination .............................................. 985

24.4.3.3.1.9.2 Variation 2: 1,4- and 1,6-Eliminations .............................................. 986

24.4.3.3.1.10 Methods 10: Additional Methods .............................................. 986

24.4.3.3.2 Applications of 1-(Alkylsulfanyl)- and 1-(Arylsulfanyl)alk-1-ynes and Their Selenium and Tellurium Analogues .............................................. 988

24.4.3.3.2.1 Method 1: Generation of Alk-1-ynylmetals from 1-(Organoselenanyl)- and 1-(Organotellanyl)alk-1-ynes .............................................. 988

24.4.3.3.2.2 Method 2: Cross-Coupling Reactions .............................................. 989

24.4.3.3.2.3 Method 3: Synthesis of Stereodefined Alkenes .............................................. 990
### 24.4 Method 4: Cycloaddition Reactions

24.4.3.2.4 Method 4: Cycloaddition Reactions .................................................. 992

### 24.4 Method 5: Oxidation of 1-(Organosulfonyl)alk-1-ynes to 1-(Organosulfinyl)- and 1-(Organosulfonyl)alk-1-ynes

24.4.3.2.5 Method 5: Oxidation of 1-(Organosulfonyl)alk-1-ynes to 1-(Organosulfinyl)- and 1-(Organosulfonyl)alk-1-ynes .................................................. 993

### 24.4 Methods 6: Additional Methods

24.4.3.2.6 Methods 6: Additional Methods ................................................ 994

### 24.4 Synthesis of 1-(Vinylsulfanyl)-, 1-(Vinylselanyl)-, and 1-(Vinyltellanyl)-alk-1-ynes

24.4.3.4.1 Synthesis of 1-(Vinylsulfanyl)-, 1-(Vinylselanyl)-, and 1-(Vinyltellanyl)-alk-1-ynes ............................................................... 996

#### 24.4.3.4.1.1 Method 1: Synthesis from Lithium Acetylides and Vinylsulfenamides

24.4.3.4.1.1 Method 1: Synthesis from Lithium Acetylides and Vinylsulfenamides 996

#### 24.4.3.4.1.2 Method 2: Dehydrohalogenation Reactions

24.4.3.4.1.2 Method 2: Dehydrohalogenation Reactions .......................... 997

### 24.4 Applications of 1-(Vinylsulfanyl)-, 1-(Vinylselanyl)-, and 1-(Vinyltellanyl)-alk-1-ynes in Organic Synthesis

24.4.3.4.2 Applications of 1-(Vinylsulfanyl)-, 1-(Vinylselanyl)-, and 1-(Vinyltellanyl)-alk-1-ynes in Organic Synthesis ........................................... 998

#### 24.4.3.4.2.1 Method 1: Synthesis of Heterocyclic Compounds from 1-(Vinylsulfanyl)alk-1-ynes

24.4.3.4.2.1 Method 1: Synthesis of Heterocyclic Compounds from 1-(Vinylsulfanyl)alk-1-ynes ................................ 998

### 24.4.4 Product Subclass 4: 1-Nitrogen-Functionalized Alk-1-ynes

24.4.4 Alk-1-yn-1-amines

B. Witulski and C. Alayrac

#### 24.4.4.1 Alk-1-yn-1-amines

24.4.4.1 Alk-1-yn-1-amines ................................................................. 1007

#### 24.4.4.1.1 Synthesis of Alk-1-yn-1-amines

24.4.4.1.1 Synthesis of Alk-1-yn-1-amines ........................................... 1009

#### 24.4.4.1.1.1 Method 1: Electrophilic Amination of Metal Acetylides

24.4.4.1.1.1 Method 1: Electrophilic Amination of Metal Acetylides ............ 1009

#### 24.4.4.1.1.2 Method 2: Synthesis from 1-Haloalk-1-ynes

24.4.4.1.1.2 Method 2: Synthesis from 1-Haloalk-1-ynes .......................... 1010

#### 24.4.4.1.1.3 Method 3: Synthesis from Alk-1-ynyliodonium Salts

24.4.4.1.1.3 Method 3: Synthesis from Alk-1-ynyliodonium Salts ................ 1011

#### 24.4.4.1.1.4 Method 4: Synthesis from 1-Alkoxyalk-1-ynes

24.4.4.1.1.4 Method 4: Synthesis from 1-Alkoxyalk-1-ynes ....................... 1012

#### 24.4.4.1.1.5 Method 5: Synthesis from 1,1-Dihaloalkenes

24.4.4.1.1.5 Method 5: Synthesis from 1,1-Dihaloalkenes .......................... 1013

#### 24.4.4.1.1.6 Method 6: Elimination Reactions of Halogenated Enamines

24.4.4.1.1.6 Method 6: Elimination Reactions of Halogenated Enamines ..... 1014

#### 24.4.4.1.1.6.1 Variation 1: From β-Halogenated Enamines

24.4.4.1.1.6.1 Variation 1: From β-Halogenated Enamines ...................... 1014

#### 24.4.4.1.1.6.2 Variation 2: From α,β-Di- or Trihalogenated Enamines

24.4.4.1.1.6.2 Variation 2: From α,β-Di- or Trihalogenated Enamines ... 1014

#### 24.4.4.1.1.7 Method 7: Shapiro-Type Eliminations

24.4.4.1.1.7 Method 7: Shapiro-Type Eliminations .................................. 1016

#### 24.4.4.1.1.8 Method 8: Fragmentation Reactions

24.4.4.1.1.8 Method 8: Fragmentation Reactions .................................... 1016

#### 24.4.4.1.1.8.1 Variation 1: Lithiation and Fragmentation of 1-Phenyl-1,2,3-triazoles

24.4.4.1.1.8.1 Variation 1: Lithiation and Fragmentation of 1-Phenyl-1,2,3-triazoles ... 1017

#### 24.4.4.1.1.8.2 Variation 2: By Flash-Vacuum Pyrolysis

24.4.4.1.1.8.2 Variation 2: By Flash-Vacuum Pyrolysis .......................... 1017

#### 24.4.4.1.1.8.3 Variation 3: Flash-Photolytic Generation of Primary, Secondary, and Tertiary Alk-1-yn-1-amines

24.4.4.1.1.8.3 Variation 3: Flash-Photolytic Generation of Primary, Secondary, and Tertiary Alk-1-yn-1-amines .......... 1018

#### 24.4.4.1.1.9 Method 9: Base-Catalyzed Isomerization of Propargylamines

24.4.4.1.1.9 Method 9: Base-Catalyzed Isomerization of Propargylamines ...... 1019

#### 24.4.4.1.2 Applications of Alk-1-yn-1-amines in Organic Synthesis

24.4.4.1.2 Applications of Alk-1-yn-1-amines in Organic Synthesis .......... 1020

#### 24.4.4.1.2.1 Method 1: Stereochemically Defined Enamines by the Carbo- or Silylmetalation of Alk-1-yn-1-amines

24.4.4.1.2.1 Method 1: Stereochemically Defined Enamines by the Carbo- or Silylmetalation of Alk-1-yn-1-amines ................................. 1021

#### 24.4.4.1.2.2 Method 2: One-Carbon Homologation of Carboxylic Acids

24.4.4.1.2.2 Method 2: One-Carbon Homologation of Carboxylic Acids .... 1021

#### 24.4.4.1.2.3 Method 3: Alkylation of Alk-1-yn-1-amines by Claisen Rearrangements

24.4.4.1.2.3 Method 3: Alkylation of Alk-1-yn-1-amines by Claisen Rearrangements 1022

#### 24.4.4.1.2.4 Method 4: [2 + 2] Cycloadditions with Cyclopentenones and Cyclohexenones

24.4.4.1.2.4 Method 4: [2 + 2] Cycloadditions with Cyclopentenones and Cyclohexenones .......................... 1023
24.4.1.2.5 Method 5: Hetero [2 + 2] Cycloadditions ........................................ 1024
24.4.1.2.6 Method 6: [4 + 2] Cycloadditions ............................................. 1025
24.4.1.2.7 Method 7: Pauson–Khand Reactions of Acetylen-1-amines ............ 1026
24.4.1.2.8 Method 8: Peptide Synthesis .................................................. 1026

24.4.2 N-acyl- and N-sulfonylalk-1-yn-1-amines
B. Witulski and C. Alayrac

24.4.2.1 Synthesis of N-acyl- and N-sulfonylalk-1-yn-1-amines ................ 1033
24.4.2.1.1 Method 1: N-Alkynylation with Alkynyliodonium Salts ................. 1033
24.4.2.1.2 Method 2: Copper-Promoted Cross Coupling of 1-Haloalk-1-ynes with Amides ................................................ 1034
24.4.2.1.2.1 Variation 1: With a Stoichiometric Amount of a Copper(I) Salt .... 1035
24.4.2.1.2.2 Variation 2: With Catalytic Amounts of Copper(I) or Copper(II) Salts 1036
24.4.2.1.3 Method 3: Elimination Reactions ............................................ 1037
24.4.2.1.3.1 Variation 1: By a Formamide to Ynamide Homologation ............. 1037
24.4.2.1.3.2 Variation 2: From \( \text{C}_{226}\), \( \text{C}_{226}\)-Dichloroenamides by Suzuki–Miyaura Coupling and Dehydrochlorination ................. 1038
24.4.2.1.3.3 Variation 3: Bromination/Dehydrobromination of Enamides ......... 1039
24.4.2.1.3.4 Variation 4: Dechlorination of Trichlorinated Enamides Derived from Pyrimidine Bases .......................................... 1040
24.4.2.1.4 Method 4: Functionalization of Ynamides .................................. 1041
24.4.2.1.4.1 Variation 1: Deprotonation/Alkylation of Ynamides ................. 1041
24.4.2.1.4.2 Variation 2: Desilylation of 1-Silyl Ynamides ......................... 1042
24.4.2.1.4.3 Variation 3: Homocoupling of Ynamides ................................ 1043
24.4.2.1.4.4 Variation 4: Negishi Coupling with Ynamides ......................... 1043
24.4.2.1.4.5 Variation 5: Sonogashira Coupling with Ynamides ................... 1044
24.4.2.1.5 Method 5: Base-Catalyzed Isomerization of Propargylamides ........ 1045
24.4.2.1.6 Method 6: Synthesis from 1-Phenyl-1,2,3-triazoles ....................... 1046

24.4.2.2 Applications of N-acyl- and N-sulfonylalk-1-yn-1-amines in Organic Synthesis 1047
24.4.2.2.1 Method 1: Regioselective Hydrometalation or Carbometalation of Ynamides .................................................. 1048
24.4.2.2.2 Method 2: Transition-Metal-Catalyzed Cross-Coupling Reactions with Ynamides ................................................. 1049
24.4.2.2.3 Method 3: Intramolecular Cyclizations ..................................... 1050
24.4.2.2.4 Method 4: Ring-Closing Ene–yne Metathesis with Ynamides ................. 1051
24.4.2.2.5 Method 5: Pauson–Khand Reactions with Ynamides .................... 1052
24.4.2.2.6 Method 6: [4 + 2] Cycloadditions ............................................. 1054
24.4.2.2.7 Method 7: [2 + 2 + 2] Cycloadditions ....................................... 1054
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.4.3</td>
<td>Alk-1-ynyldiazonium Salts, 1-Azidoalk-1-ynes, and 1-Nitroalk-1-ynes</td>
<td>1059</td>
</tr>
<tr>
<td>24.4.3.1</td>
<td>Synthesis of Alk-1-ynyldiazonium Salts, 1-Azidoalk-1-ynes, and 1-Nitroalk-1-ynes</td>
<td>1059</td>
</tr>
<tr>
<td>24.4.3.1.1</td>
<td>Method 1: Synthesis of Alk-1-ynyldiazonium Salts</td>
<td>1059</td>
</tr>
<tr>
<td>24.4.3.1.1.1</td>
<td>Variation 1: From a 1-Nitrosoalk-1-yne</td>
<td>1059</td>
</tr>
<tr>
<td>24.4.3.1.1.2</td>
<td>Variation 2: From a 1-Chloro-1-(tosylazo)alk-1-ene</td>
<td>1060</td>
</tr>
<tr>
<td>24.4.3.1.2</td>
<td>Method 2: Synthesis of 1-Azidoalk-1-ynes</td>
<td>1061</td>
</tr>
<tr>
<td>24.4.3.1.2.1</td>
<td>Variation 1: Introduction of the Azido Group by Nucleophilic Substitution</td>
<td>1061</td>
</tr>
<tr>
<td>24.4.3.1.2.2</td>
<td>Variation 2: Formation of the C==C Bond by Elimination of Halogen</td>
<td>1062</td>
</tr>
<tr>
<td>24.4.3.1.3</td>
<td>Method 3: Synthesis of 1-Nitroalk-1-ynes</td>
<td>1064</td>
</tr>
<tr>
<td>24.4.3.1.3.1</td>
<td>Variation 1: Formation of the C==C Bond by Elimination</td>
<td>1064</td>
</tr>
<tr>
<td>24.4.3.1.3.2</td>
<td>Variation 2: Introduction of the Nitro Group by Substitution Reactions</td>
<td>1065</td>
</tr>
<tr>
<td>24.4.3.1.3.3</td>
<td>Variation 3: Oxidation of 1-Nitrosoalk-1-ynes</td>
<td>1067</td>
</tr>
<tr>
<td>24.4.3.2</td>
<td>Applications of Alk-1-ynyldiazonium Salts, 1-Azidoalk-1-ynes, and 1-Nitroalk-1-ynes in Organic Synthesis</td>
<td>1068</td>
</tr>
<tr>
<td>24.4.5</td>
<td>Product Subclass 5: 1-Phosphorus-Functionalized Alk-1-ynes</td>
<td>1073</td>
</tr>
<tr>
<td>24.4.5.1</td>
<td>Synthesis of Product Subclass 5</td>
<td>1073</td>
</tr>
<tr>
<td>24.4.5.1.1</td>
<td>Method 1: Nucleophilic Substitution Reactions at Phosphorus with Alkali Metal Acetylides</td>
<td>1073</td>
</tr>
<tr>
<td>24.4.5.1.2</td>
<td>Method 2: Reaction of Phosphorus Nucleophiles with Electrophilic Alkynes</td>
<td>1074</td>
</tr>
<tr>
<td>24.4.5.1.2.1</td>
<td>Variation 1: From Triorgano Phosphites (Michaelis–Arbuzov Reaction)</td>
<td>1074</td>
</tr>
<tr>
<td>24.4.5.1.2.2</td>
<td>Variation 2: From Diorgano Phosphites (Michaelis–Becker Reaction)</td>
<td>1075</td>
</tr>
<tr>
<td>24.4.5.1.2.3</td>
<td>Variation 3: From Tertiary Phosphines by Quaternization</td>
<td>1076</td>
</tr>
<tr>
<td>24.4.5.1.3</td>
<td>Method 3: Elimination</td>
<td>1076</td>
</tr>
<tr>
<td>24.4.5.1.3.1</td>
<td>Variation 1: From Phosphorus-Substituted Alkenes</td>
<td>1076</td>
</tr>
<tr>
<td>24.4.5.1.3.2</td>
<td>Variation 2: From α-Phosphorus-Substituted Ketones</td>
<td>1077</td>
</tr>
<tr>
<td>24.4.5.1.4</td>
<td>Method 4: Coupling of Phosphorus Derivatives with Alkynes and Alkenes</td>
<td>1078</td>
</tr>
<tr>
<td>24.4.5.1.5</td>
<td>Method 5: Structural Modification of Other Phosphorus-Substituted Alkenes</td>
<td>1079</td>
</tr>
<tr>
<td>24.4.5.1.5.1</td>
<td>Variation 1: Modification of the Phosphorus Functionality</td>
<td>1079</td>
</tr>
<tr>
<td>24.4.5.1.5.2</td>
<td>Variation 2: Modification of the Alkyne Fragment</td>
<td>1080</td>
</tr>
<tr>
<td>24.4.5.2</td>
<td>Applications of Product Subclass 5 in Organic Synthesis</td>
<td>1081</td>
</tr>
<tr>
<td>Keyword Index</td>
<td>1087</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Author Index</td>
<td>1145</td>
<td></td>
</tr>
<tr>
<td>Abbreviations</td>
<td>1189</td>
<td></td>
</tr>
</tbody>
</table>