Volume 1:
Compounds with Transition Metal–Carbon π-Bonds
and Compounds of groups 10–8 (Ni, Pd, Pt, Co, Rh,
Ir, Fe, Ru, Os)

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**1.5**

**Product Class 5: Organometallic Complexes of Rhodium**

I. Ojima, A. T. Vu, and D. Bonafoux

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### Section 1.6

**Product Class 6: Organometallic Complexes of Iridium**

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M. Nilsson†

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J. Pietruszka

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**4.4.27**

**Product Subclass 27: α-Haloacysilanes**
N. J. Lawrence

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J. Pernet

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B. A. Keay

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P. B. Wyatt

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G. T. Crisp

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H. Abu Ali, V. M. Dembitsky, and M. Srebnik

6.1.29 Product Subclass 29: α-Boryl Carbonyl Compounds

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H. Abu Ali, V. M. Dembitsky, and M. Srebnik

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P. J. Murphy

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Method 3: Hydroboration of Vinysilanes

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Variation 2: Using Borane–Dimethyl Sulfide Complex

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Variation 4: Using Hindered Boranes

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Variation 6: Of Divinylsilanes

Variation 7: Using (−)-Diisopinocampheylborane

Method 4: Heterocycles by Hydroboration

Variation 1: Using tert-Butylborane–Trimethylamine Complex

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Variation 3: Using 1,1-Dimethyl-1,4-silaborinane

Method 5: Silylation of Vinylboranes

Method 6: From a Diborirane

Method 7: From Tetrahaldoboranes(4) and Vinysilanes

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Method 9: Addition to Z-2-Boryl-1-stannylalkenes with Rearrangement

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Method 12: Synthesis of Methoxyboranes and Methylboronates via Butylsulfanylboranes

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Product Subclass 33: Propargylboranes

D. E. Kaufmann and C. Burmester

Synthesis of Product Subclass 33

Method 1: By Transmetalation Reactions

Variation 1: Borylation of Lithium or Magnesium Compounds

Variation 2: Borylation of Stannanes

Method 2: By Rearrangement of “Ate” Complexes

Variation 1: By One-Carbon Homologation of Boronates

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Applications of Product Subclass 33 in Organic Synthesis

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Method 4: Oxidation
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M. Zaidlewicz and J. Meller

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Y. Bubnov

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8.1.18 Product Subclass 18: β-Lithio Aldehydes, β-Lithio Ketones, and Related Compounds

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S. MacNeil

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Synthesis by Ring Transformation

Oxidation of Thiophenes

Method 1: Oxidation of Thiophenes

Aromatization

Method 1: From Dihydro- or Tetrahydrothiophene 1,1-Dioxides by Elimination

Variation 1: From Dihydro- or Tetrahydrothiophene 1,1-Dioxides by Hydrogen Halide Elimination

Variation 2: From Dihydro- or Tetrahydrothiophene 1,1-Dioxides by Nitrous Acid Elimination

**Product Subclass 3: Thiophene 1-Oxides**

Synthesis by Ring Transformation

Formal Exchange of Ring Members

Method 1: From Zirconocenes

**Product Class 11: Selenophenes**

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Synthesis by Ring-Closure Reactions

By Formation of Two Se—C Bonds

Fragments C—C—C and Se

Method 1: Reaction of C$_4$ Building Blocks with Sources of Selenium

Variation 1: Reaction of 1,4-Dilithio- or 1,4-Diiodobutadienes with a Selenium Source

Variation 2: Reaction of Butadiynes with Selenides

Variation 3: Reaction of 1-Alkynyl-2-bromobenzenes with Elemental Selenium

Variation 4: Reaction of Chloroalkynols or Alkynyloxiranes with Selenides

By Formation of Two C—C Bonds

Fragments C—Se—C and C—C

Method 1: From 1,2-Diketones and a Selenodiacetate (Hinsberg Synthesis)

By Formation of One C—C Bond

Fragment C—C—Se—C—C

Method 1: Reductive Cyclization of Diphenacyl Selenides
9.11 Synthesis by Formal Exchange of Ring Members

9.11.2 Method 1: Exchange of Zirconium by Selenium

9.11.3 Synthesis by Substituent Modification

9.12 Product Class 12: Tellurophenes

J. Schatz

9.12.1 Synthesis by Ring-Closure Reactions

9.12.1.1 By Formation of Two Te—C Bonds

9.12.1.1.1 Method 1: Reaction of C₄ Building Blocks with Sources of Tellurium

9.12.1.1.2 Variation 1: Reaction of 1,4-Dilithio- or 1,4-Diodobutadienes with a Tellurium Source

9.12.1.1.3 Variation 2: Reaction of Butadiynes with Tellurides

9.12.1.1.4 Variation 3: Reaction of 1-Alkynyl-2-bromobenzenes or But-1-en-3-ynes with Elemental Tellurium

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9.12.1.2.1 Fragment C—Te—C—C

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9.12.1.2.4 Method 2: Reaction of Zirconium and Titanium Complexes with Alkynes and Carbonyl Compounds

9.13 Product Class 13: 1H-Pyrroles

D. St.C. Black

9.13.1 Synthesis by Ring-Closure Reactions

9.13.1.1 By Formation of Two N—C Bonds and One C—C Bond

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9.13.1.1.3 Method 3: Condensation Reaction of Aliphatic Aldehydes or Ketones and Hydrazines (The Piloty Synthesis)

9.13.1.1.4 Method 4: Reaction of Trimethylsilyl Cyanide with Alkynes, Catalyzed by Palladium(II) or Nickel(II) Chloride

9.13.1.1.5 Method 5: Reaction of Zirconium and Titanium Complexes with Alkynes and Carbonyl Compounds

9.13.1.2 By Formation of One N—C Bond and Two C—C Bonds

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R. A. Aitken

Synthesis by Ring-Closure Reactions

By Annulation to a Benzene Ring

By Formation of Two P—C Bonds

Method 1: From Phthaloyl Chloride

Method 2: From a Bis(phosphonium salt)

Aromatization

Of a 1,3-Dihydrobenzo[c]phosphole

Method 1: Formation of 1H-Benzophospholes

Method 2: Formation of 2H-Benzophospholes

Product Class 19: Dibenzophospholes
R. A. Aitken

Synthesis by Ring-Closure Reactions

By Annulation to an Arene

By Formation of Two P—C Bonds

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D. Gudat

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W.-D. Pfeiffer

Product Subclass 1: Isotellurazoles (1,2-Tellurazoles)

Synthesis by Ring-Closure Reactions

By Formation of One Te—N, One Te—C, and One N—C Bond

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By Formation One Te—C and One N—C Bond

Fragments Te—C and N

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Variation 3: From 3-[Dibromo(methyl)-4-tellanyl]prop-2-enals and Arylamines

Product Subclass 2: 1,2-Benzisotellurazoles

Synthesis by Ring-Closure Reactions

By Formation of One Te—N and One N—C Bond

Fragments Te—C—C and N

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Variation 1: From 2-(Butyltellanyl)benzaldehyde

Variation 2: From 2-(Iminomethyl)benzenetellurenyl Chlorides

Product Subclass 3: Arenotellurazoles

Synthesis by Ring-Closure Reactions

By Formation of One Te—N Bond

Fragment Te—Arene—C—N

Method 1: From 2-(Butyltellanyl)benzaldehyde

Method 2: Cyclization of 2-(Iminomethyl)benzenetellurenyl Chlorides

Modification of 1,2-Benzisotellurazole Iodide by Alkylation

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**Product Class 18: Diazaphospholes and Dizaoarsoles**  
R. K. Bansal and Neelima Gupta

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13.18.2  
**Product Subclass 2: 1,2,3-Diazaphospholo[1,5-a]pyridines**

13.18.3  
**Product Subclass 3: Monocyclic 1,2,4-Diazaphospholes and 1,2,4-Diazaoarsoles**

13.18.4  
**Product Subclass 4: 1,2,4-Diazaphospholo[1,5-a]pyridines and 1,2,4-Diazarsolo[1,5-a]pyridines**

13.18.5  
**Product Subclass 5: Monocyclic 1,3,2-Diazaphospholes**

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Product Class 20: Triphospholes and Diphospharsolides

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Aromatization

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Product Subclass 3: Dibenzo[b,d]pyrylium Salts

Synthesis by Ring-Closure Reactions

By Formation of One O–C and One C–C Bond

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By Formation of One C–C Bond

Method 1: Ring Closure of a 3-(2-Carboxymethylaryl)-2-benzopyrylium Salt with Phosphorus Pentachloride

Synthesis by Ring Transformation

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Product Subclass 4: Dibenzo[b,e]pyrylium Salts (Xanthylium Salts)

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1. **Method 1:** By Condensation of an α,β-Unsaturated Ketone and an α-Acyloxy Ketone
2. **Method 2:** By Deacylation of 3-(Acyloxy)pyrylium or 3-(Acyloxy)thiopyrylium Salts
3. **Method 3:** By Oxidation of Thiopyran-3-ones
4. **Method 4:** By Oxidation of Thiabenzenes with Molecular Oxygen

#### 14.5.2 Applications of Product Class 5 in Organic Synthesis

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3. **Variation 2:** In Situ Generation of the 3-Oxidopyrylium Salt from Methyl 2-(Diazoacetyl)benzoate
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### Product Class 6: Thiopyrylium Salts

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#### 14.6.1.3 Method 3: Reaction of 1,5-Diketones with Sulfur Transfer Reagents

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#### 14.6.1.7 Variation 3: With Hydrogen Sulfide in the Presence of Hydride Acceptors

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Product Class 7: Benzothiopyrylium Salts
W.-D. Rudorf

Product Subclass 1: 1-Benzothiopyrylium Salts

Synthesis by Ring-Closure Reactions

By Annulation to an Arene

By Formation of One S—C and One C—C Bond

Method 1: Cyclization of Benzenethiols with 1,3-Diketones
Method 2: Cyclization of Benzenethiols with Alkynals
Method 3: Cyclization of Benzenethiols with Haloalkenones
Method 4: Condensation of Benzenethiols with (2Z)-2-(Hydroxymethylene)cyclohexanones

By Formation of Two C—C Bonds

Method 1: Reaction of Diarylsulfanes with 1,1-Dichlorodimethyl Ether
Method 2: Intramolecular Condensation of (Arylsulfanyl)ketones and Subsequent Intermolecular Disproportionation
Method 2: Intramolecular Condensation of (Arylsulfanyl)ketones in the Presence of Trityl Chloride/Perchloric Acid

Aromatization

By Elimination

Method 1: From 2H-1-Benzothiopyrans
Method 2: From 4H-1-Benzothiopyrans
Method 3: From 4-Hydroxy-3,4-dihydro-2H-1-benzothiopyran S-Oxides
Method 4: From 1-Benzothiopyran-4(4H)-ones with Phosphoryl Chloride
Method 5: From 2-Hydroxy-2H-1-benzothiopyrans
Method 6: From 4-Hydroxy-4H-1-benzothiopyrans
Method 7: From 4-Hydroxy-3,4-dihydro-2H-1-benzothiopyrans

By Dehydrogenation

Method 1: From 2H-1-Benzothiopyrans
Method 2: From 4H-1-Benzothiopyrans
Method 3: From 3,4-Dihydro-2H-1-benzothiopyrans

By Reduction or Grignard Addition and Dehydration

Method 1: Grignard Addition and Dehydration of 1-Benzothiopyran-4(4H)-ones
Method 2: Reduction–Dehydration of 1-Benzothiopyran-4(4H)-ones
Method 1: From 1-Benzothiopyran-2(2H)- or 1-Benzothiopyran-4(4H)-ones

By Oxidation
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14.8 Product Class 8: Thiopyranones and Thiopyranthiones
S. Faulkner, R. C. Whitehead, and R. J. Aarons

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Of Metals
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Product Class 14: Pyrazines
N. Sato

Synthesis by Ring-Closure Reactions
By Formation of Four N–C Bonds
Fragments C–C, C–C, and Two N Fragments
Method 1: From a 1,2-Bifunctional Compound and Ammonia or Ammonium
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16.15 Product Class 15: Quinoxalines
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Product Class 18: Pyridopyridazines

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Product Subclass 1: Pyrido[2,3-c]pyridazines

Synthesis by Ring-Closure Reactions

By Formation of Two N—C Bonds and One C—C Bond

Method 1: Intermolecular Cyclizations of Malononitrile Dimer and
Hydrazones, or Acetonitriles and Pyridazinediones

By Formation of Two N—C Bonds

Method 1: Cycloamination with Diazenes and Hydrazines

By Formation of One N—C and One C—C Bond

Method 1: Condensation of Enamines, Acetamide Acetals,
and Acetoacetates with Suitably Activated Pyridazines

By Formation of One N—C Bond

Method 1: Intramolecular Cyclization of Suitably Modified
Diazocompounds, Hydrazones, Azides, and Hydrazides

By Formation of One C—C Bond

Method 1: Intramolecular Cyclizations Induced by Base Treatment of
Active Methylene and Methine Compounds

Synthesis by Ring Transformation

Formal Exchange of Ring Members with Retention of the Ring Size

Method 1: Intramolecular [4 + 2] Cycloaddition of
3-(Alkynylamino)-1,2,4,5-tetrazines

Aromatization

Synthesis by Substituent Modification

Substitution of Existing Substituents

Addition Reactions

Product Subclass 2: Pyrido[2,3-d]pyridazines

Synthesis by Ring-Closure Reactions

By Formation of Two N—C Bonds and One C—C Bond

Method 1: Condensation of Hydrazones with Malononitriles

By Formation of Two N—C Bonds

Method 1: Condensation of Pyridine-2,3-dicarbonyl Compounds with
Hydrazines

By Formation of One N—C and One C—C Bond

Method 1: Condensation of 5-Chloropyridazine-4-carbonyl Chloride
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By Formation of Two N—C Bonds

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Method 2: Cycloamination of 4-Vinylpyridazine-3-carboxylates

By Formation of One N—C and One C—C Bond

Method 1: Cycloamination of 3-Hydrazonopyridines with Aldehydes

Method 2: Cyclocondensation of Pyridazine-3-carbohydrazides with Aldehydes

By Formation of One C—C Bond

Method 1: Intramolecular Cyclization of 3-Pyridylhydrazones

Product Subclass 5: Pyrido[3,4-d]pyridazines

Synthesis by Ring-Closure Reactions

By Formation of Two N—C Bonds

Method 1: Cycloamination of Pyridine-3,4-dicarboxylates with Hydrazines

Method 2: Cycloamination of 4-Carbofunctional 5-Vinylpyridazines

By Formation of One N—C and One C—C Bond

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By Formation of One C—C Bond

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Synthesis by Ring Transformation

By Ring Enlargement

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Formal Exchange of Ring Members with Retention of the Ring Size

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16.20 Product Class 20: Pyridopyrazines

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#### 17.1.1 Product Subclass 1: Two Unlike Oxygen, Sulfur, Selenium, or Tellurium Atoms

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### Product Subclass 2: One Oxygen and One Nitrogen or Phosphorus Atom

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Product Subclass 1: 1,2,3-Triazines and Phosphorus Analogues
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Monocyclic 1,2,3-Triazines

Synthesis by Ring-Closure Reactions

By Formation of One N—N and One N—C Bond

Method 1: Condensations of 3-Diazo-2-oxopropanoic Acid Derivatives with Hydrazine Hydrate or Hydroxylamine

By Formation of Two N—C Bonds

Method 1: Cyclization of Triazenes with (Chloroformyl)ketenes

By Formation of One N—N Bond

Method 1: Cyclization of \(N\)-Benzyl-3-diazo-2-oxopropanamide

Synthesis by Ring Transformation

By Ring Enlargement

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Variation 1: From 4-Methyl-\(N\)¢-[aryl(3-arylaziridin-2-yl)methylene]-benzenesulfonylhydrazides

Method 2: From Tetrahalocyclopropenes and Trimethylsilyl Azide

Method 3: By Rearrangement of Cyclopropenyl Azides

Method 4: By Oxidation of Pyrazol-1-amines

Variation 1: From Pyrazol-1-amines by Oxidation and Halogenation

Method 5: Reactions of Substituted 1,2,3-Triazole 1-Oxides with Dialkyl Acetylenedicarboxylates

Variation 1: By Thermal Rearrangement of Pyrrolo[2,3-\(d\)][1,2,3]triazoles

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Method 1: Metalation

Method 2: Introduction of Amide Functions at C5

Method 3: Vicarious Nucleophilic Substitution

Method 4: C-Alkylation with Silyl Enol Ethers or Ketene Silyl Acetals in the Presence of 1-Chloroethyl Chloroformate

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**Method 2:** Hydrazine Condensation with Oxo Esters and Oxo Acids

**By Formation of One N—N Bond**

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**By Formation of One C—C Bond**

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**Product Subclass 2: 1,3-Diazepines**

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**Variation 2:** Using 2,5-Di-unsubstituted 1H-Pyrroles and Aldehydes

**Method 2:** From Dipyroles

**Method 3:** From a,c-Biladiene Salts

**Method 4:** By Porphyrin Ring Contraction

17.8.3.3

**Expanded Porphyrins**

17.8.3.3.1

**Method 1:** Syntheses of Sapphyrins

**Variation 1:** The [3 + 2] Approach

**Variation 2:** The [3 + (1)²] Approach

**Variation 3:** The [4 + 1] Approach

**Variation 4:** The [1]² Approach

**Method 2:** Syntheses of Pentaphyrins

17.8.4

**Reactions around the Porphyrin Periphery**

17.8.4.1

**Method 1:** Electrophilic Substitution Reactions

**Variation 1:** Halogenation

**Variation 2:** Nitration

**Variation 3:** Formylation and Acylation

**Variation 4:** Peripheral Metalation

**Variation 5:** Reactions with Carbenes and Nitrenes

**Method 2:** Reactions with Nucleophiles

**Method 3:** Oxidation Reactions

**Method 4:** Cycloaddition Reactions

**Variation 1:** Intermolecular Reactions

**Variation 2:** Intramolecular Reactions

17.9

**Product Class 9: Phthalocyanines and Related Compounds**

N. B. McKeown

17.9.1

**Product Class 9: Phthalocyanines and Related Compounds**

**Product Subclass 1: Metal-Free Phthalocyanine**

**Method 1:** From Phthalonitrile

**Variation 1:** From Generation and Demetalation of a Labile Metal Complex

**Method 2:** From Isoindolinediimine

**Product Subclass 2: Metal–Phthalocyanine Complexes**

**Method 1:** From Phthalonitrile

**Method 2:** From Phthalic Anhydride

**Method 3:** From Phthalimide

**Method 4:** From Isoindolinediimine

**Method 5:** From 2-Cyanobenzamide

**Method 6:** From Phthalocyanine

**Method 7:** Metal Exchange of Dilithium or Disodium Complex
17.9.3 Product Subclass 3: 1,8(11),15(18),22(25)-Tetrasubstituted Phthalocyanines and 1:25,11:15-Bridged Phthalocyanines

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17.9.4.1 Method 1: From 4-Substituted Phthalonitriles

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J. Schmidt and L. A. Silks

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# Product Class 5: α-Heteroatom-Substituted Alkanamides

M. Pätz, S. Pritz, and J. Liebscher

## Product Class 5: α-Heteroatom-Substituted Alkanamides

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### 22.5 Product Class 5: 2-Functionalized Alkylidenephosphines

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Synthesis of Product Subclass 6

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Product Class 13: Alkenylketenes

R. L. Danheiser, G. B. Dudley, and W. F. Austin

Product Subclass 1: Vinylketenes

Synthesis of Product Subclass 1

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Method 2: Wolff Rearrangement of $\alpha'$-Diazo-$\alpha,\beta$-unsaturated Ketones

Method 3: Electrocyclic Ring Opening of Cyclobutenones

Applications of Product Subclass 1 in Organic Synthesis

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Variation 2: Intramolecular Cycloadditions

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Applications of Product Subclass 3 in Organic Synthesis

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Product Class 16: Sulfur, Selenium, and Tellurium Analogues of Ketenes
C. Spanka and E. Schaumann

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R. Zimmer

Synthesis of Product Subclass 6

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R. Zimmer

Synthesis of Product Subclass 7

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R. Zimmer

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Method 3: Alkylation of 2-Ethynylbenzothiazolium Salts

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

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

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**J. G. Schantl**

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Synthesis by Hydration of Alkynes

M. Oestreich

Synthesis by Direct Hydration

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T. J. J. Müller

Synthesis by Formylation of Enolates

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Product Class 2: 2-Oxoaldehydes and Heteroatom Analogues
T. Olpp

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Product Class 9: 3-Heteroatom-Substituted Aldehydes

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25.9.1.1

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## 26.4 Product Class 4: 1,2-Diketones and Related Compounds

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### 26.4.1 Product Subclass 1: 1,2-Diketones

#### 26.4.1.1 Synthesis of Product Subclass 1

- **Method 1:** Coupling Reactions
  - **Variation 1:** Coupling of Aldehydes
  - **Variation 2:** Coupling of Carboxylic Acid Derivatives
- **Variation 3:** Coupling of $\alpha$-Oxonitriles
- **Variation 4:** Carbonylative Coupling of Alkyl Halides with Organometallic Reagents
- **Variation 5:** Nucleophilic Acylation of Carboxylic Acid Derivatives by Acyllithium Reagents
- **Variation 6:** Addition of Organometallic Reagents to 1,2-Diacyl Derivatives
- **Variation 7:** Friedel–Crafts Acylation

#### 26.4.1.2 Substitution of Heteroatoms

- **Variation 1:** Hydrolysis of $\alpha$-Oxo Ketals
- **Variation 2:** Hydrolysis of $\alpha$-Oxo Thioketals
- **Variation 3:** Hydrolysis of $\alpha$-Oxo Imines
- **Variation 4:** Hydrolysis of $\alpha,\alpha$-Dihalo Ketones
- **Variation 5:** From $\alpha$-Diazo Ketones

#### 26.4.1.3 Oxidation

- **Variation 1:** Of Ketones
- **Variation 2:** Of Enones by Ozonolysis
- **Variation 3:** Of $\alpha$-Hydroxy Ketones
- **Variation 4:** Of 1,2-Diols
- **Variation 5:** Of Alkenes
- **Variation 6:** Of Alkynes
- **Variation 7:** Of Arenes, Phenols, and Catechols
- **Variation 8:** Of $\alpha$-Oxo Phosphorus Ylides
- **Variation 9:** Of $\alpha$-Bromo Ketones

#### 26.4.1.4 Rearrangements of $\alpha,\beta$-Epoxy Ketones

**Method 4:**
- **Variation 1:** Of 1,2-Bis(siloxy)alkenes

#### 26.4.1.5 Additional Methods

**Method 5:**
- **Variation 1:** Rearrangements of $\alpha,\beta$-Epoxy Ketones

**Method 6:**
- **Variation 1:** Additional Methods

#### 26.4.1.6 Applications of Product Subclass 1 in Organic Synthesis

- **Method 1:** Oxidation of 1,2-Diketones to Carboxylic Acids
- **Method 2:** Addition Reactions with 1,2-Diketones
  - **Variation 1:** Addition of Hydrogen
  - **Variation 2:** Addition of Organometallic Reagents
  - **Variation 3:** Addition of Carbon Functionalities
  - **Variation 4:** Addition of Heteroatoms
  - **Variation 5:** Cycloadditions of 1,2-Diketones
- **Method 3:** Ring Contraction of Cyclic 1,2-Diketones
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Product Subclass 12: α-Amino-α-sulfanyl Ketones

Synthesis of Product Subclass 12

Method 1: Via Pummerer Reaction from α-Sulfoxy Ketones

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Method 5: Using α-Amino-α-(sulfonylmethyl)lithium Reagents

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Product Subclass 13: α,α-Diselanyl Ketones

Synthesis of Product Subclass 13

Method 1: By Addition of Metal Enolates to Elemental Selenium

Method 2: From α-Selanyl Ketones

Method 3: From α-Diazo Ketones

Method 5: Using α-Amino-α-(sulfonylmethyl)lithium Reagents

Method 6: From 1,2-Diketones or 1,2-Oxoaldehydes

Product Subclass 14: α,α-Diamino Ketones

Synthesis of Product Subclass 14

Method 1: By Substitution of Halogen

Method 2: Via Cycloaddition

Method 3: By Addition of Diaminoalkylmetal Reagents

Method 4: From 1,2-Diketones or α-Oxoaldehydes

Product Class 6: α-Heterosubstituted Ketones

J. Suffert

Product Class 6: α-Heterosubstituted Ketones

Product Subclass 1: α-Fluoro Ketones

Synthesis of Product Subclass 1

Method 1: Substitution of a Hydrogen Atom from an Alkanone

Variation 1: Direct Fluorination of Ketones without a Base

Variation 2: Deprotonation with an External Base

Variation 3: From an Alkanone via a Preformed Acetate Enol Ether

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Product Subclass 2: \(\alpha\)-Chloro Ketones

Synthesis of Product Subclass 2

Method 1: Substitution of a Hydrogen Atom from an Alkanone

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Variation 2: Opening of an \(\alpha\),\(\beta\)-Epoxy Ketone with Benzoyl Chloride

Product Subclass 3: \(\alpha\)-Bromo Ketones

Synthesis of Product Subclass 3

Method 1: Substitution of Hydrogen by Bromine

Variation 1: Direct Bromination with Bromine in Acetic Acid/Water or in the Presence of Urea

Variation 2: Direct Bromination with Bromine in Concentrated Sulfuric Acid

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Variation 11: Bromination with Bromine Donors: N-Bromosuccinimide in the Presence of Ammonium Acetate

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Product Class 9: Enones
S. P. Marsden

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R. A. Pilli and G. B. Rosso

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D. M. Wilson and Y. Zhang

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Y. Zhang and D. M. Wilson

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J. G. Schantl

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Method 4: Transformation of Diphenyl Dithioacetals into Titanium–Carbene Complexes

Product Subclass 2: 1,3-Dithietanes

T.-Y. Luh and M.-k. Leung

Synthesis of Product Subclass 2

Symmetrical Dithietanes

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Variation 2: Thioketones Formed In Situ from Disulfides

Variation 3: Thioketones Formed In Situ from \(-\)Chlorosulfenyl Chloride

Variation 4: Thioketones Formed In Situ from Carbon Suboxide

Method 2: Dimerization of Dithioacetic Acid

Method 3: Dimerization of 1,2-Dithiole-3-thiones

Method 4: Synthesis from Thiophosgene

Method 5: Dimerization of Thioketenes

Variation 1: Thioketenes Formed In Situ from Isothiazole-5(2H)-thione

Variation 2: Thioketenes Formed In Situ from Terminal Alkynes

Variation 3: Thioketenes Formed In Situ from Octafluoroisobutene

Method 6: Dimerization of Isothiocyanates

Method 7: Synthesis Using Carbon Disulfide

Variation 1: Reaction with Ketones

Variation 2: Reaction with Wittig Reagents

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Unsymmetrical Dithietanes

Method 1: Synthesis from Ethene-1,1-dithiols

Method 2: Synthesis from Xanthates

Method 3: Synthesis from Thioketenes and Imines

Method 4: Synthesis from Ketones

Method 5: Synthesis from Bis(chloromethyl) Sulfoxide

Method 6: Cycloaddition of a Sulfinylalkane with a Thioketone

Variation 1: Sequential Oxidation of Disulfides

Variation 2: Thermolysis of Sulfenic Esters

Variation 3: Rearrangement Reactions

Method 7: Substitution Reactions of Dithietane

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### Acid Hydrolysis

Variation 2: Acid Hydrolysis

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31.5 Product Class 5: Phenols and Phenolates

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C. González-Bello and L. Castedo

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C. González-Bello and L. Castedo

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J. Chen and C. K.-F. Chiu

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31.10.1.3.1 Variation 1: Nucleophilic Addition to α,β-Unsaturated Sulfones

31.10.1.3.2 Variation 2: Radical Addition to α,β-Unsaturated Sulfones

31.10 Product Class 10: Aryl Sulfones and Nitrogen Derivatives

31.10. Product Class 10: Aryl Sulfones and Nitrogen Derivatives

31.10.1 Product Subclass 1: Aryl Sulfones

31.10.1.1 Synthesis of Product Subclass 1

31.10.1.1.1 Method 1: Synthesis by Formation of the C—S Bond

31.10.1.1.2 Variation 1: Addition of Arenesulfonic Acids to Alkenes and Alkynes

31.10.1.1.3 Variation 2: Nucleophilic Displacement with Arenesulfinates

31.10.1.1.4 Variation 3: Addition of Arenesulfonyl Radicals to Alkenes and Alkynes

31.10.1.1.5 Variation 4: Reaction of Arenesulfonic Esters or Arenesulfonyl Halides with Nucleophiles

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31.10.1.2 Method 2: Oxidation of Aryl Sulfides and Sulfoxides

31.10.1.3 Method 3: Synthesis from α,β-Unsaturated Sulfones

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O. A. Rakitin

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O. A. Rakitin

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Synthesis of Product Subclass 4

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A. Schmidt

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S. Bräse, D. Keck

31.35  **Product Class 35: Aryl Azides**

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31.36  **Product Class 36: Aryltriazenes, Aryltetrazenes, and Related Compounds**  
S. Bräse and T. Muller

31.36  **Product Class 36: Aryltriazenes, Aryltetrazenes, and Related Compounds**

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Synthesis of Product Subclass 4

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Synthesis of Product Subclass 5

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Synthesis of Product Subclass 6

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Product Class 37: N-Phosphinoarylamines

M. Alajarín, C. López-Leonardo, and J. Berná
Product Class 38: Cyclic Arylamines

P. J. Stevenson

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I. B. Gorrell and T. P. Kee

31.39  **Product Class 39: Arylphosphonic Acids and Derivatives**  
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H.-J. Cristau and D. Virieux

31.40  **Product Class 40: Arylphosphinic Acids and Derivatives**  
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Product Class 41: Arylphosphine Oxides

C. A. Ramsden

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B. List, C. Chandler, R. R. Torres, and A. Erkkilä

32.3.15 Product Subclass 15: 1-Nitrogen-Functionalized 2-Phosphorus-Functionalized Alkenes

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B. List, C. Chandler, R. R. Torres, and A. Erkkilä

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A. Pollex

32.4  **Product Class 4: Haloalkenes**  
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V. Milata, S. Rádl, and S. Voltrová

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**N. Ono**

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W. D. Pfeiffer
Synthesis by Substitution of \( \alpha \)-Bonded Heteroatoms

M. Braun

Method 1: Substitution of Other Halogens

Method 2: Substitution of Oxygen Functionalities

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Synthesis by Addition across C=C Bonds

T. Troll

Method 1: Bromination of Aromatic Compounds

Method 2: Bromination of 1,3-Dienes

Method 3: Bromination of Alkenes

Variation 1: Bromination with Bromine–Amine Complexes

Variation 2: Generation of Electrophilic Bromine by In Situ Oxidation of Bromide

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Method 5: Sulfobromination of Alkenes

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Synthesis by Addition across C=O Bonds

K. Rück-Braun and T. Freysoldt

Method 1: Hydrobromination of Epoxides Using Hydrogen Bromide

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Variation 1: Catalyzed by Lewis Acids

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Method 7: Enantioselective Hydrobromination of Epoxides Using Azidotrialkyilsilanes and Allyl Bromide

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- **T. Troll**

#### 35.3.5.1 Synthesis by Addition across C=C Bonds

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#### 35.3.5.3 Synthesis by Addition across C–S Bonds

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H. Adolfsson

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Product Subclass 6: Alkylthiosulfino Transition-Metal Complexes

Product Subclass 7: Alkanethiosulfonic Acid Esters

Product Subclass 8: Alkanesulfamicides

Product Class 4: Acyclic Dialkyl Sulfoxides and Derivatives

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Variation 5: Sulfuration Using Polymer- or Solid-Supported Reagents or Catalysts

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Product Subclass 2: Alkaneseleninyl Chlorides

Synthesis of Product Subclass 2

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Product Subclass 3: Alkaneseleninic Acids and Their Salts

Synthesis of Product Subclass 3

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- Method 2: Hydrolysis of Alkylselenium Trihalides
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Applications of Product Subclass 3 in Organic Synthesis

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T. Shimizu and N. Kamigata

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Product Class 20: Acyclic Dialkyl Selenides
M. Segi

Synthesis of Product Class 20

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Y. Tang and X.-L. Sun

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J. B. Sweeney

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E. Kruiswijk and J. A. Deck

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W. Maison

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Abbreviations
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**Synthesis by Elimination**
S. Sankararaman

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Product Class 3: Cyclic Allenes
T. Kawase

Product Subclass 1: Cyclohexa-1,2-dienes

Method 1: Ring Enlargement by the Doering–Moore–Skattebøl Reaction

Variation 1: From 1,1-Dibromocyclopropanes

Variation 2: From 1-Bromo-1-fluorocyclopropanes

Method 2: Dehydrohalogenation of 1-Halocyclohexenes

Variation 1: Base-Promoted Reactions

Variation 2: Photochemical or Thermal Reaction of Intermediate Allyl Anions

Method 3: Dehalogenation of 2,3-Dihalocyclohexenes

Method 4: Elimination from 2-Halo-3-(trimethylsilyl)cyclohexenes

Product Subclass 2: Cyclohexa-1,2,4-trienes

Method 1: [4 + 2]-Cycloaddition Reactions

Variation 1: From Vinylalkynes and Alkynes

Variation 2: From Arylalkynes and Alkynes

Variation 3: From Diarylacetylenes and Alkynes

Variation 4: From Two Arylalkynes

Method 2: Electrocyclization of (Z)-Hexa-1,3-dien-5-ynes

Method 3: Ring Enlargement by the Doering–Moore–Skattebøl Reaction

Method 4: Dehydrohalogenation of 1-Halocyclohexa-1,4-dienes

Product Subclass 3: Bicyclo[4.4.0]deca-1,3,5,7,8-pentaenes

Method 1: [4 + 2]-Cycloaddition Reactions

Variation 1: Intermolecular [4 + 2]-Cycloaddition Reactions

Variation 2: Intramolecular [4 + 2]-Cycloaddition Reactions

Method 2: Ring Enlargement by the Doering–Moore–Skattebøl Reaction

Method 3: Dehydrohalogenation of 3-Bromo-1,2-dihydronaphthalenes

Product Subclass 4: Cyclohepta-1,2-dienes

Method 1: Ring Enlargement by the Doering–Moore–Skattebøl Reaction

Variation 1: From 1,1-Dihalocyclopropanes

Variation 2: From 7-Bromo-7-(trimethylstannyl)bicyclo[4.1.0]heptane

Method 2: Ring Enlargement by Cope Rearrangement from 1,2-Diethynylcyclopropanes

Method 3: Ring Enlargement by Thermolysis of Tricyclo[4.1.0.0^2,4]-hept-5-yliden or 1-Ethynyl-2-vinylcyclopropane

Method 4: Dehydrohalogenation of 1-Halocycloheptenes

Method 5: Dehalogenation of 1,7-Dihalocycloheptenes

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### 45.8

**Product Class 8: Cyclooctatetraenes**

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45.21  Product Class 21: Phenanthrenes, Helicenes, and Other Angular Acenes

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Science of Synthesis Original Edition Volume 46
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# Synthesis by Alkyldenation with Metal–Carbene Complexes and Related Reagents

T. Takeda and A. Tsubouchi

## Synthesis by Alkyldenation with Metal–Carbene Complexes and Related Reagents

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