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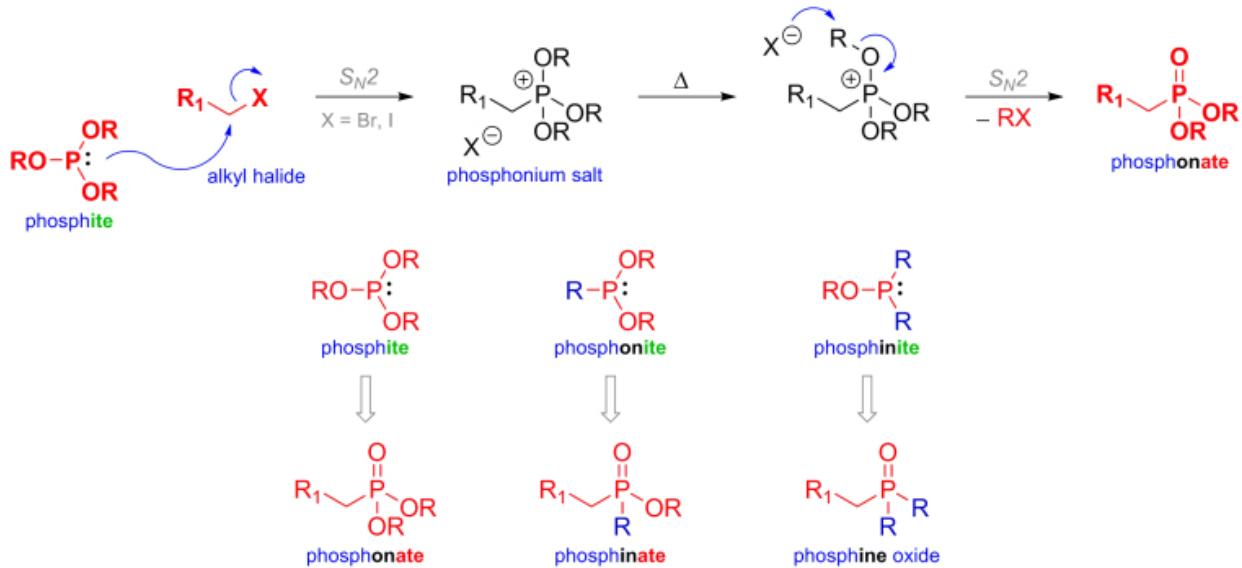
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# I. 100 Must Know Mechanisms

## 1. Arbuzov Reaction (1898–1906)

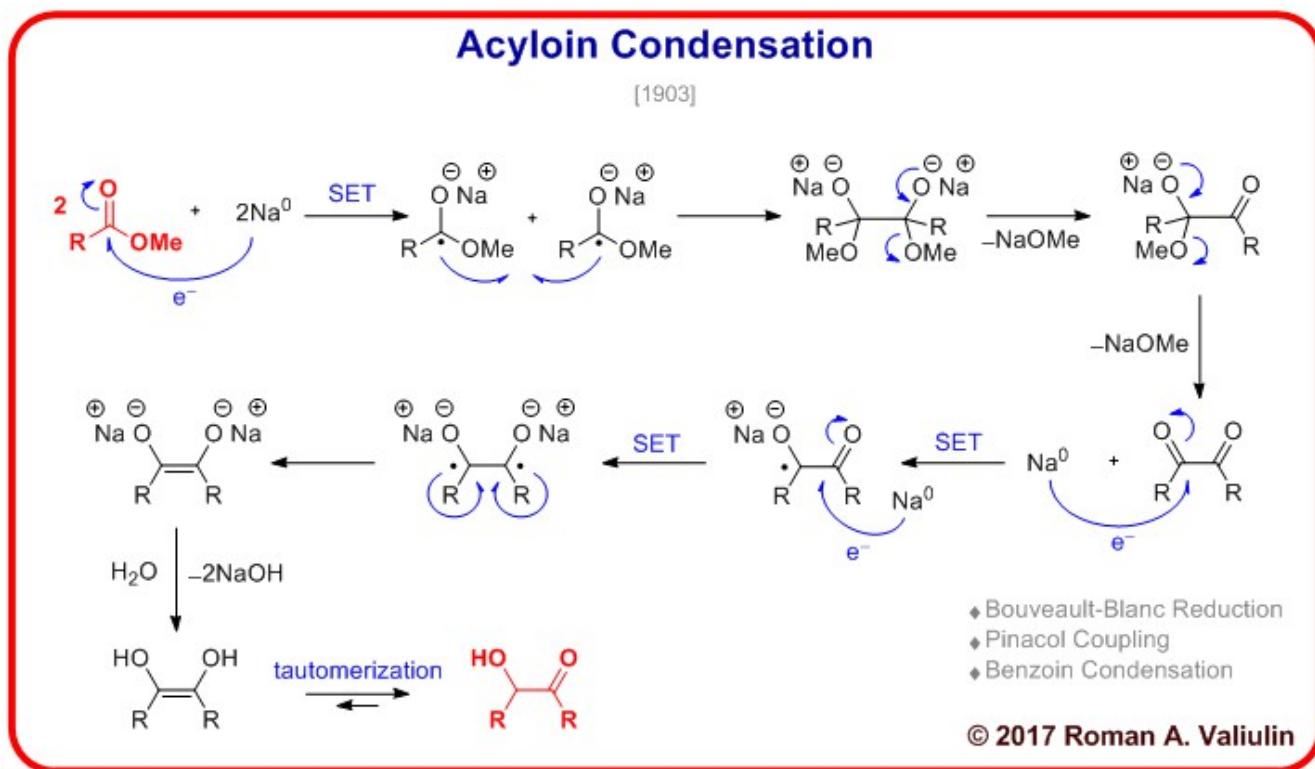
### Arbuzov Reaction

[1898-1906]

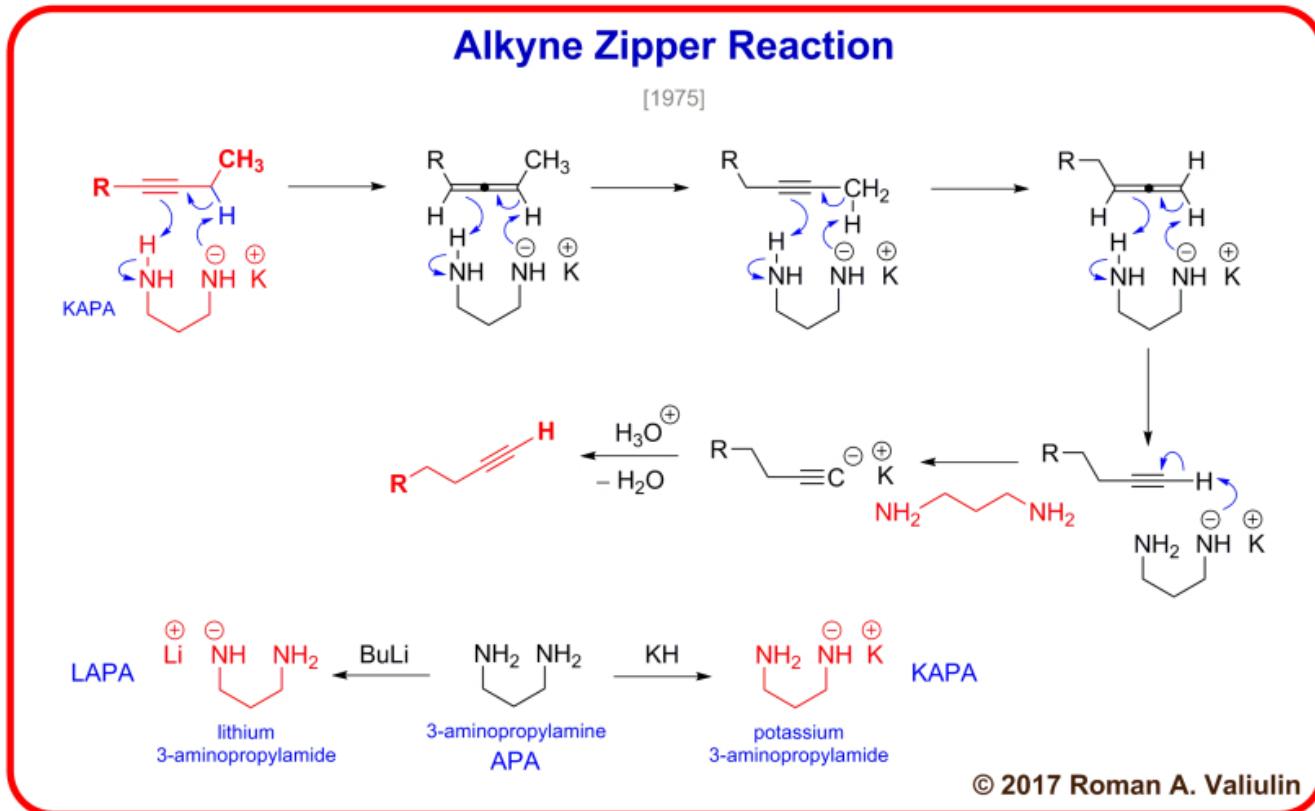


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## 2. Acyloin Condensation 1903



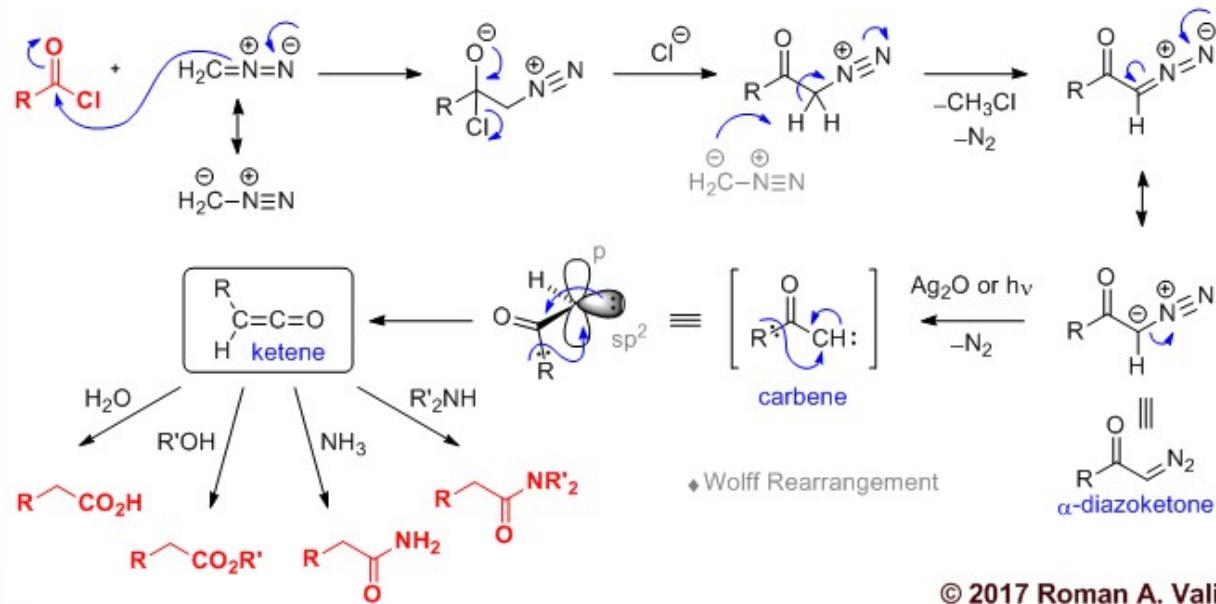
## 3. Alkyne (acetylene) Zipper 1975



## 4. Arndt-Eistert Synthesis 1935

### Arndt-Eistert Synthesis

[1935]

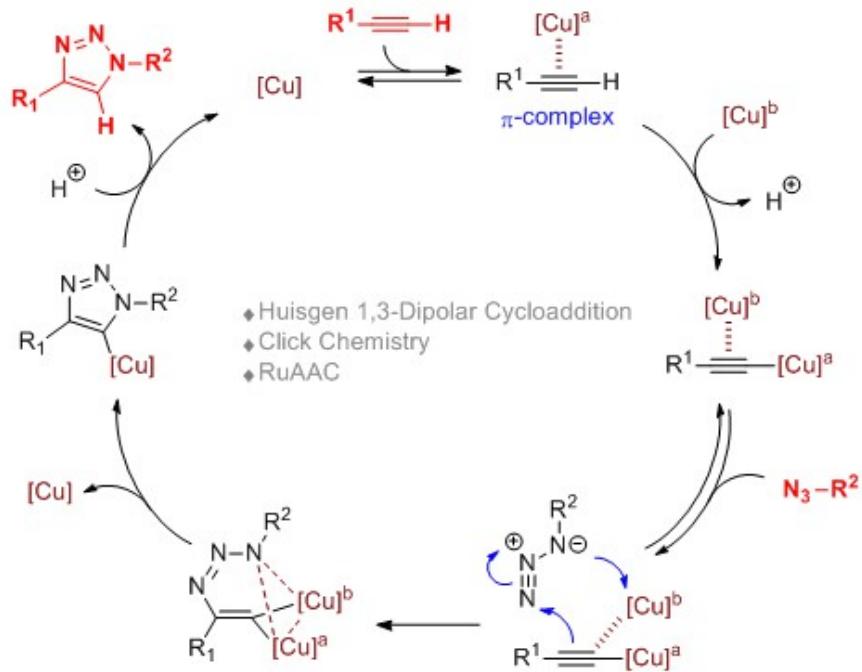


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## 5. Copper-Catalyzed Alkyne Azide Cycloaddition

### Cu Catalyzed Alkyne Azide Cycloaddition

CuAAC [2002]

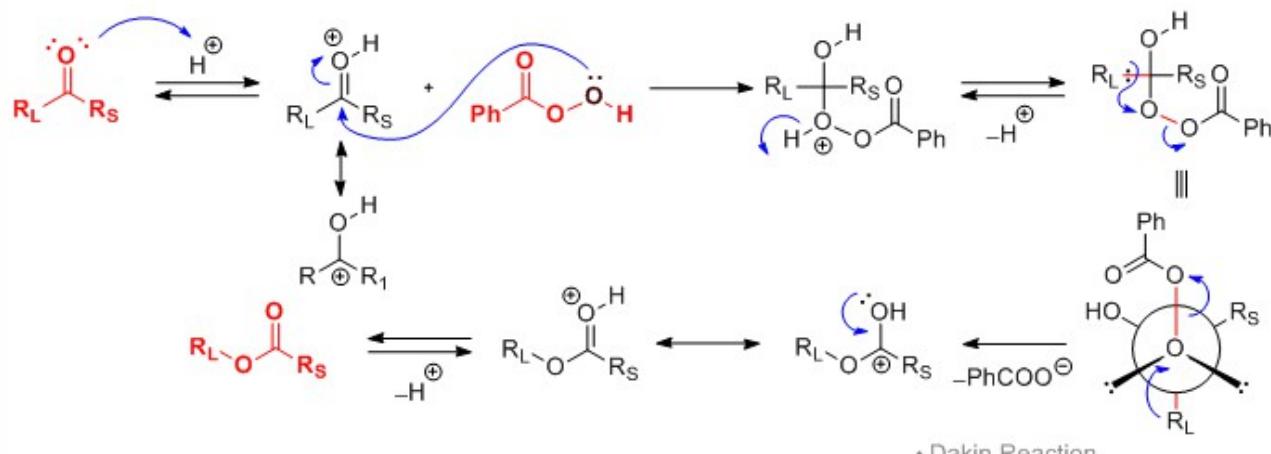


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## 6. Baeyer-Villiger Oxidation 1899

### Baeyer-Villiger Oxidation

[1899]



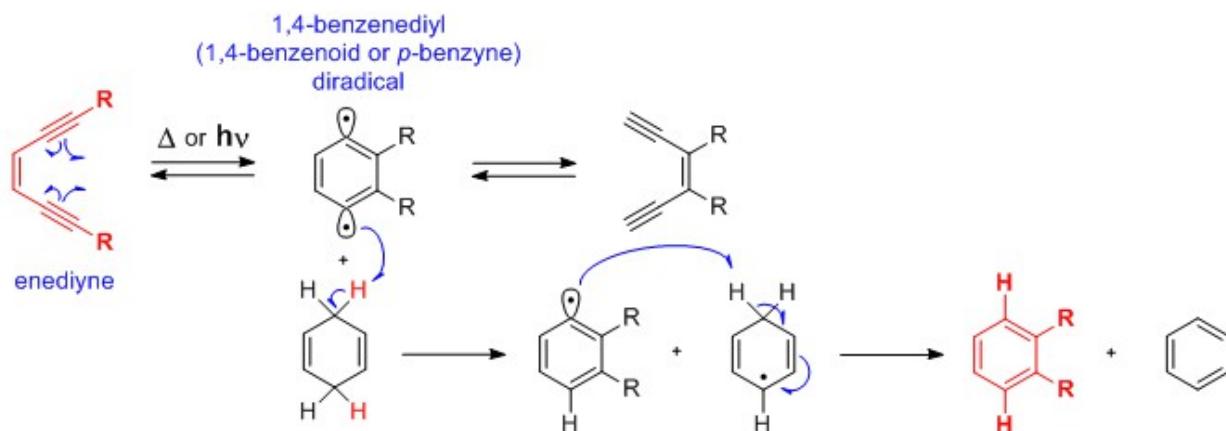
$\text{H} \gg 3^0 \text{ alkyl} > \text{cyclohexyl} > 2^0 \text{ alkyl} > \text{Ph} > 1^0 \text{ alkyl} > \text{CH}_3$

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## 7. Bergman Cyclization 1972

### Bergman Cyclization

[1972]

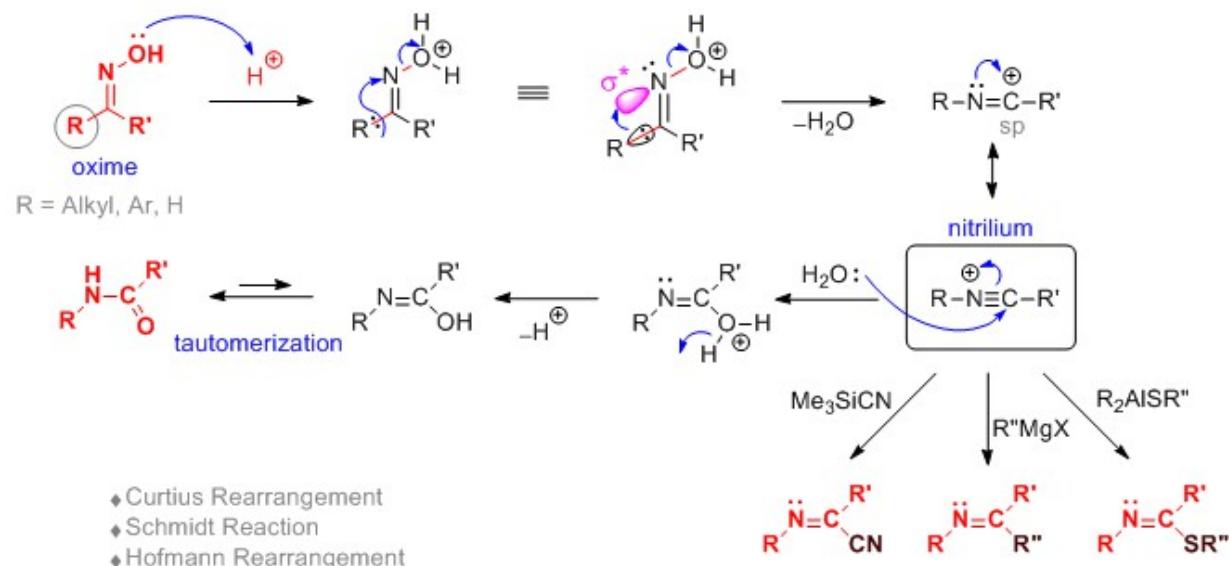


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## 8. Beckmann Rearrangement 1886

### Beckmann Rearrangement

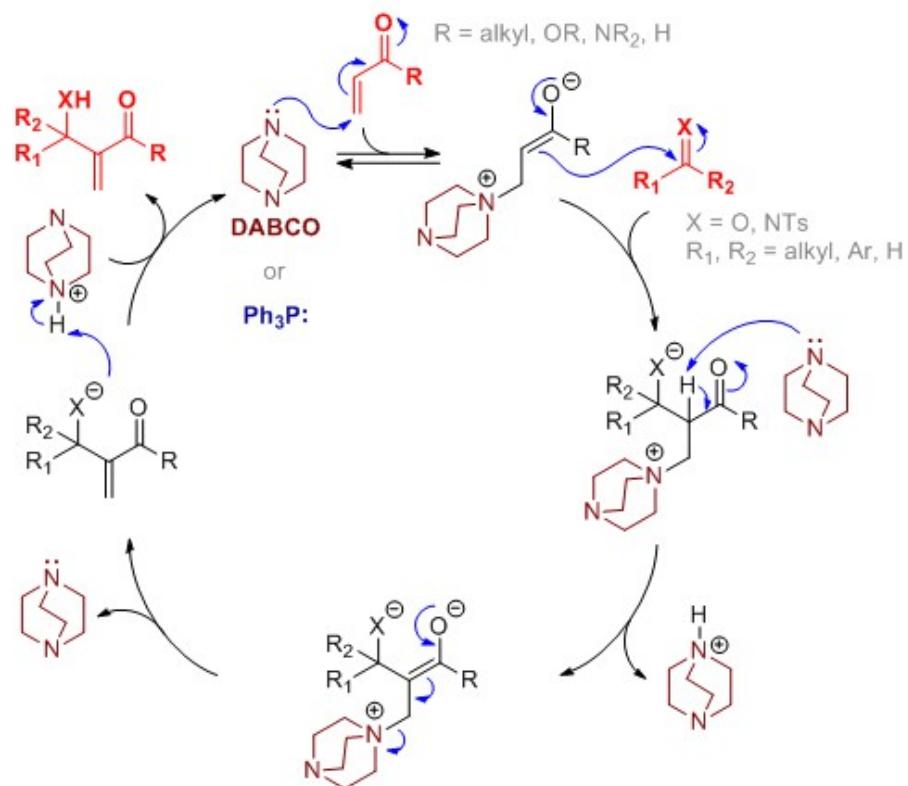
[1886]



## 9. Baylis-Hillman Reaction 1972

### Baylis-Hillman Reaction

[1972]

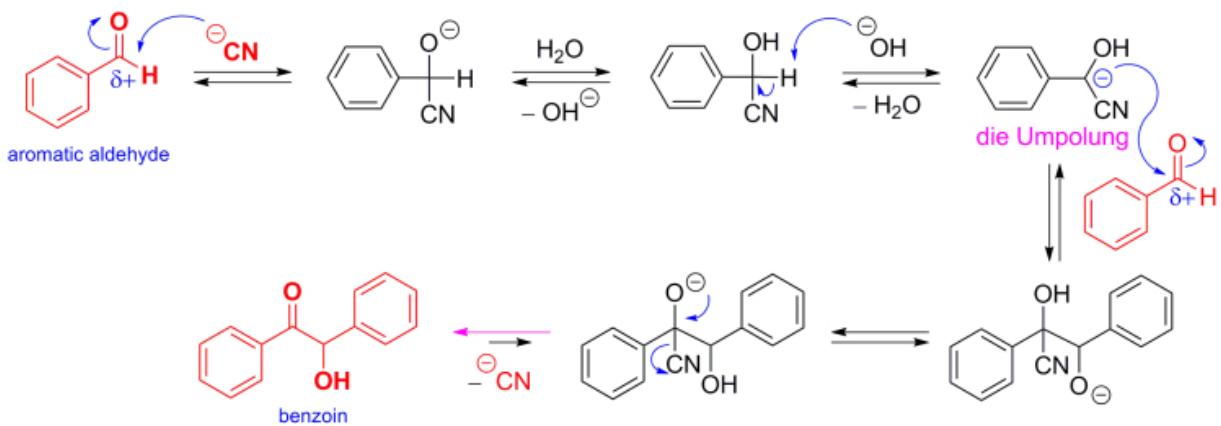


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## 10. Benzoin Condensation 1832

### Benzoin Condensation

[1832]

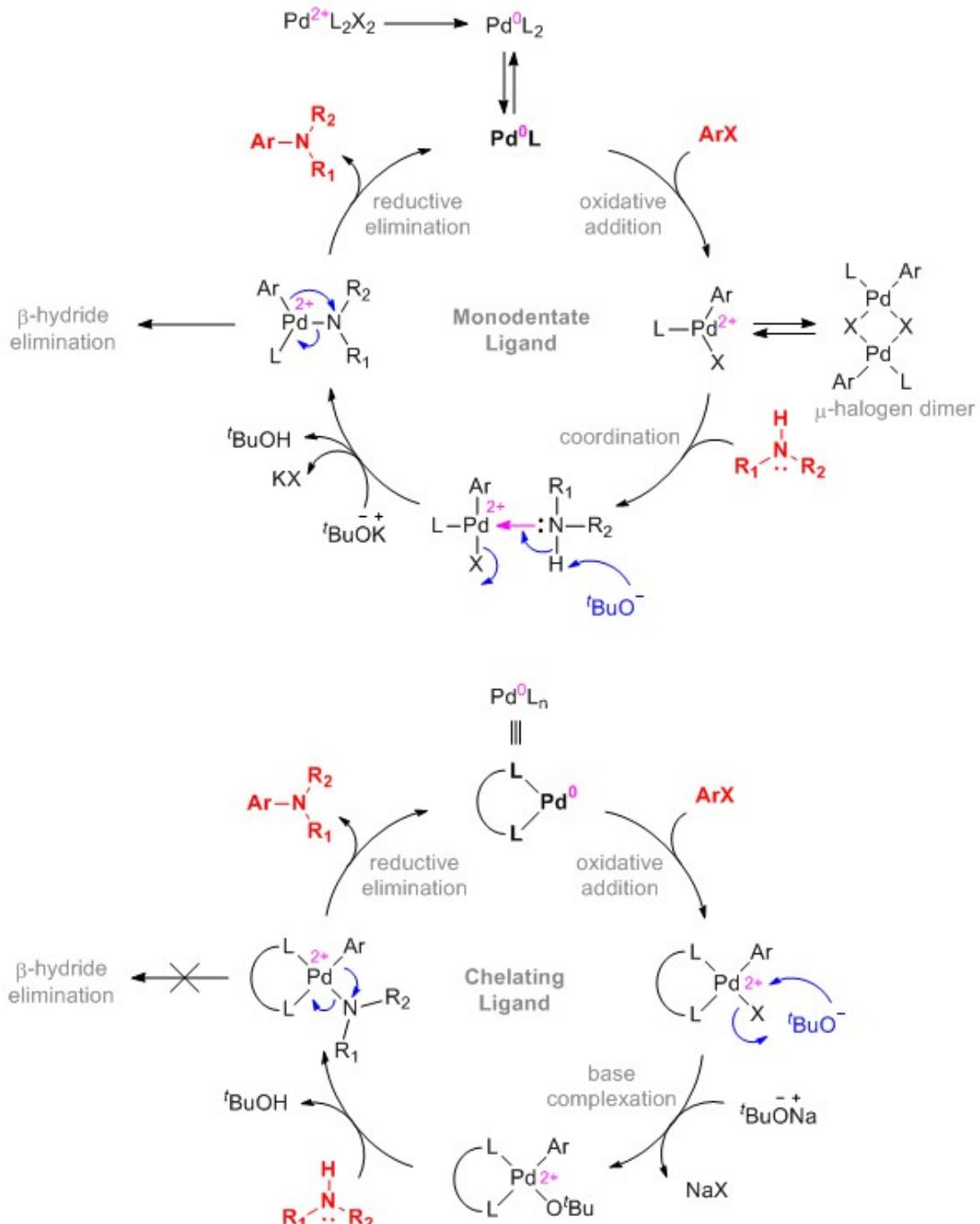


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# 11. Buchwald-Hartwig Cross Coupling 1994

## Buchwald-Hartwig Cross Coupling

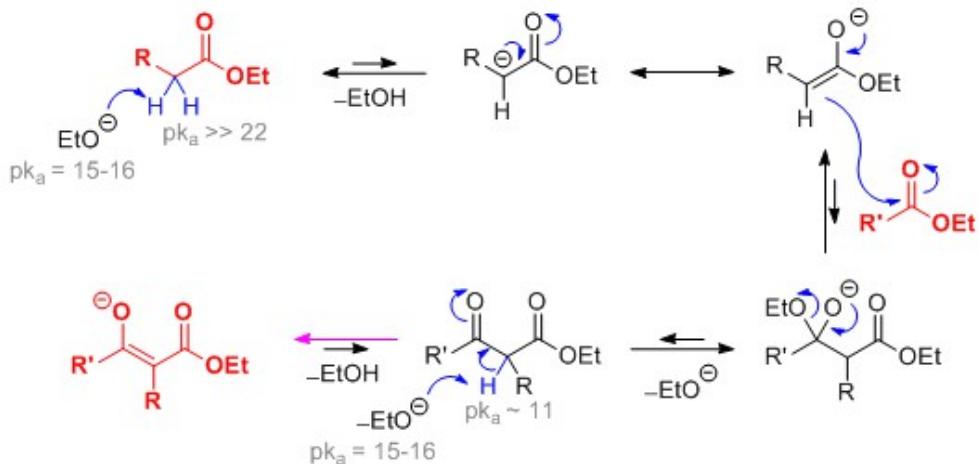
[1994]



## 12. Claisen Condensation 1887

### Claisen Condensation

[1887]



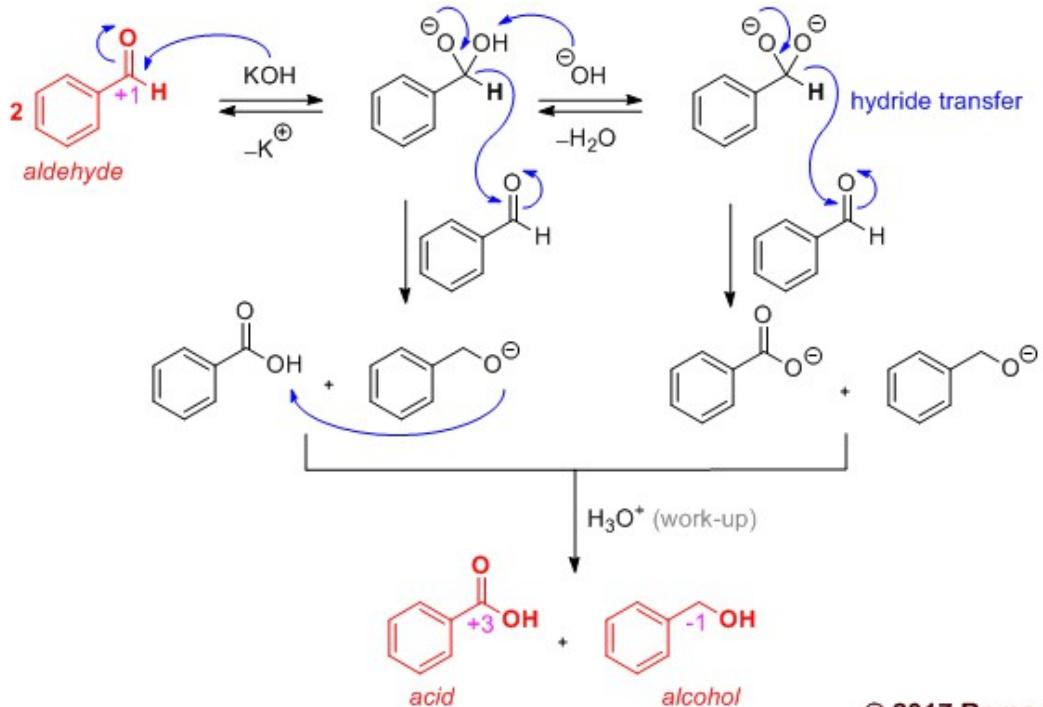
♦ Dieckmann condensation

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## 13. Cannizzaro Reaction 1853

### Cannizzaro Reaction

[1853]

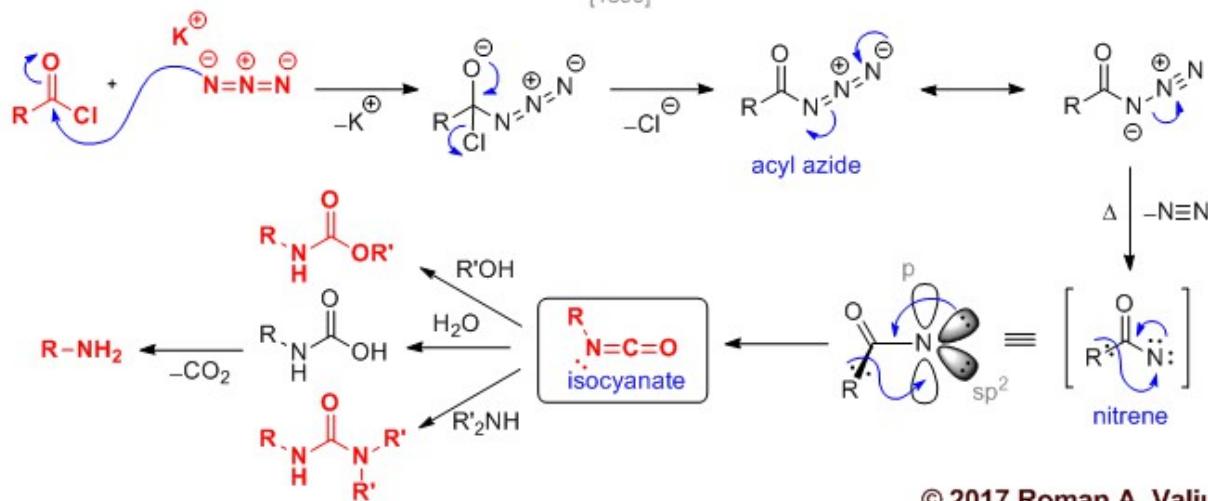


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## 14. Curtius Rearrangement 1890

### Curtius Rearrangement

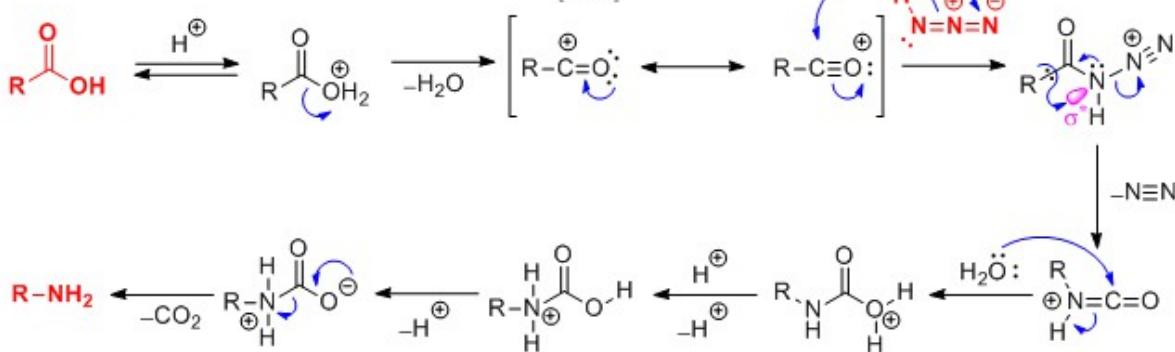
[1890]



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### Schmidt Reaction

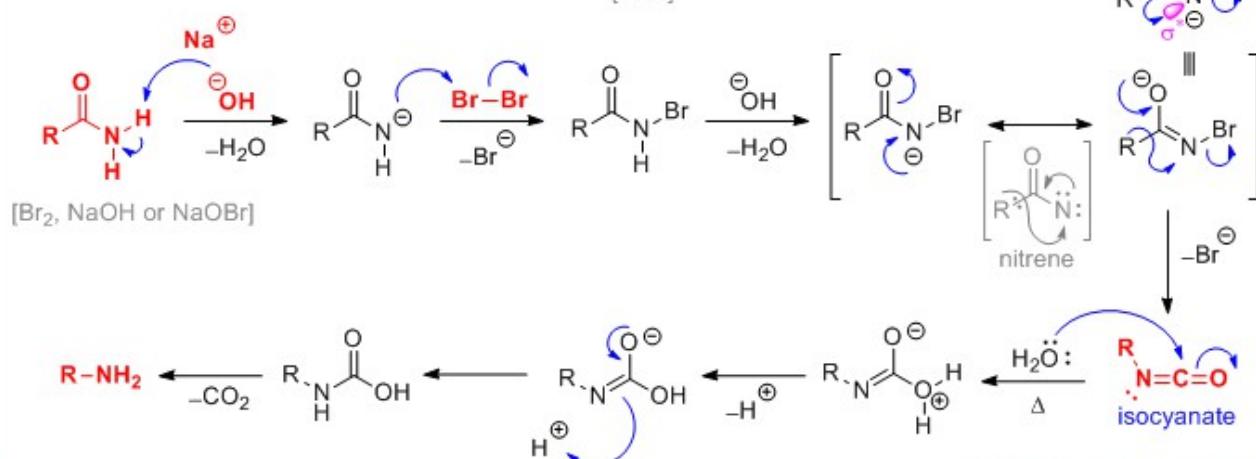
[1923]



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## Hofmann Rearrangement

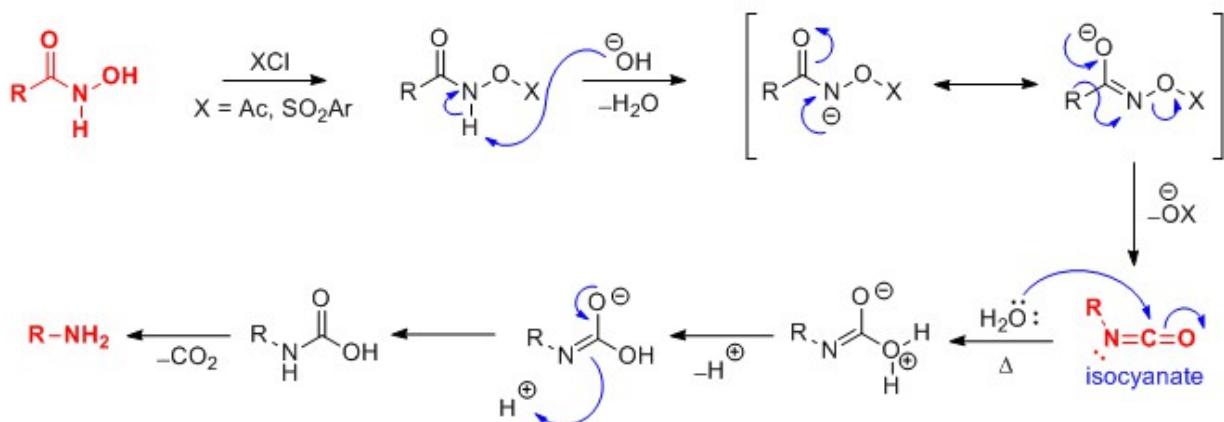
[1881]



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## Lossen Rearrangement

[1872]



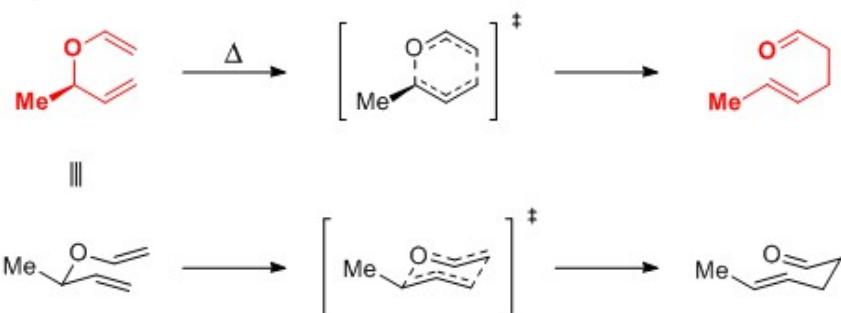
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## 15. Claisen Rearrangement 1912

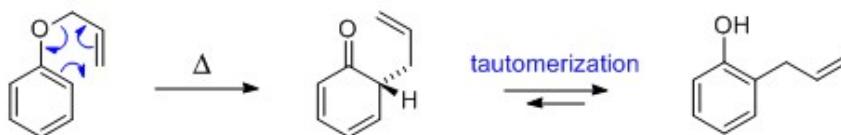
### Claisen Rearrangement

[1912]

◆ Alyphatic [3,3]-sigmatropic shift



◆ Aromatic [3,3]-sigmatropic shift



◆ Overman Rearrangement

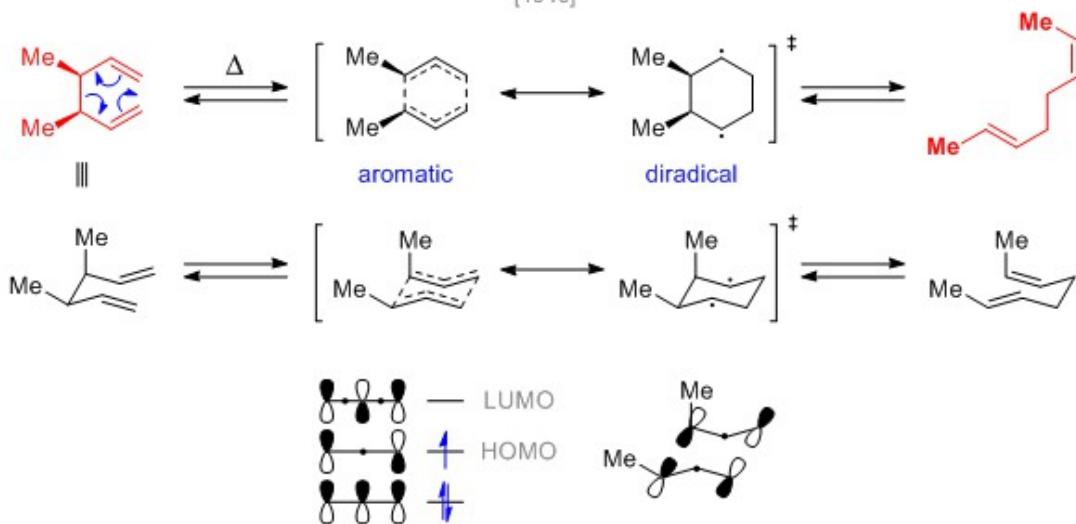
◆ Ireland-Claisen Rearrangement

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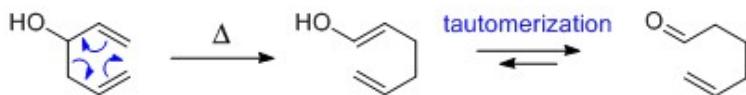
## 16. Cope Rearrangement 1940

### Cope Rearrangement

[1940]



### Oxy-Cope Rearrangement



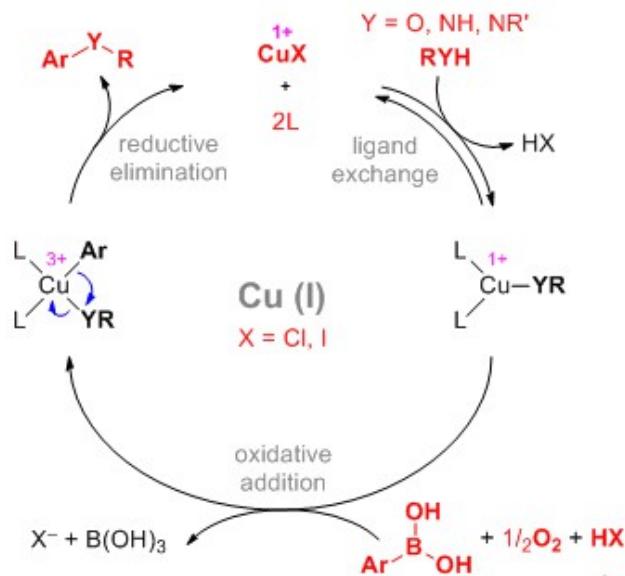
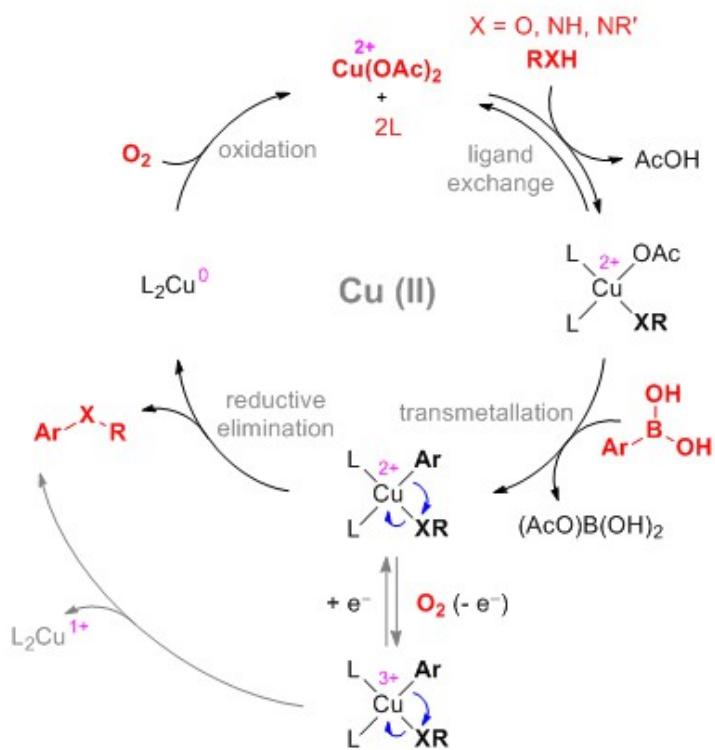
- ◆ Anionic Oxy-Cope Rearrangement
- ◆ Aza-Cope Rearrangement
- ◆ Claisen Rearrangement

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## 17. Chan-Evans-Lam Cross Coupling 1998

### Chan-Evans-Lam Cross Coupling

[1998]

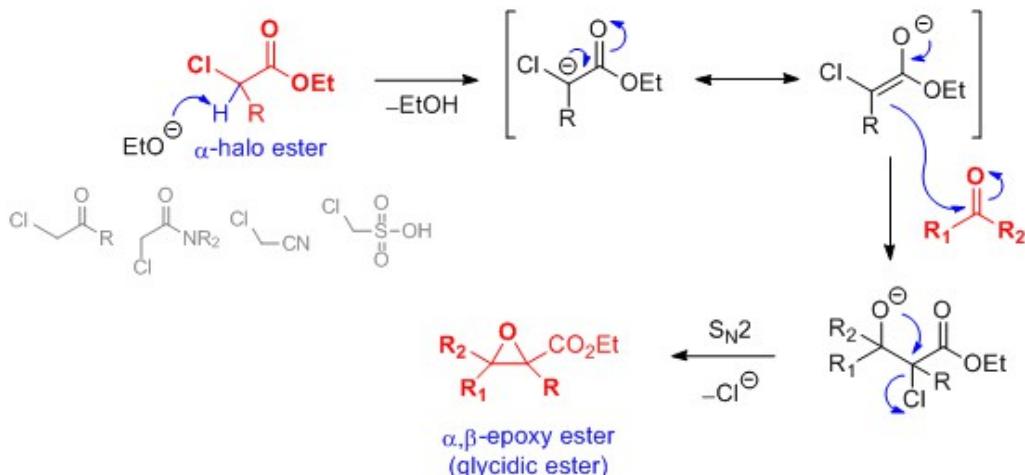


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## 18. Darzens Condensation 1904

### Darzens Condensation

[1904]

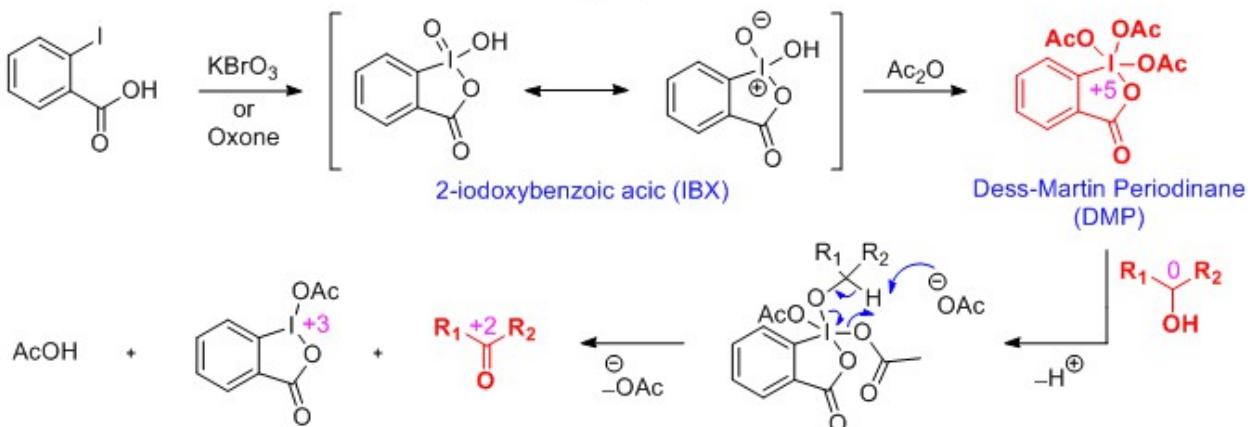


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## 19. Dess-Martin Oxidation 1983

### Dess Martin Oxidation

[1983]

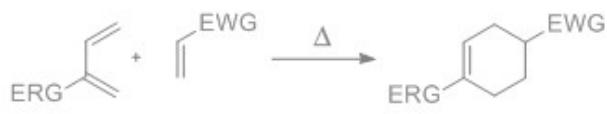
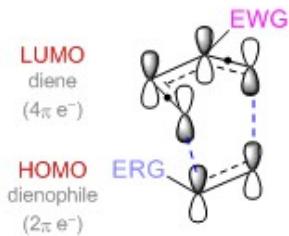
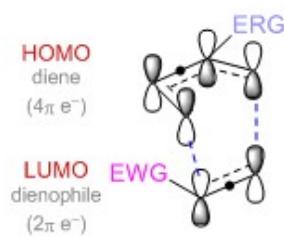
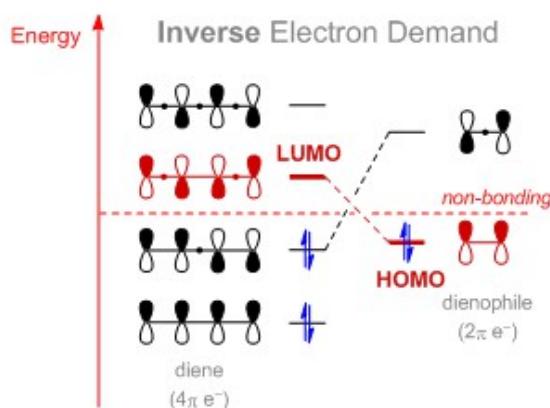
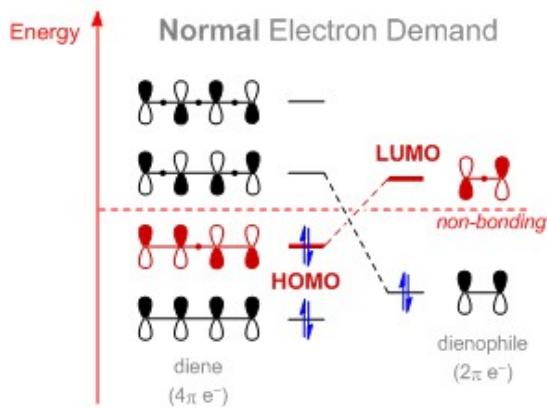
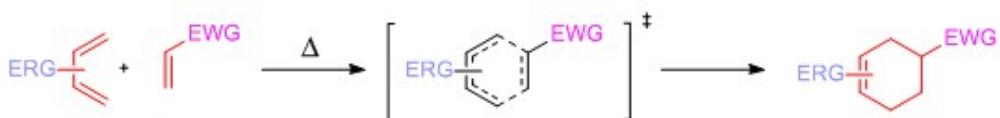


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## 20. Diels-Alder Cycloaddition 1928

### Diels-Alder Cycloaddition

[1928]



◆ Ene Reaction  
◆ [4+2] Cycloaddition



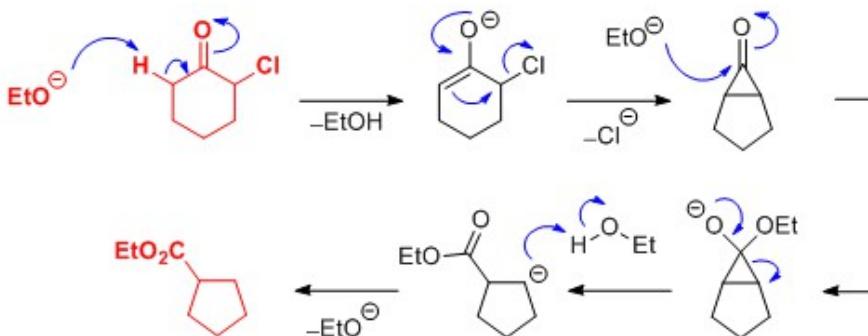
ERG = EDG = Electron Releasing/Donating Group  
EWG = Electron Withdrawing Group

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## 21. Favorskii Rearrangement 1894

### Favorskii Rearrangement

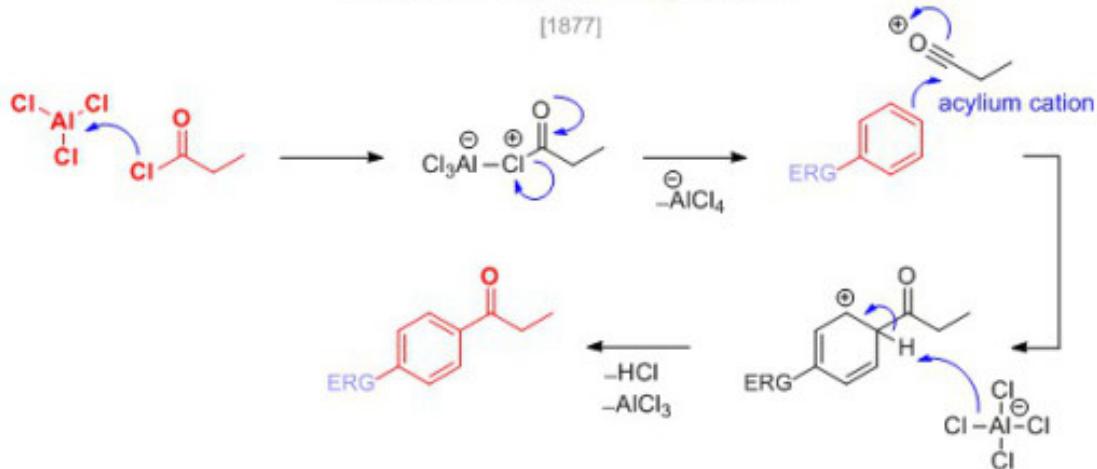
[1894]



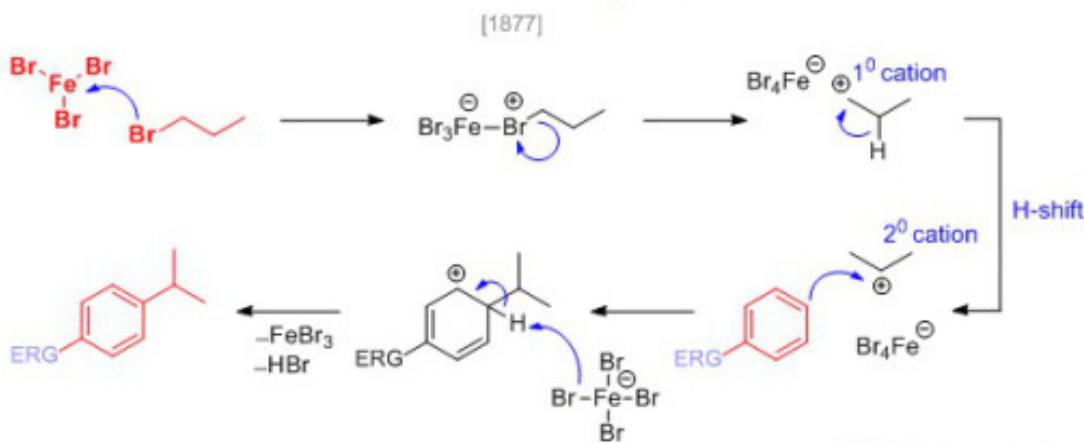
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## 22. Friedel-Crafts Acylation & Alkylation 1877

### Friedel-Crafts Acylation



### Friedel-Crafts Alkylation

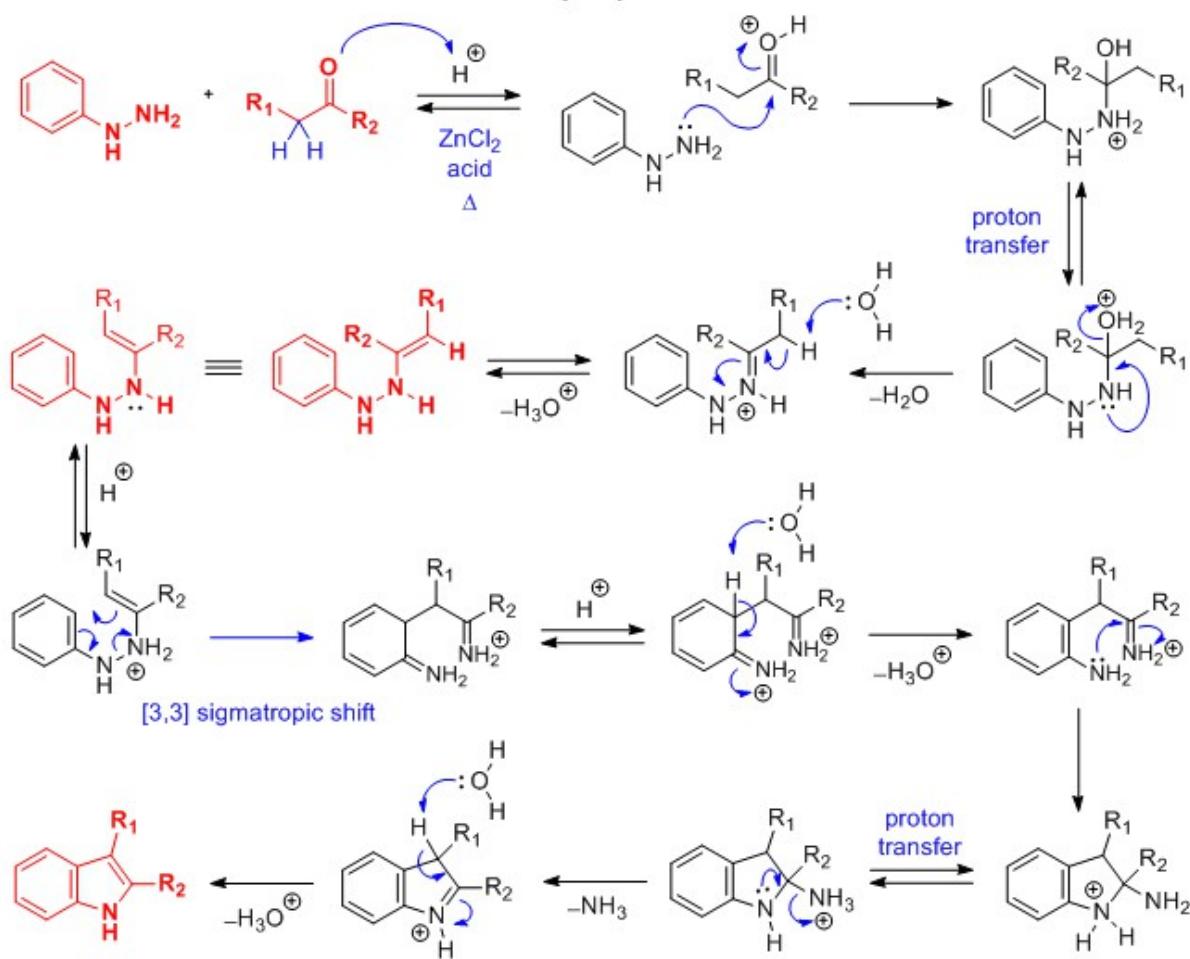


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## 23. Fischer Indole Synthesis 1883

### Fischer Indole Synthesis

[1883]

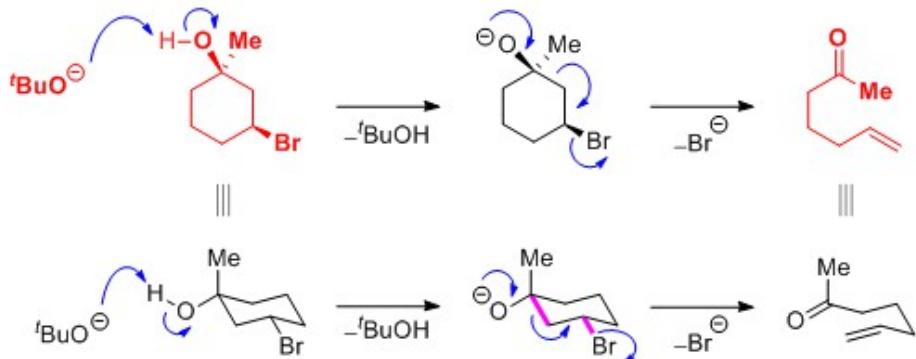


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## 24. Grob Fragmentation 1955

### Grob Fragmentation

[1955]

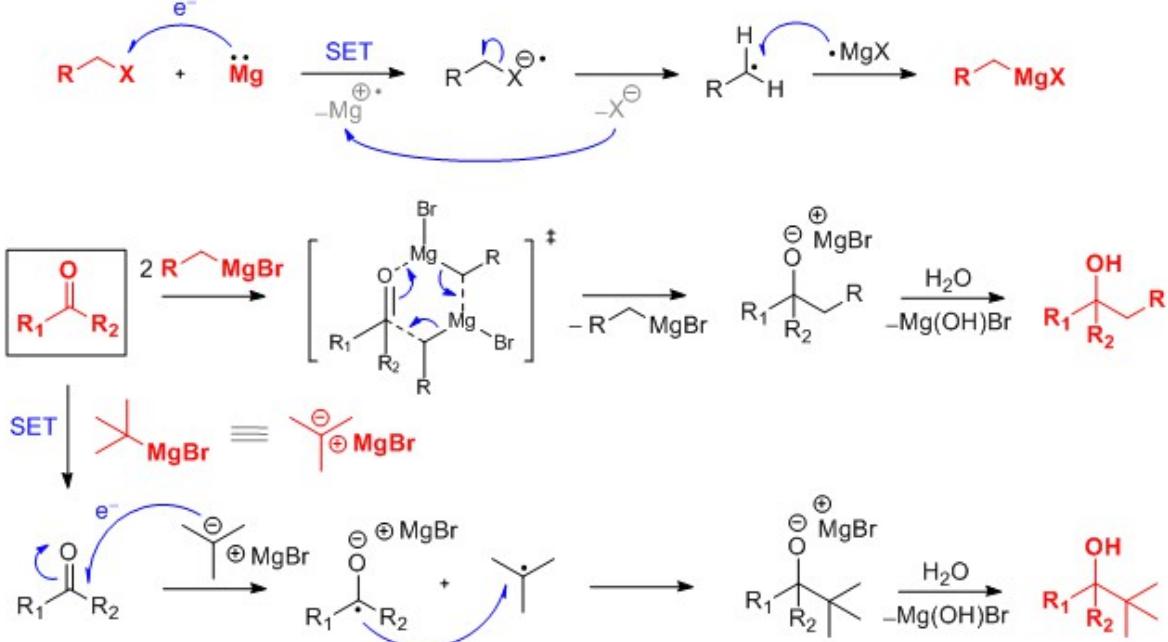


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## 25. Grignard Reaction 1900

### Grignard Reaction

[1900]

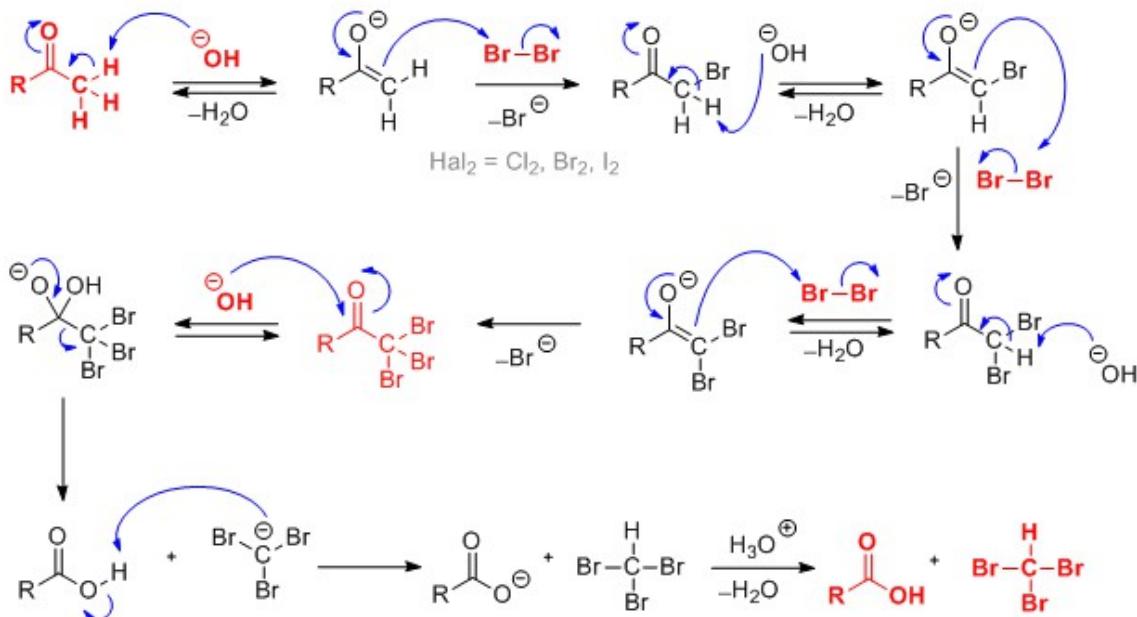


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## 26. Haloform Reaction 1822



[1822-1831-1870]

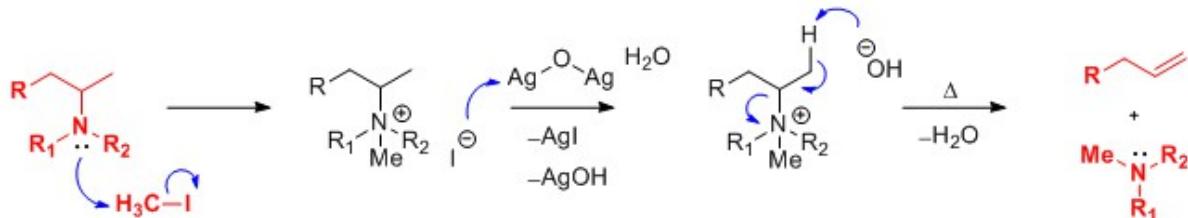


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## 27. Hofmann Elimination 1851



[1851]

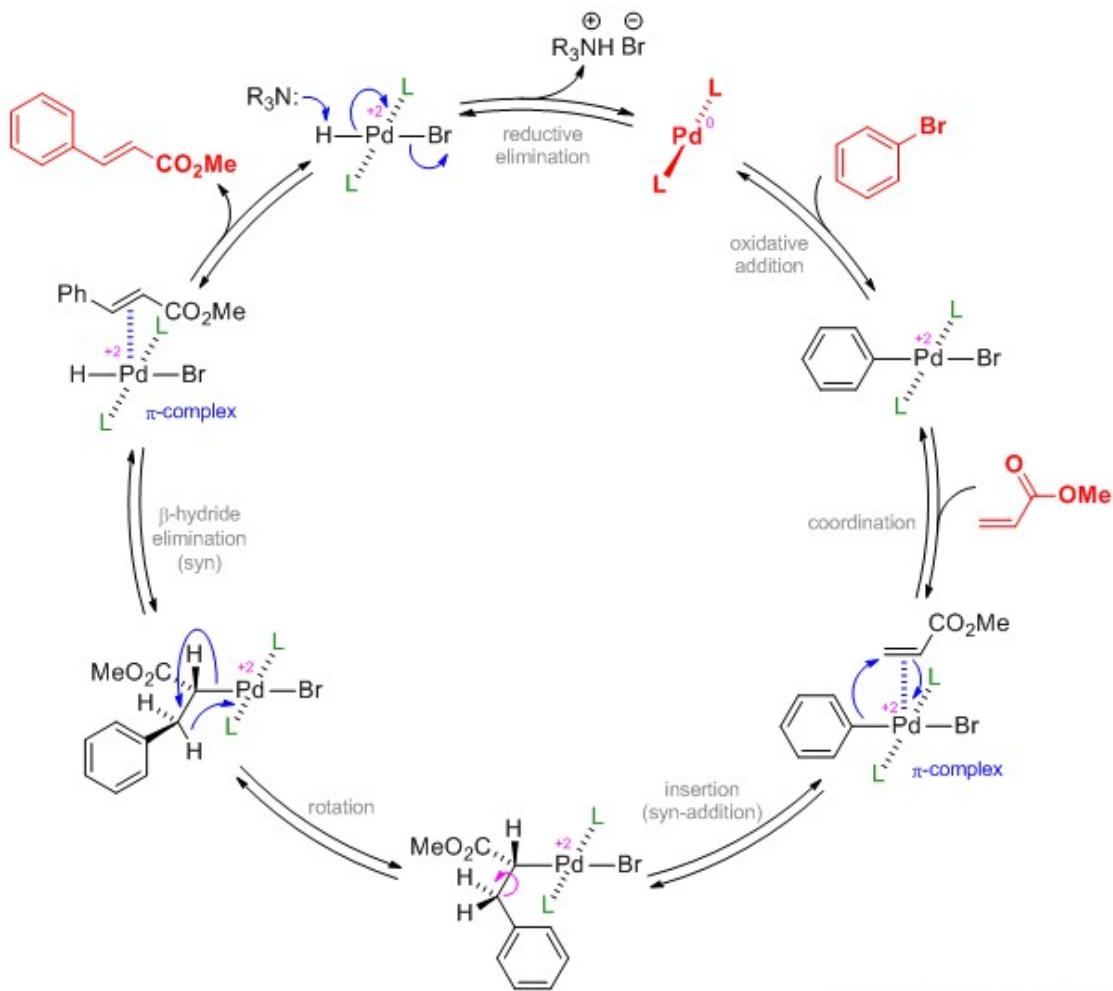


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## 28. Heck Cross Coupling 1968

### Heck Coupling

[1968]

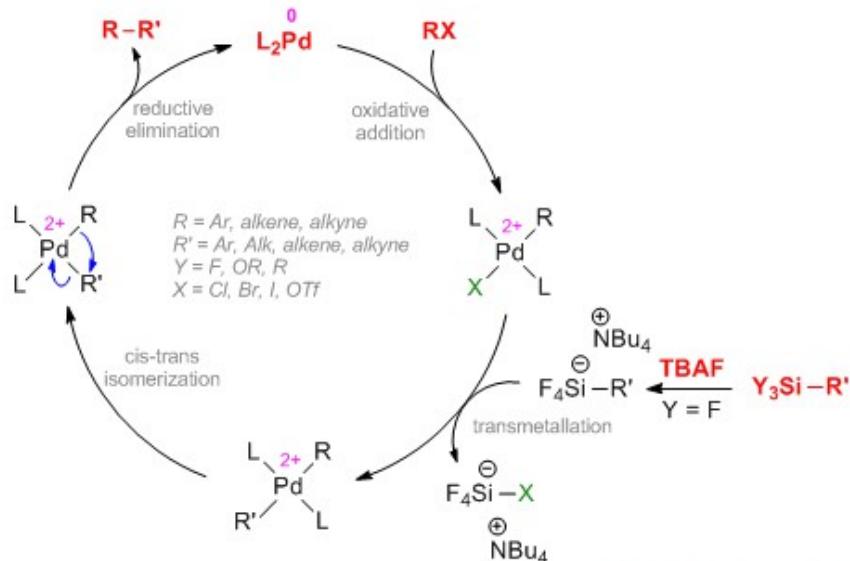


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## 29. Hiyama Cross Coupling 1988

### Hiyama Cross Coupling

[1988]

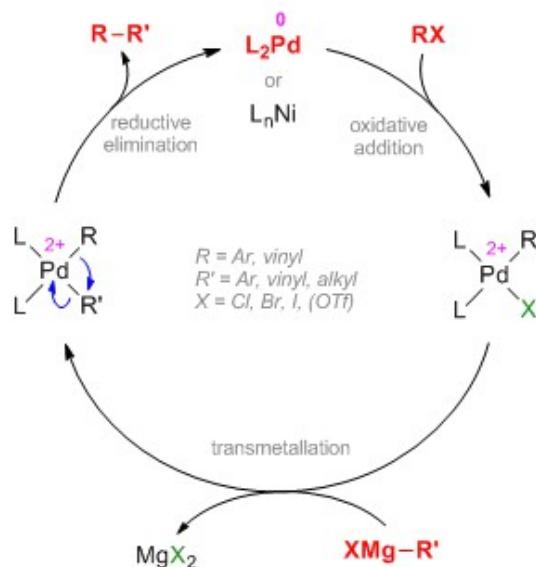


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## 30. Kumada Cross Coupling 1972

### Kumada Cross Coupling

[1972]

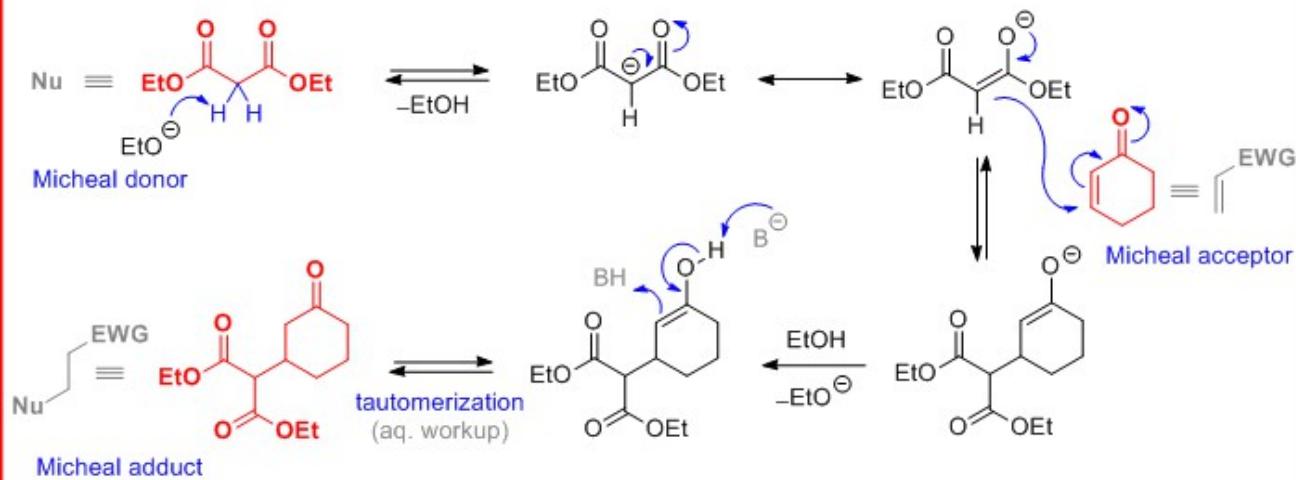


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## 31. Michael Addition 1887

### Michael Addition

[1887]



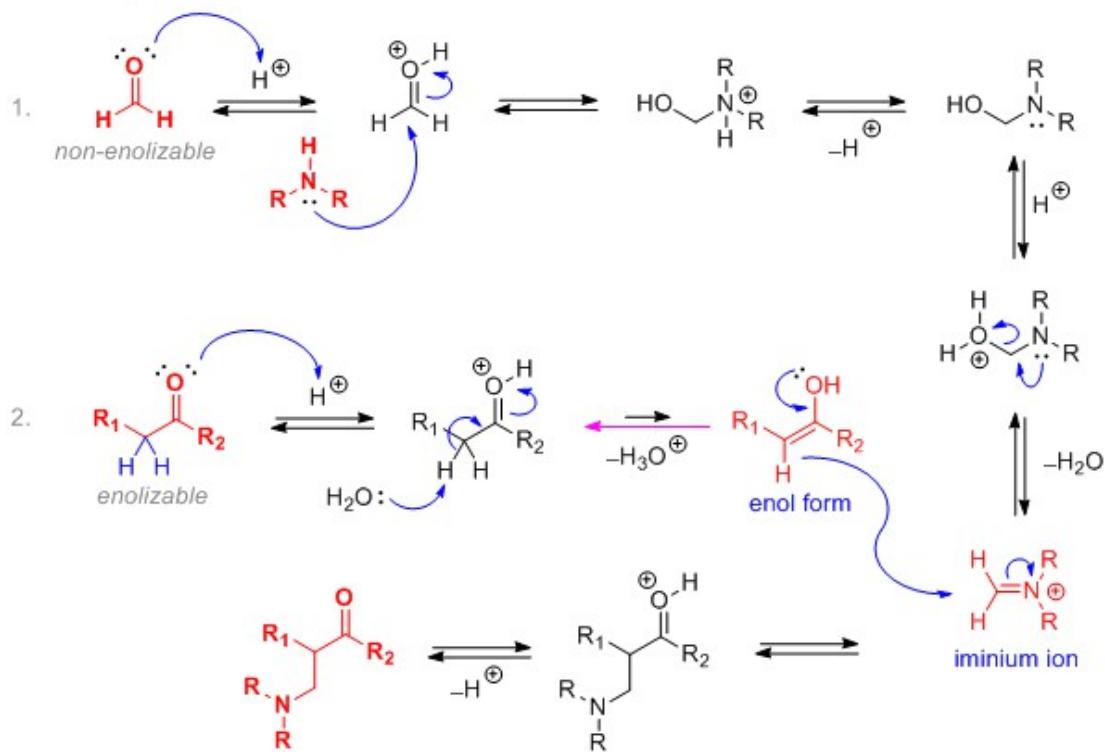
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## 32. Mannich Reaction 1912

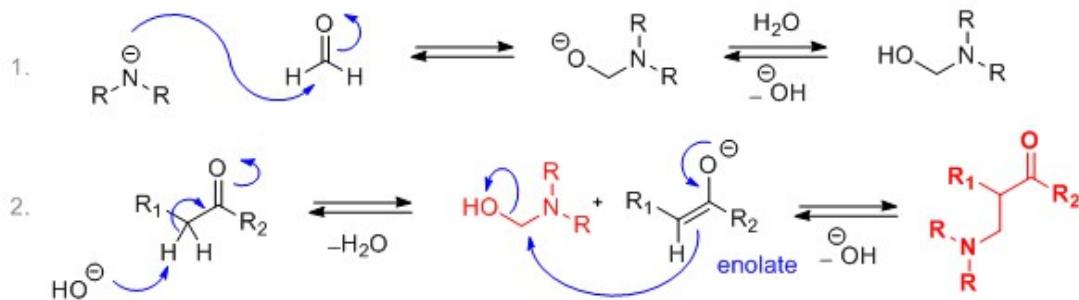
### Mannich Reaction

Acid Catalyzed:

[1912]



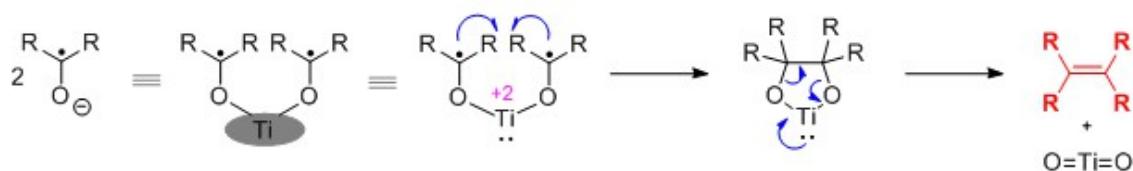
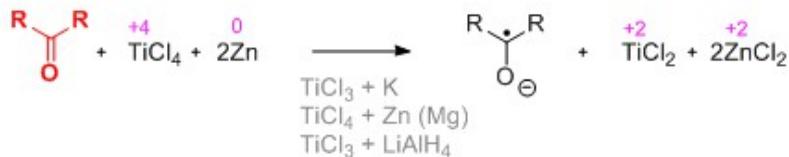
Base Catalyzed:



### 33. McMurry Coupling 1974

#### McMurry Coupling

[1974]

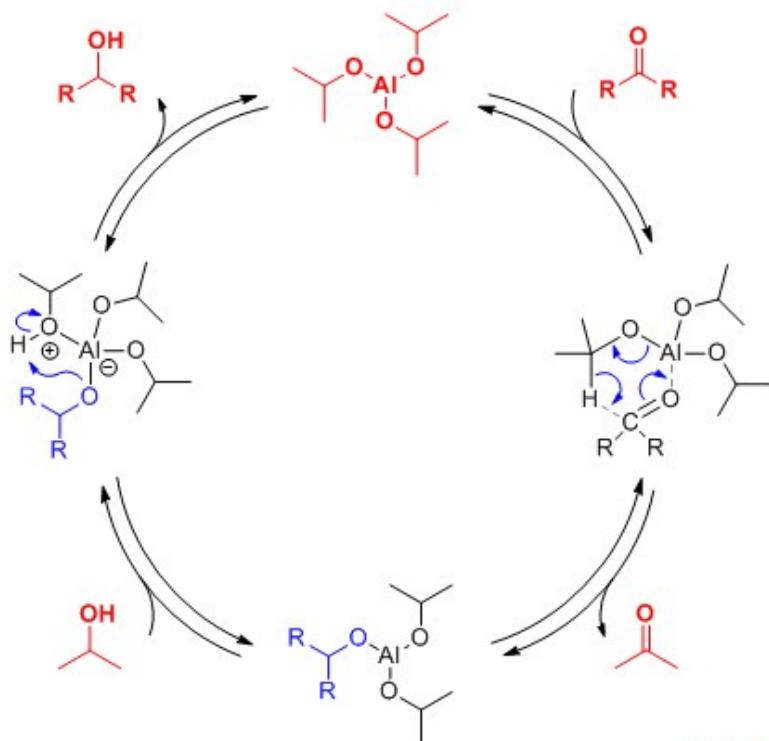


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### 34. Meerwein-Ponndorf-Verley Reduction 1924

#### Meerwein-Ponndorf-Verley Reduction

[1924]

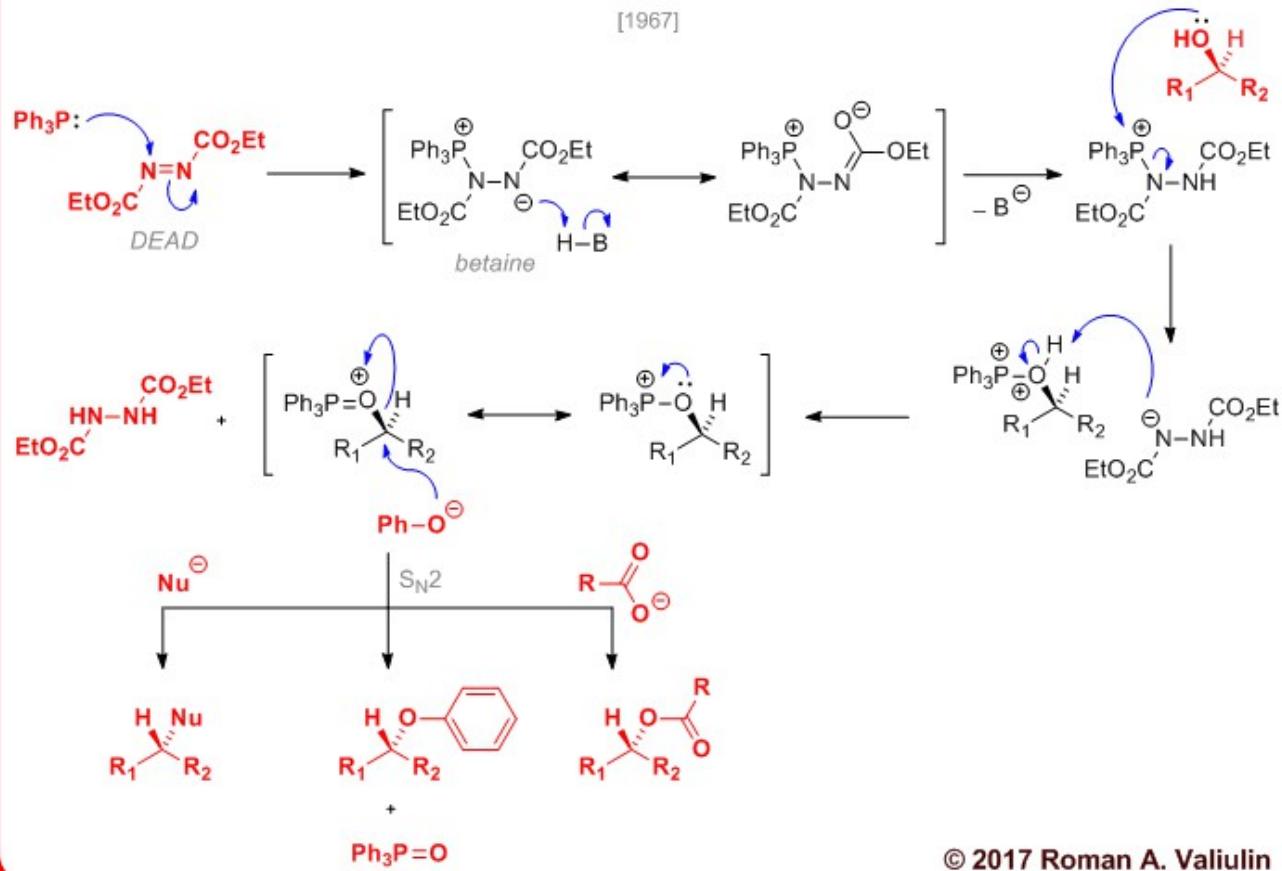


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## 35. Mitsunobu Reaction 1967

### Mitsunobu Reaction

[1967]

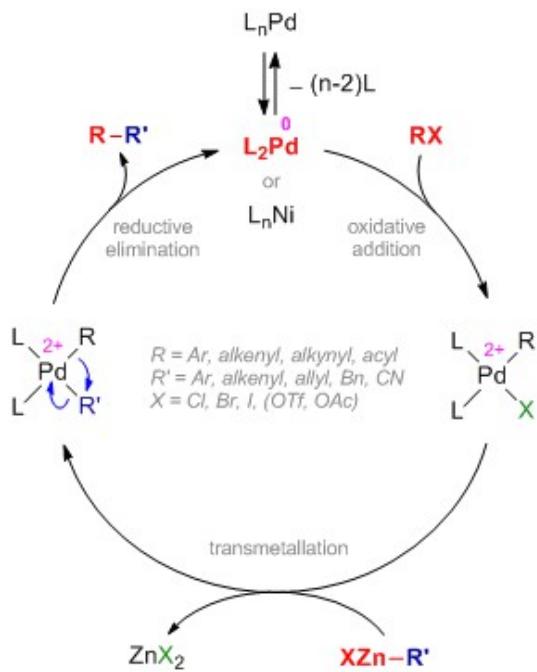


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## 36. Negishi Cross Coupling 1977

### Negishi Cross Coupling

[1977]

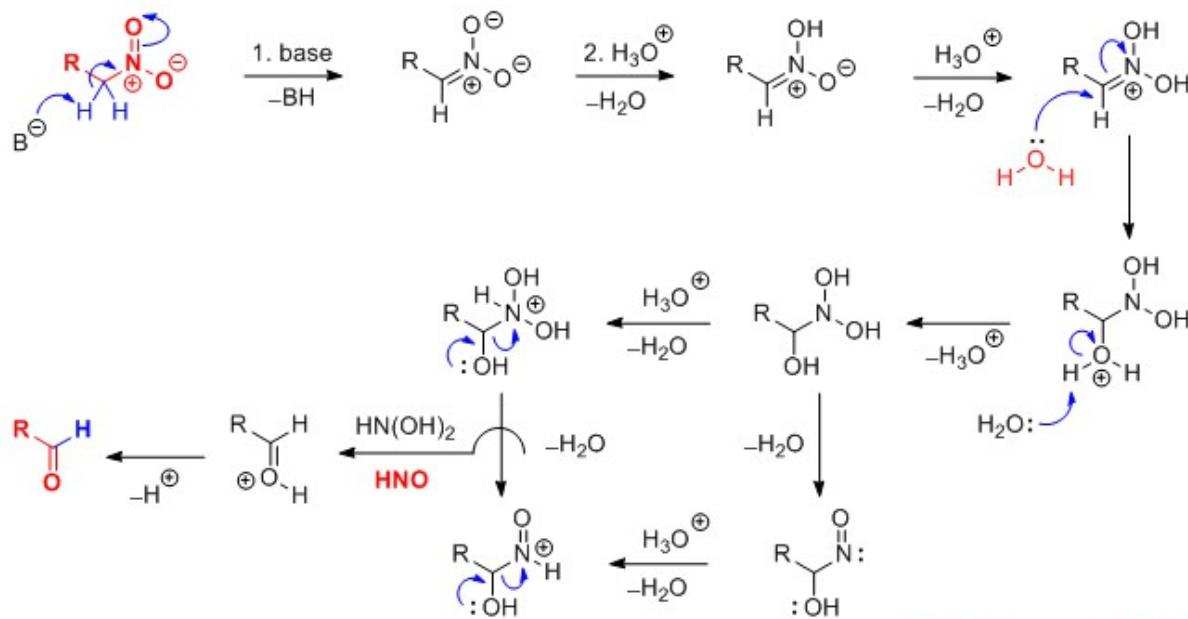


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## 37. Nef Reaction 1894

### Nef Reaction

[1894]

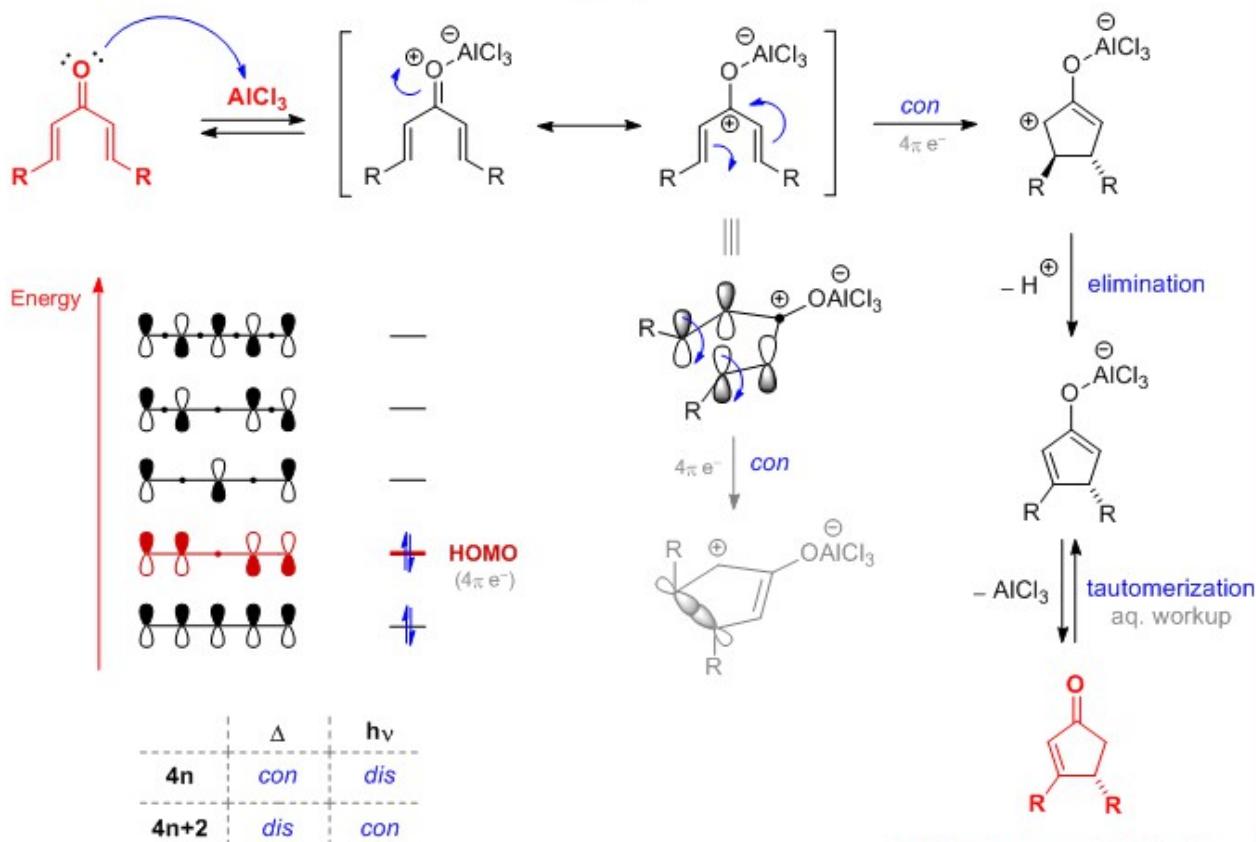


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## 38. Nazarov Cyclization 1941

### Nazarov Cyclization

[1941]

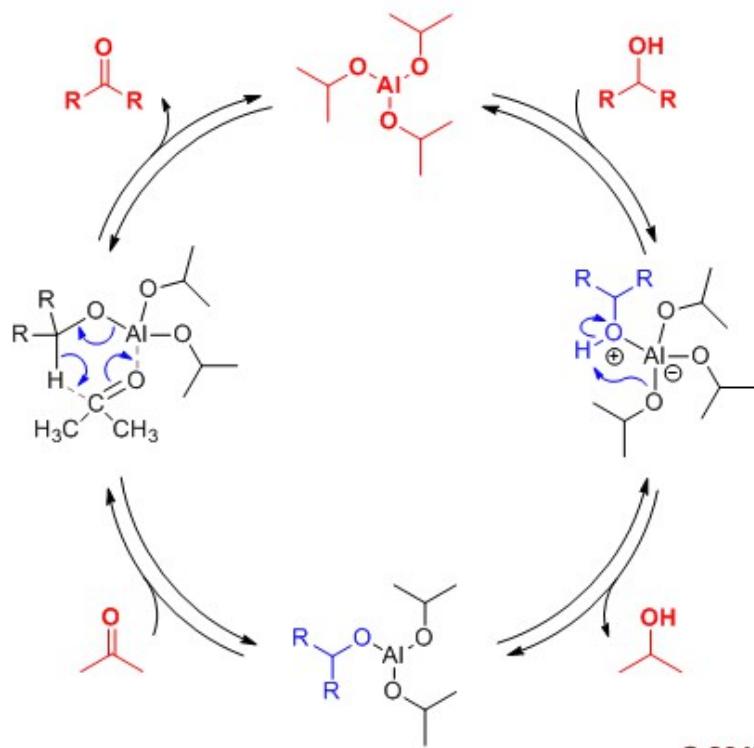


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### 39. Oppenauer Oxidation 1937

#### Oppenauer Oxidation

[1937]

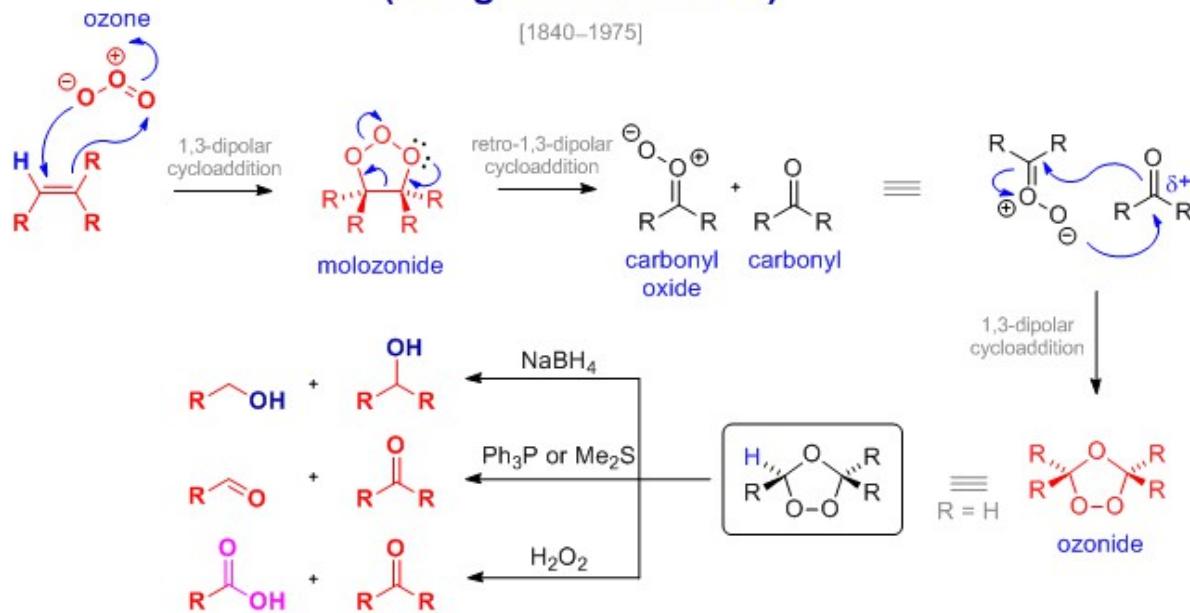


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## 40. Ozonolysis 1840

### Ozonolysis (Criegee Mechanism)

[1840–1975]

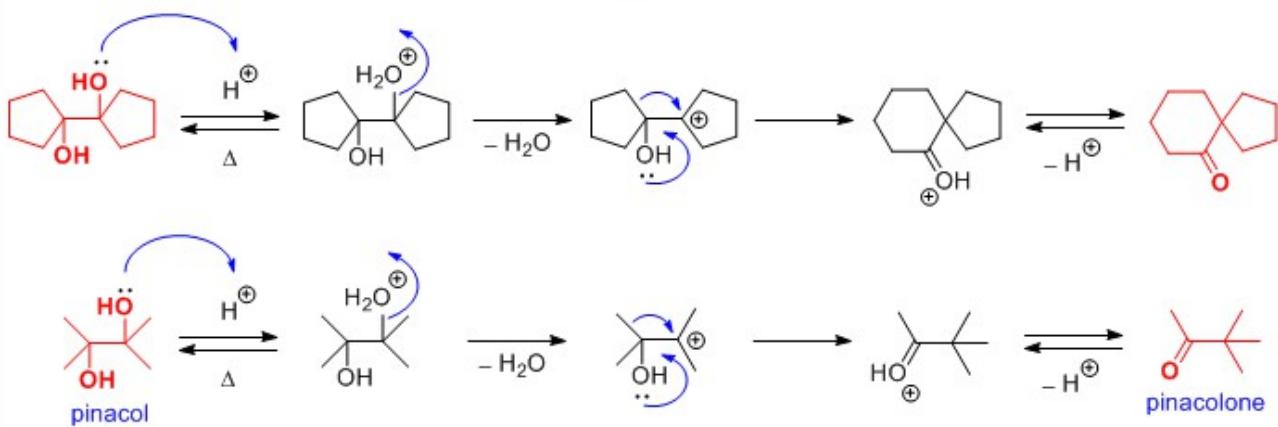


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## 41. Pinacol Rearrangement 1860

### Pinacol-Pinacolone Rearrangement

[1860]

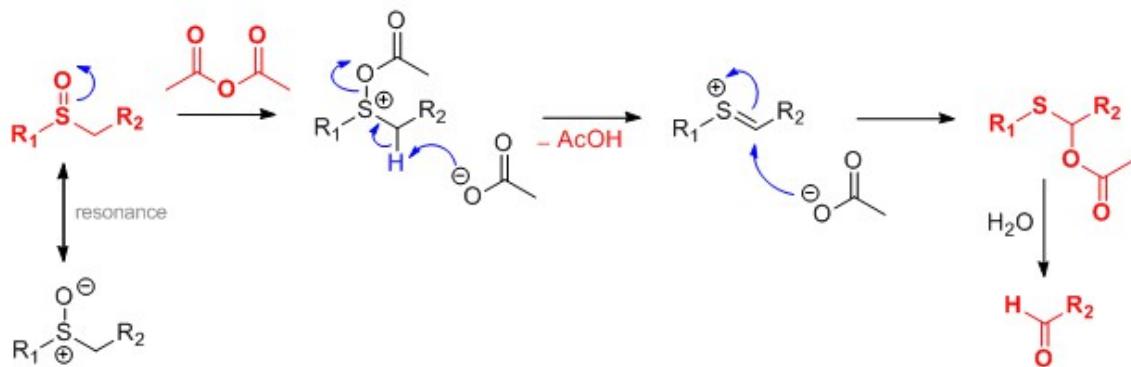


© 2017 Roman A. Valiulin

## 42. Pummerer Rearrangement 1909

### Pummerer Rearrangement

[1909]

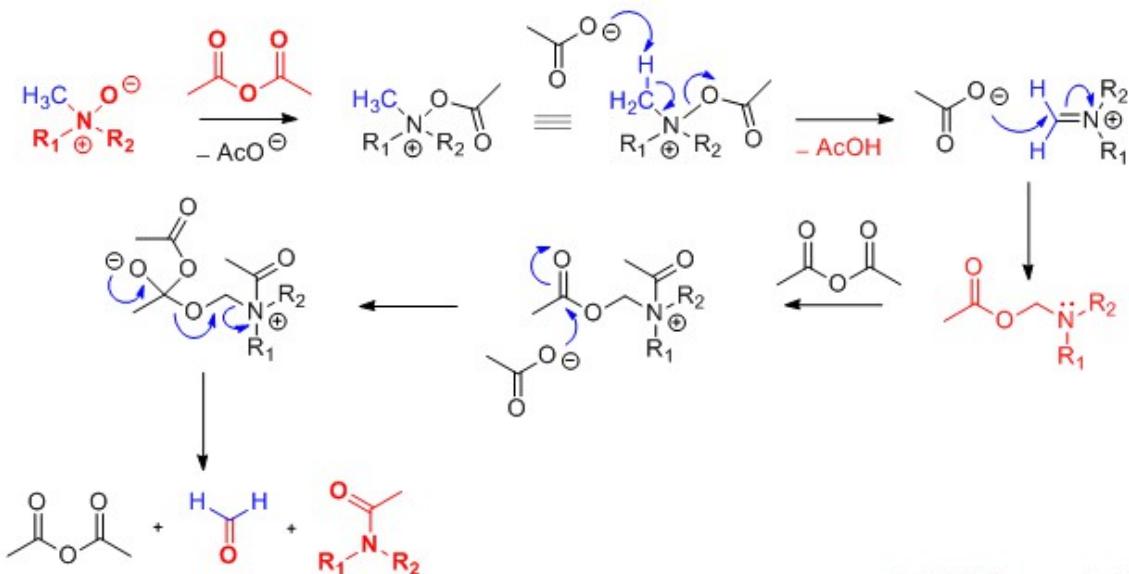


© 2017 Roman A. Valiulin

## 43. Polonovski Reaction 1927

### Polonovski Reaction

[1927]

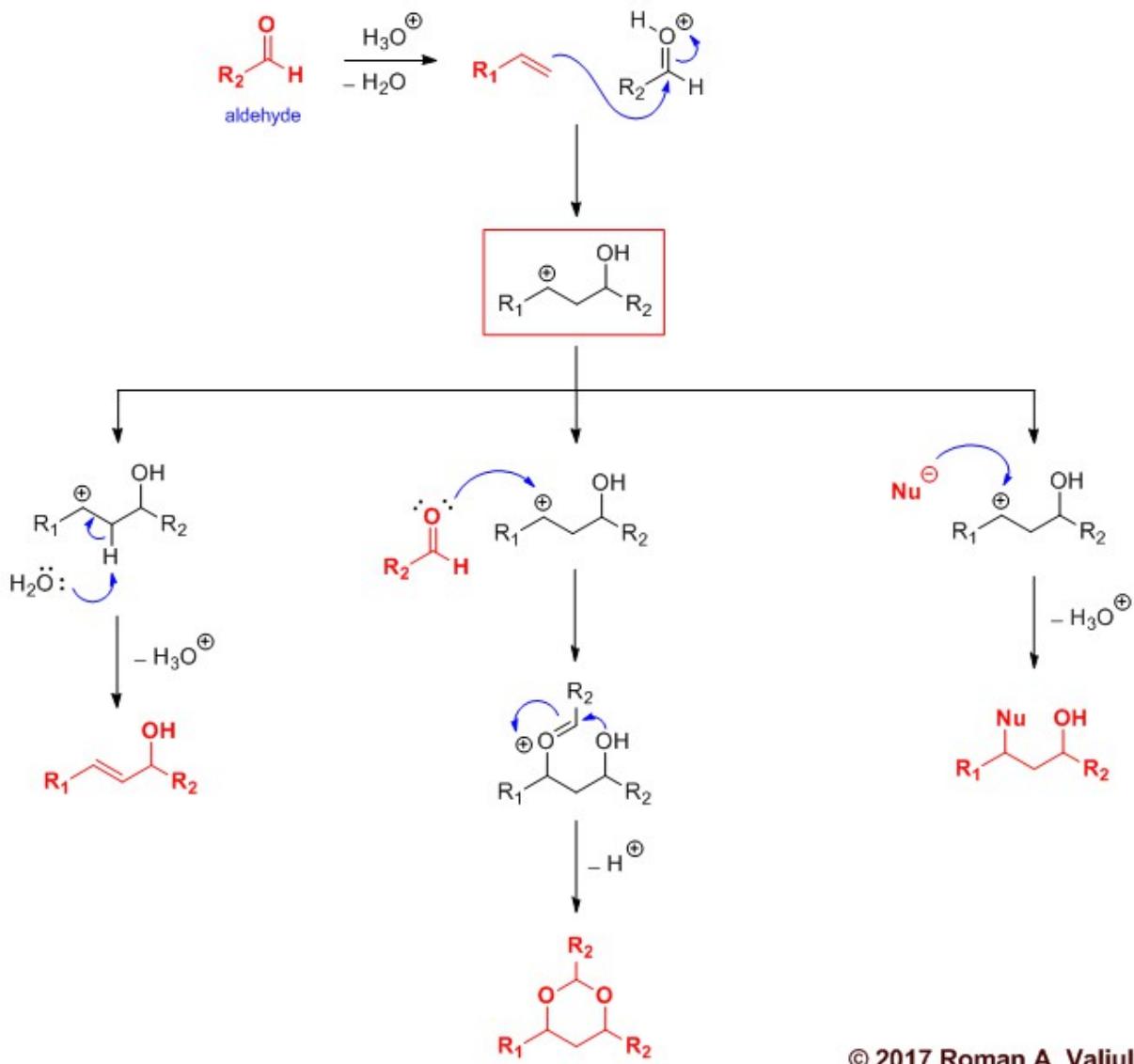


© 2017 Roman A. Valiulin

## 44. Prins Reaction 1919

### Prins Reaction

[1919]



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## 45. Paternò-Büchi Reaction (1909, 1954)

### Paternò-Büchi Reaction

[1909+1954]

Mechanism:

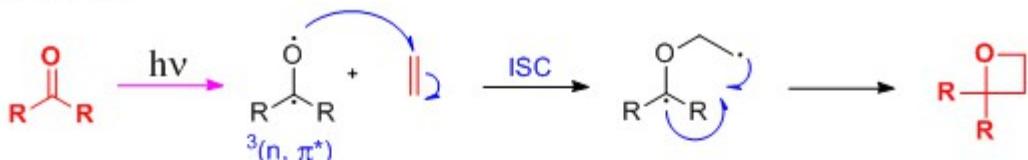
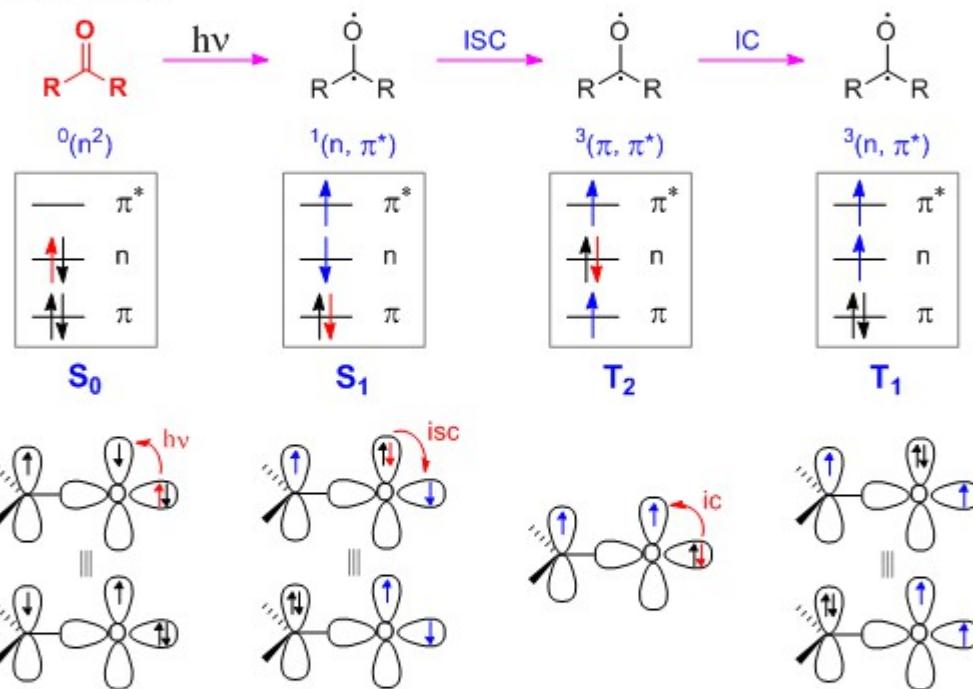
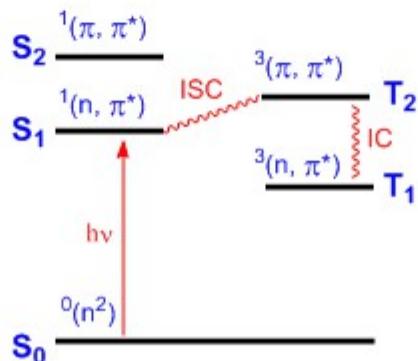


Photo-excitation:



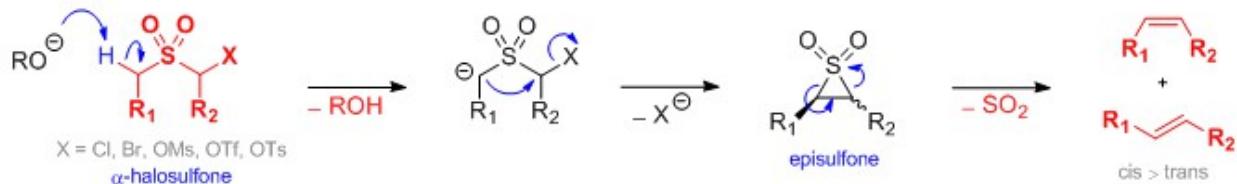
Energy Diagram:



## 46. Ramberg-Bäcklund Rearrangement 1940

### Ramberg-Bäcklund Rearrangement

[1940]

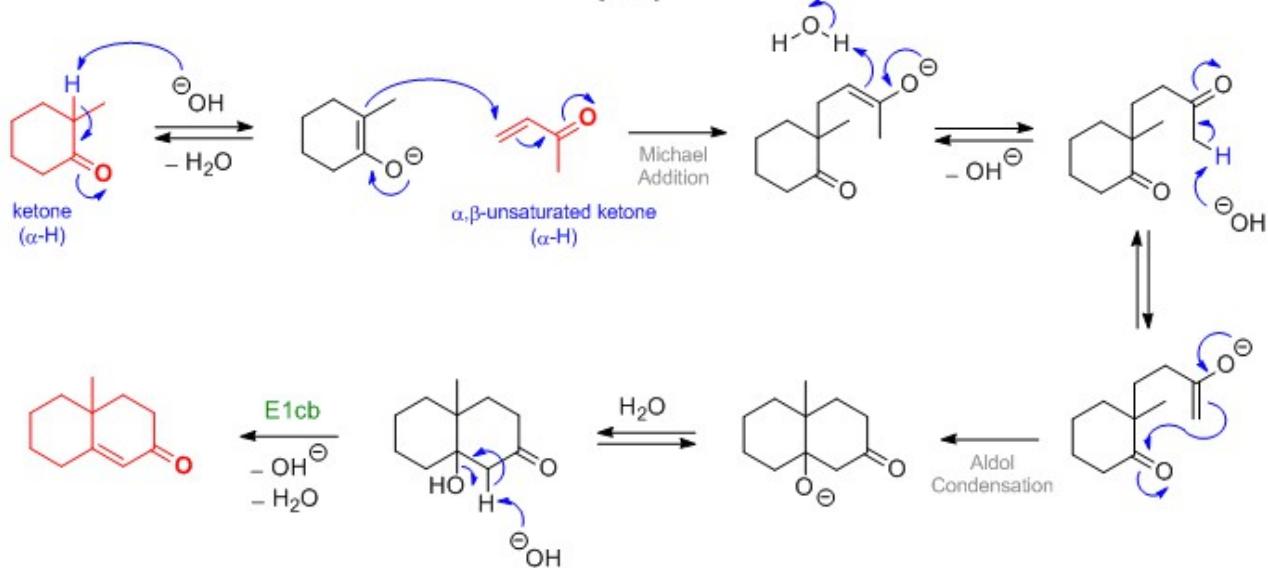


© 2017 Roman A. Valiulin

## 47. Robinson Annulation 1935

### Robinson Annulation

[1935]

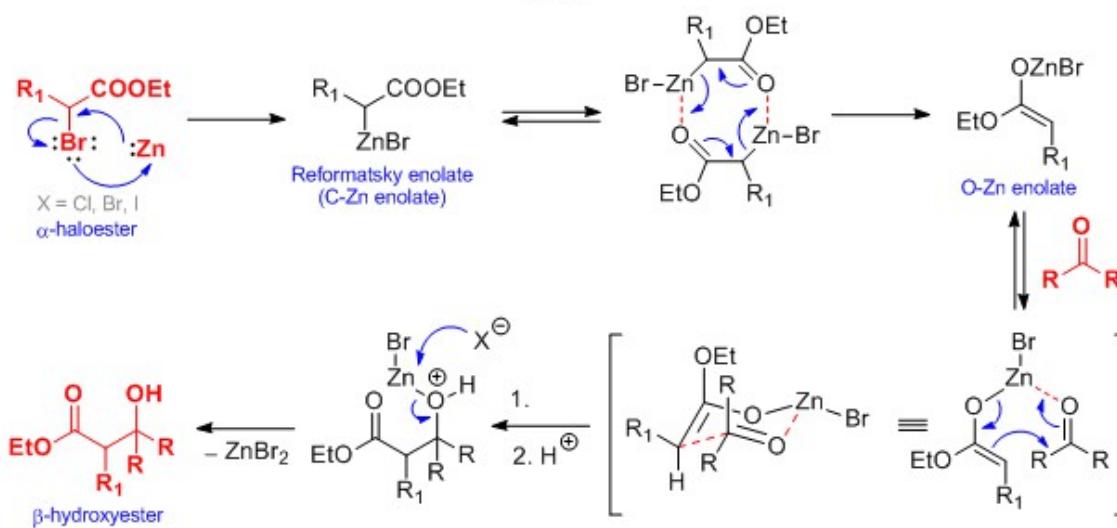


© 2017 Roman A. Valiulin

## 48. Reformatsky Reaction 1887

### Reformatsky Reaction

[1887]

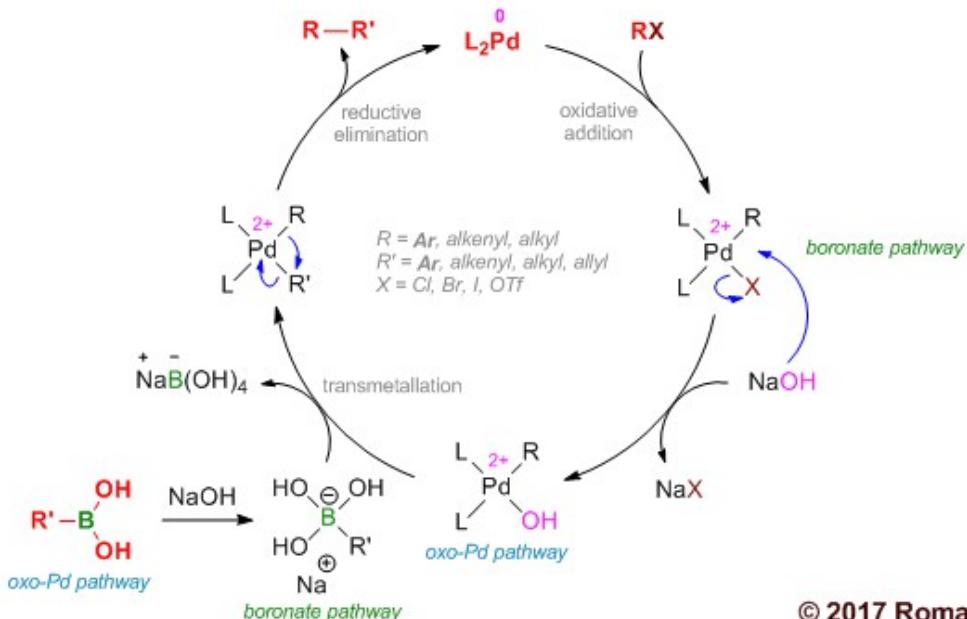


© 2017 Roman A. Valiulin

## 49. Suzuki Cross Coupling 1979

### Suzuki Cross Coupling

[1979]

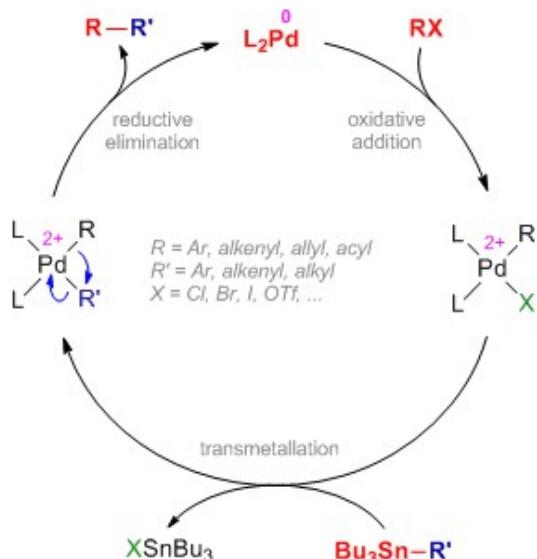


© 2017 Roman A. Valiulin

## 50. Stille Cross Coupling 1978

### Stille Cross Coupling

[1978]

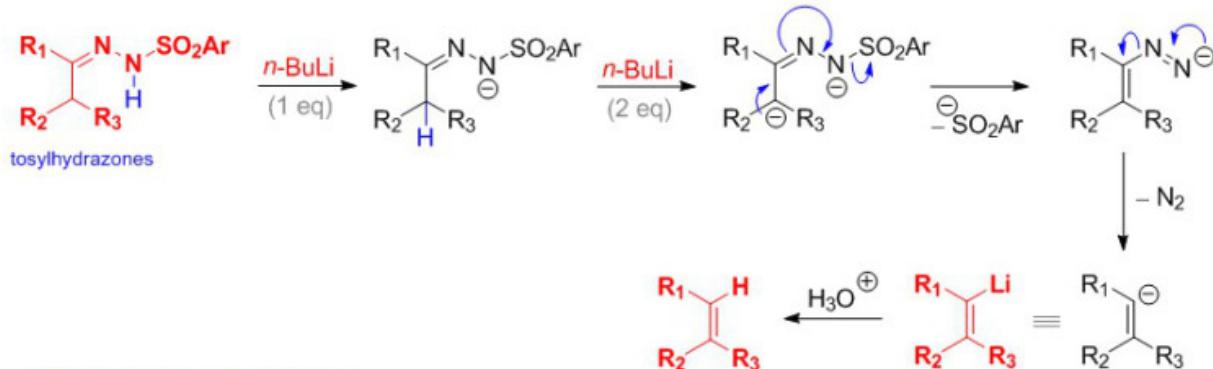


© 2017 Roman A. Valiulin

## 51. Shapiro Reaction 1975

### Shapiro Reaction

[1975]

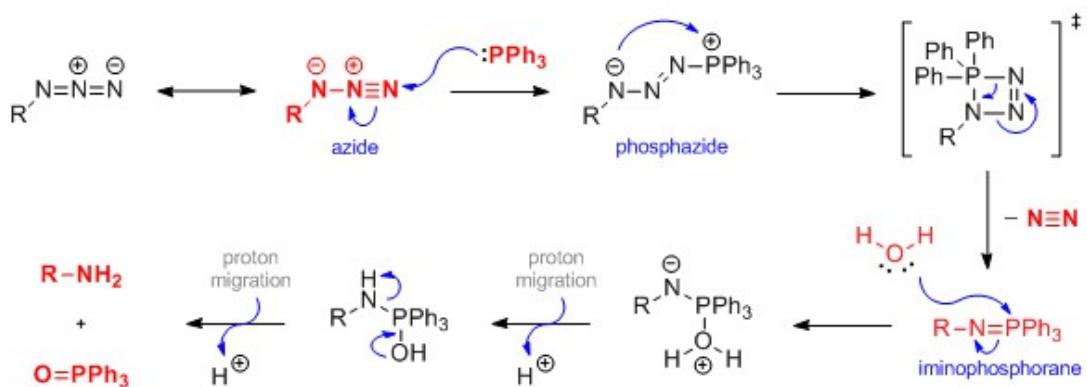


© 2017 Roman A. Valiulin

## 52. Staudinger Ligation 1919

### Staudinger Ligation

[1919]

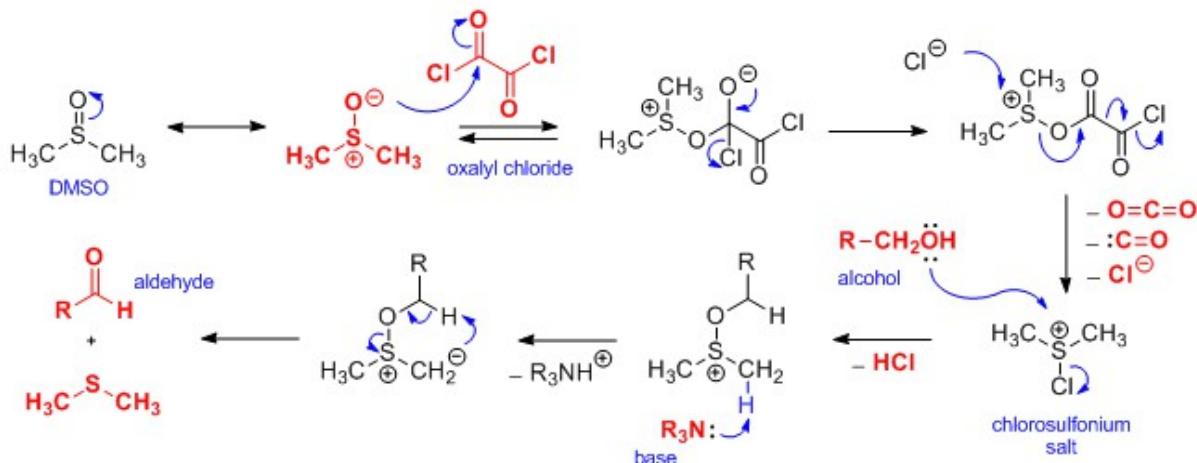


© 2017 Roman A. Valiulin

## 53. Swern Oxidation 1978

### Swern Oxidation

[1978]

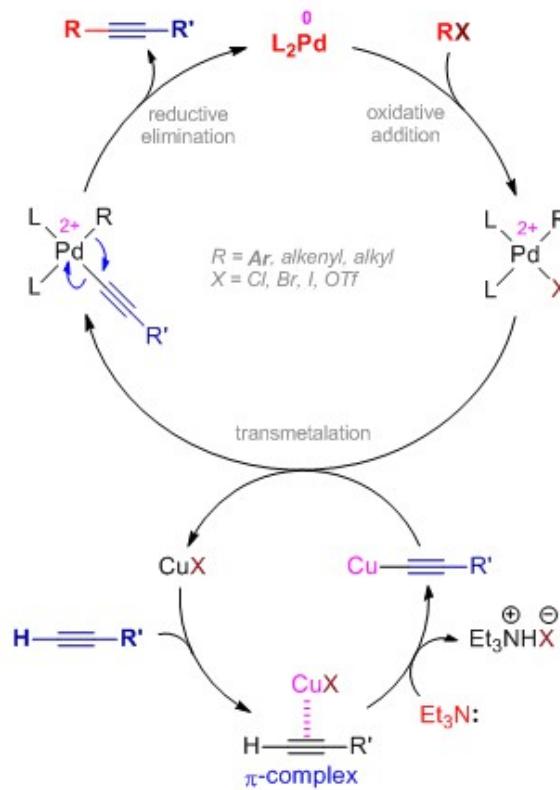


© 2017 Roman A. Valiulin

## 54. Sonogashira Cross Coupling 1975

### Sonogashira Cross Coupling

[1975]

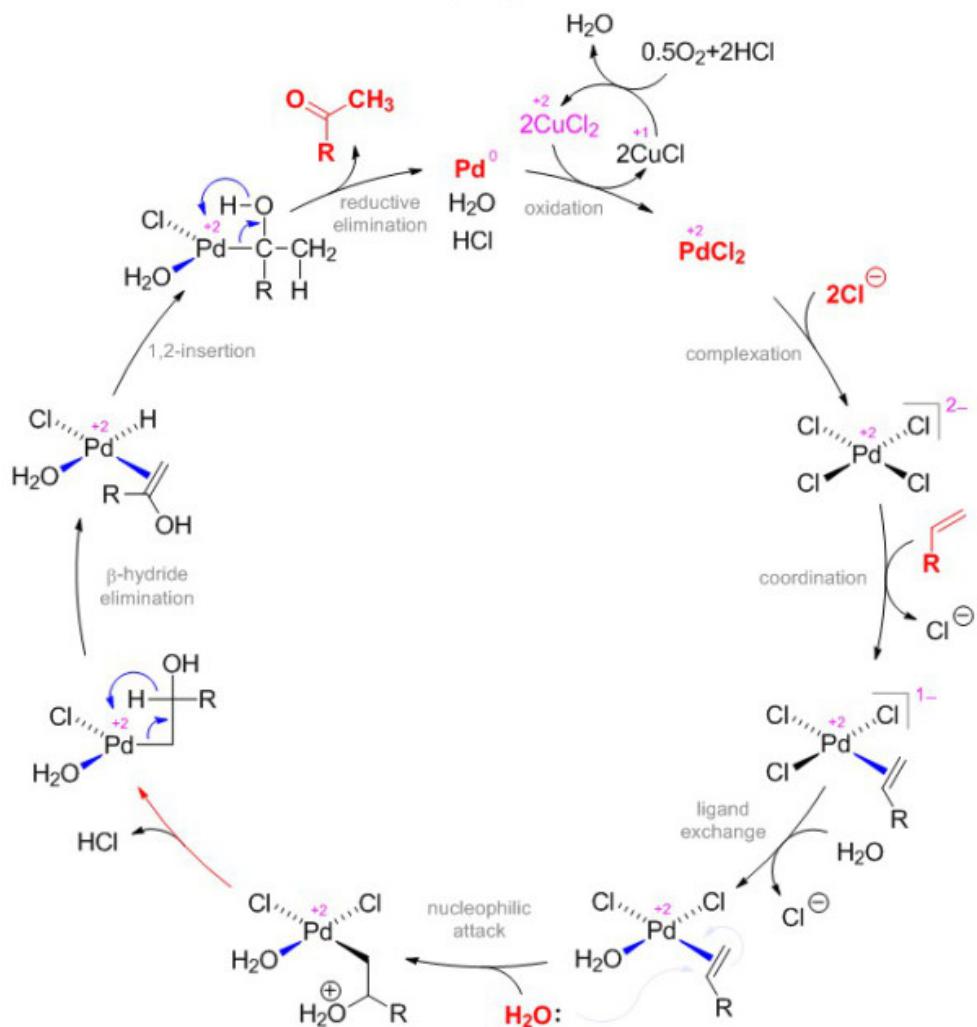


© 2017 Roman A. Valiulin

## 55. Wacker Oxidation 1959

### Wacker Oxidation

[1959]

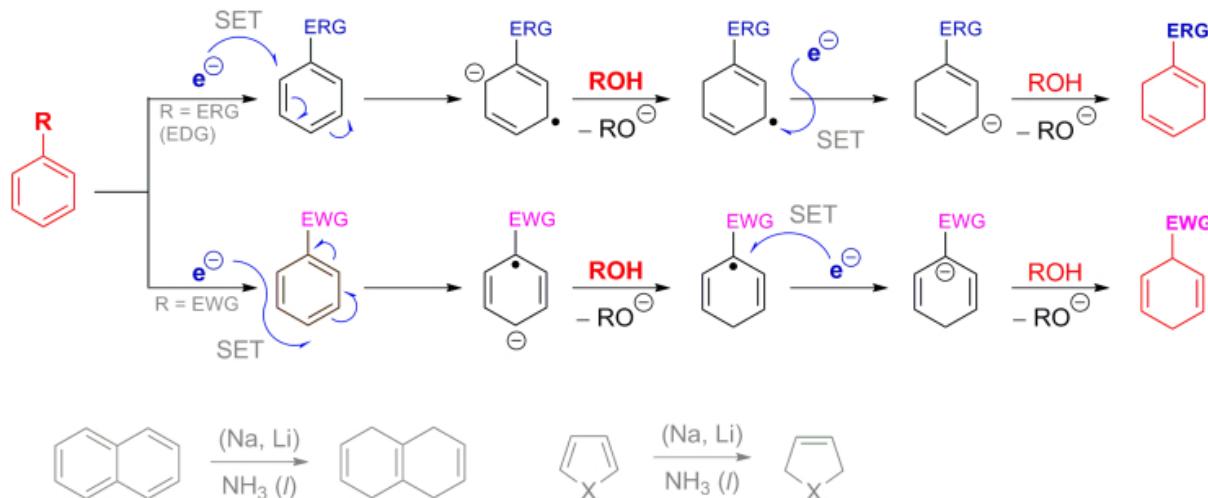


© 2017 Roman A. Valiulin

## 56. Birch Reduction 1944

### Birch Reduction

[1944]

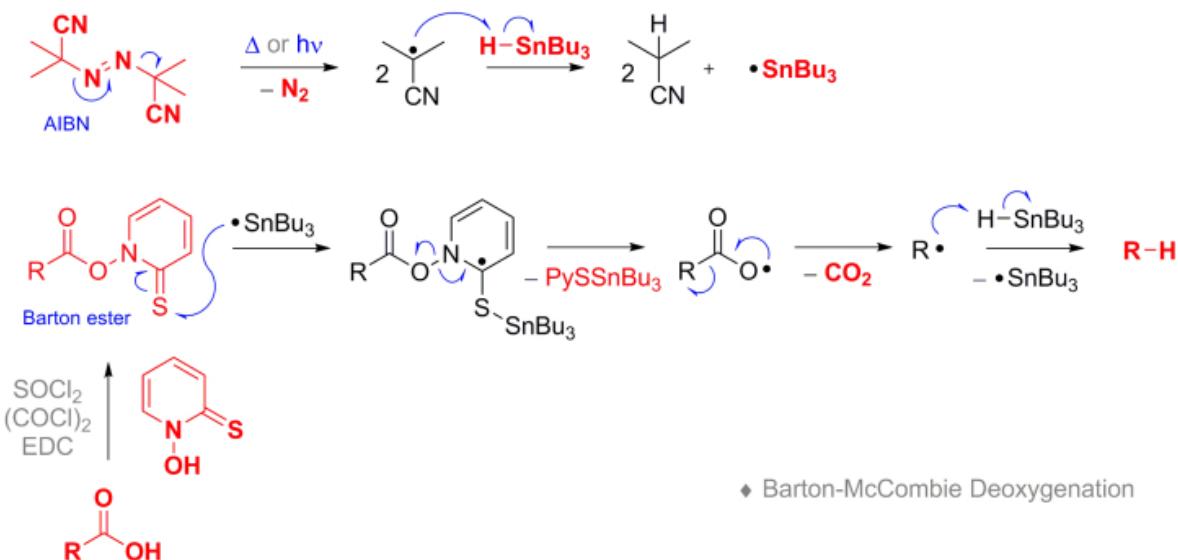


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## 57. Barton Decarboxylation 1983

### Barton Decarboxylation

[1983]



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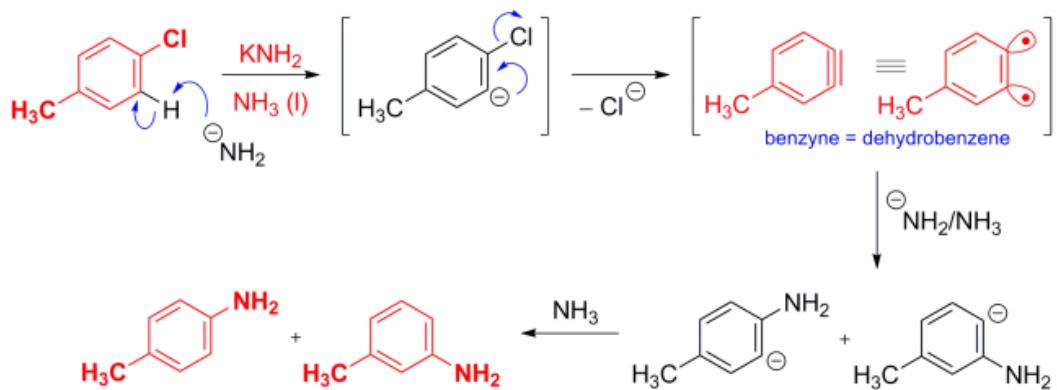
## 58. Benzyne Mechanism 1953

### Benzyne Mechanism

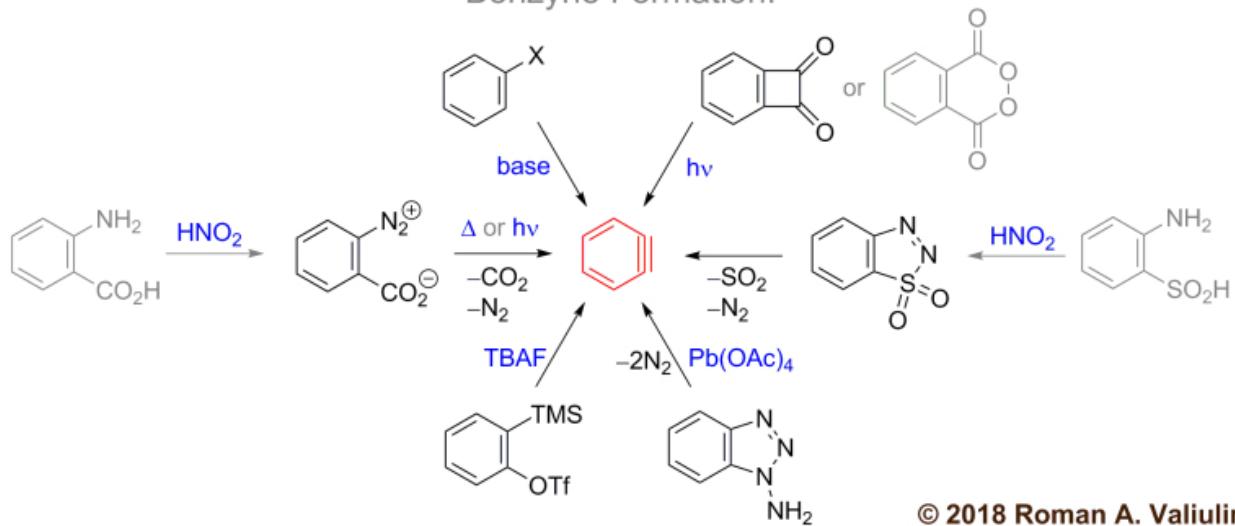
[1953]



Nucleophilic Aromatic Substitution:  
Elimination-Addition



#### Benzyne Formation:

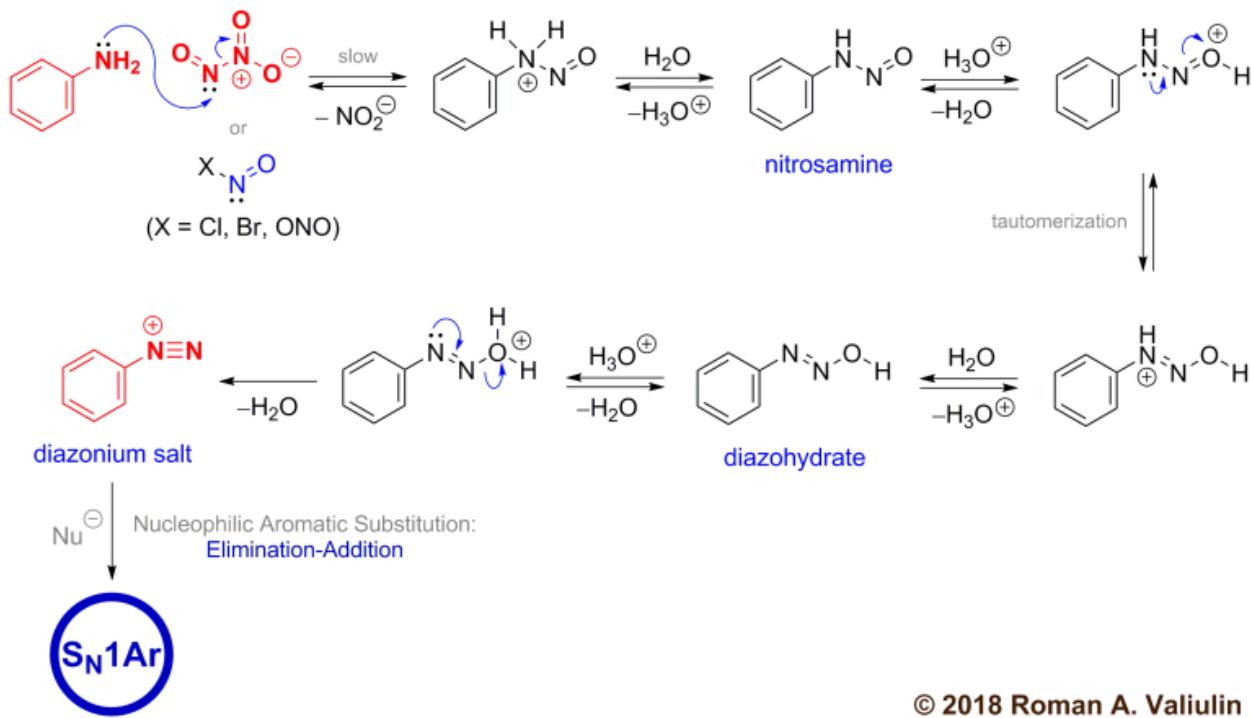
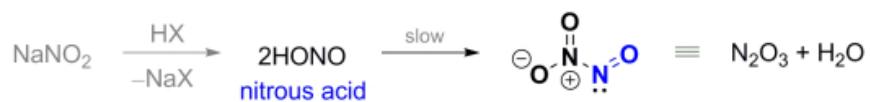


© 2018 Roman A. Valiulin

## 59. Diazotisation 1900

### Diazotisation

[1900]



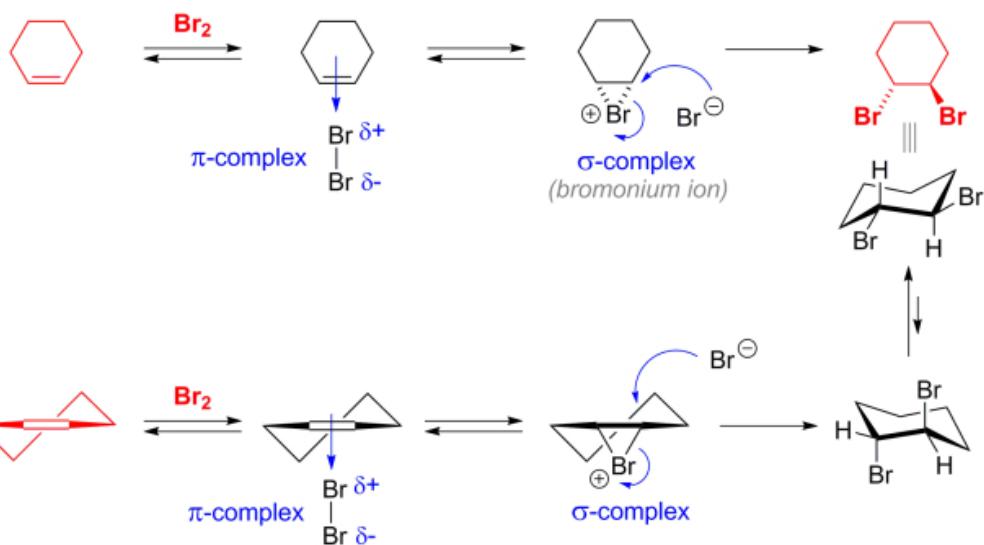
© 2018 Roman A. Valiulin

## 60. Electrophilic Addition

### Electrophilic Addition

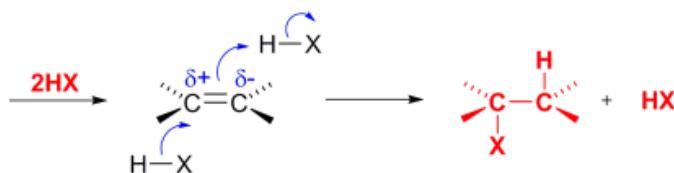
**Ad<sub>E</sub>2**

$$\text{rate} = k[\mathbf{E}^+][\text{C=C}]$$



**Ad<sub>E</sub>3**

$$\text{rate} = k[\mathbf{HCl}]^2[\text{C=C}]$$



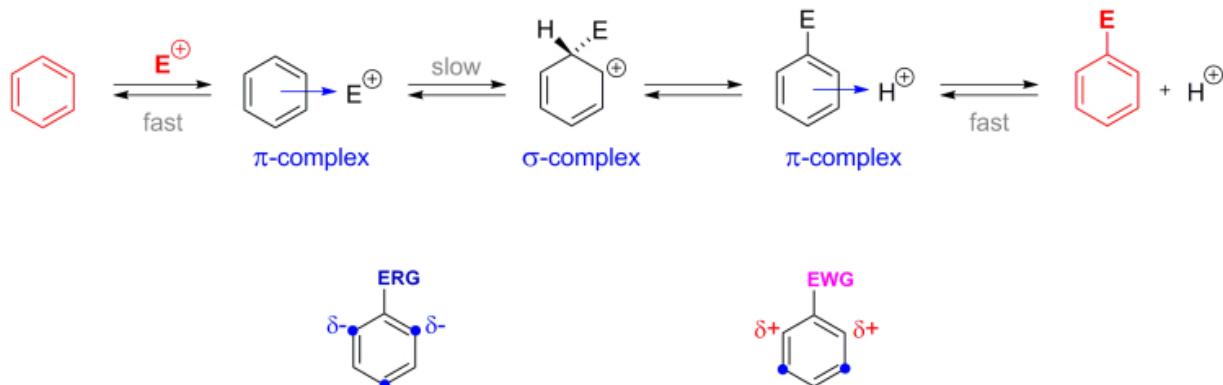
© 2018 Roman A. Valiulin

# 61. Electrophilic Aromatic Substitution

## Electrophilic Aromatic Substitution

$$\text{rate} = k[\text{E}^+][\text{ArH}] \quad \text{E}^+ = \text{Cl}^+, \text{Br}^+, \text{I}^+, \text{NO}_2^+, \text{R}^+, \text{RC(O)}^+, \text{SO}_3\text{H}^+$$

S<sub>E</sub>2Ar



Electron Releasing (Donating) Group

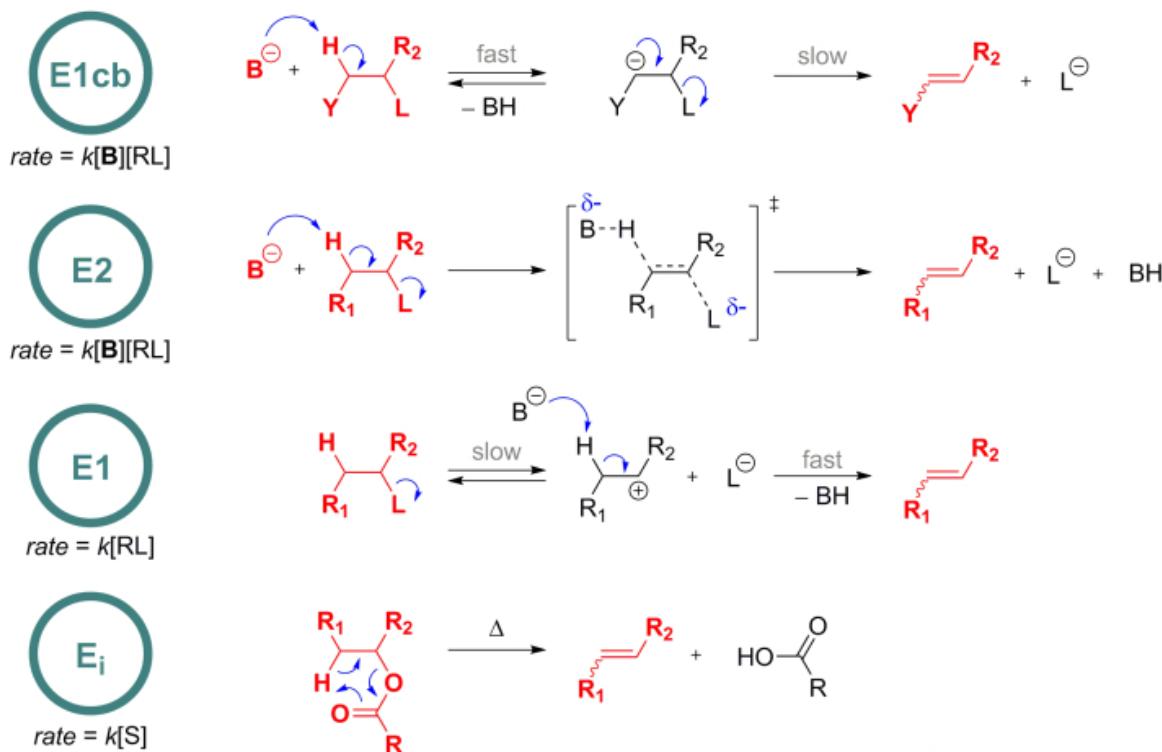
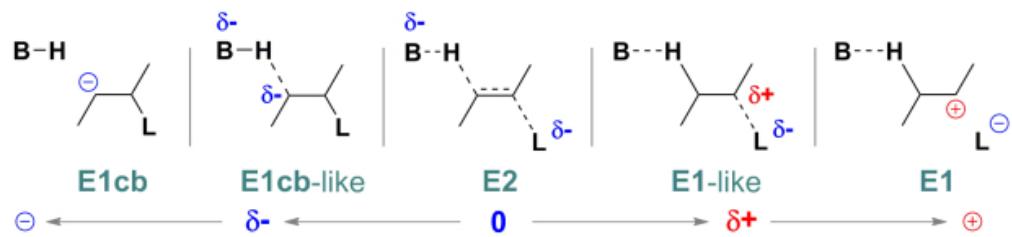


Electron Withdrawing Group

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## 62. Beta-Elimination

### $\beta$ -Elimination

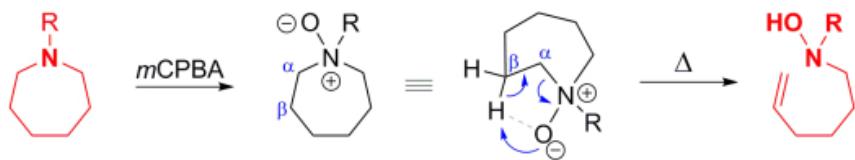
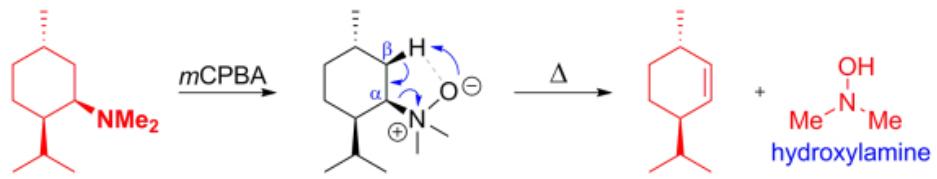


© 2018 Roman A. Valiulin

## 63. Cope Elimination 1949

### Cope Elimination

[1949]

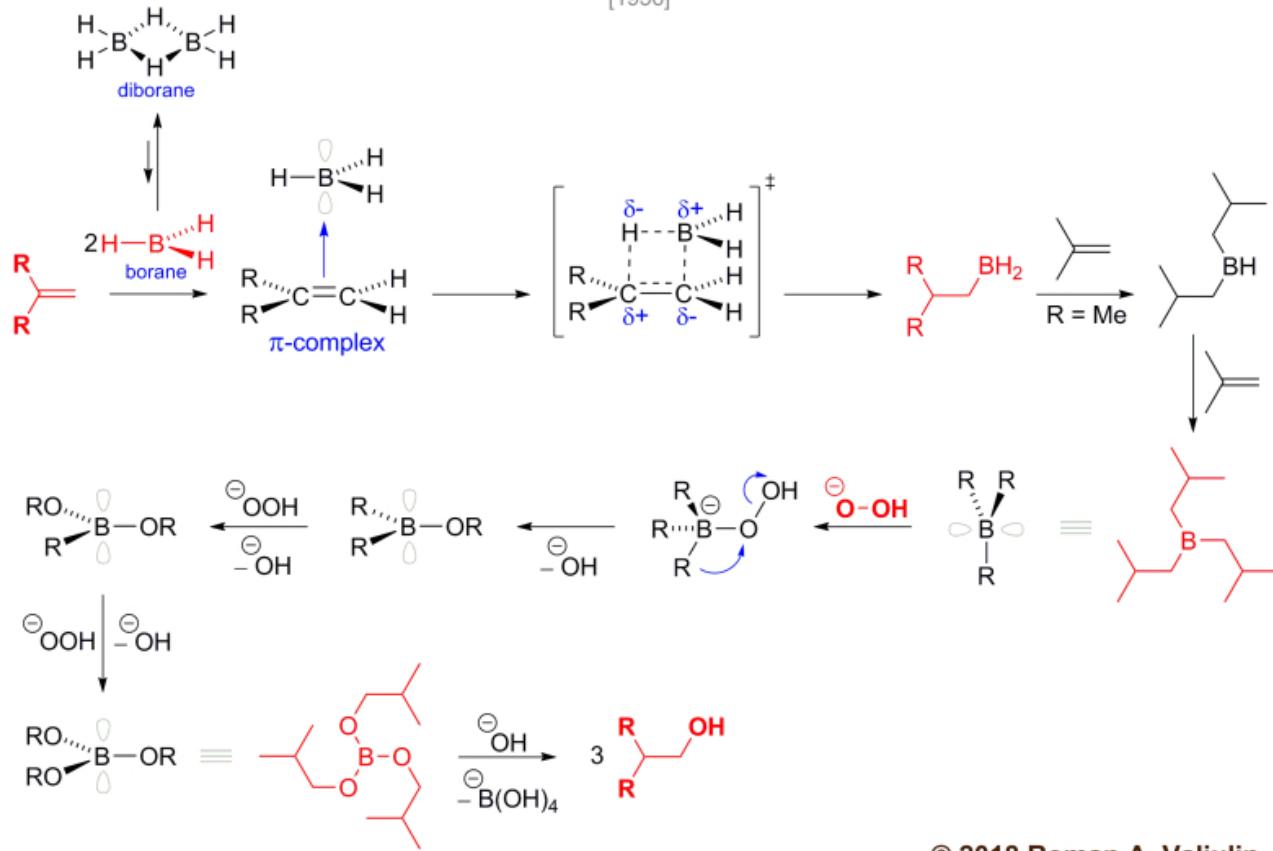


© 2018 Roman A. Valiulin

## 64. Brown Hydroboration 1956

### Brown Hydroboration

[1956]

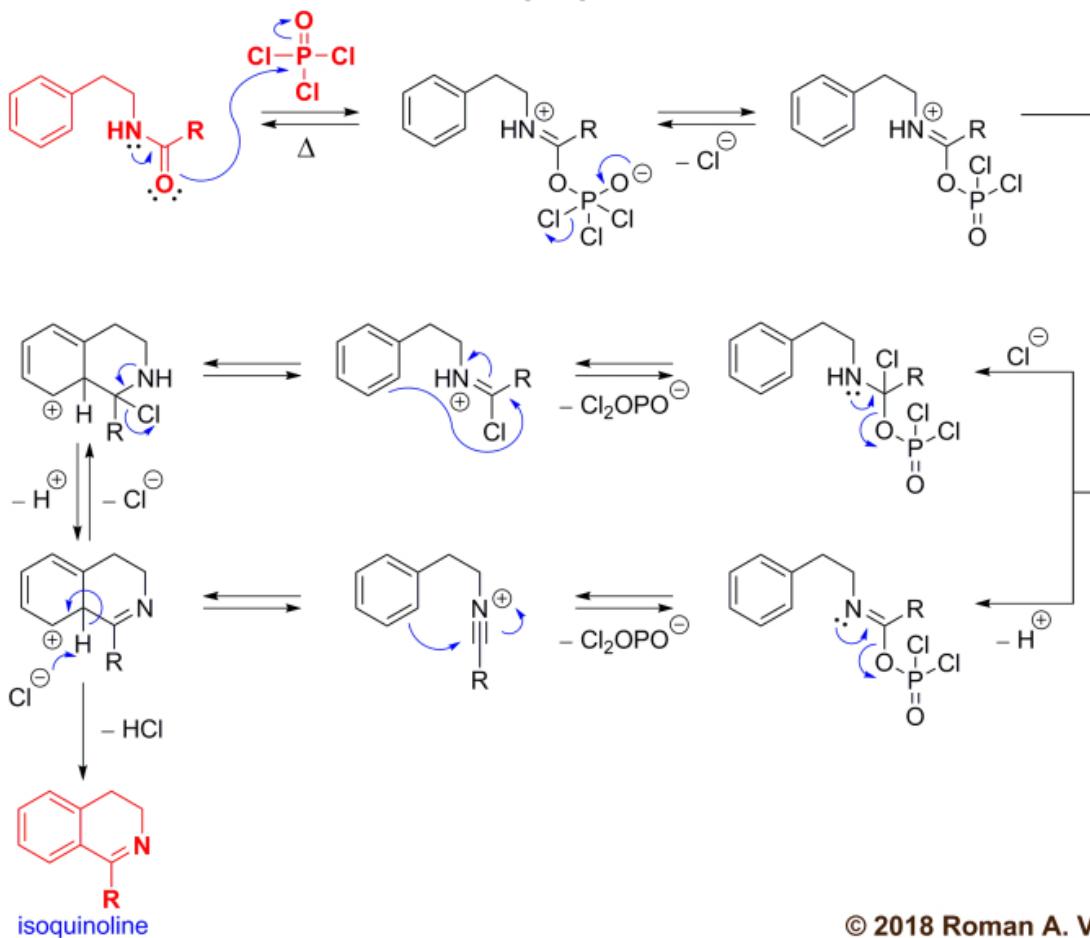


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## 65. Bischler-Napieralski Reaction 1903

### Bischler-Napieralski Cyclization

[1903]

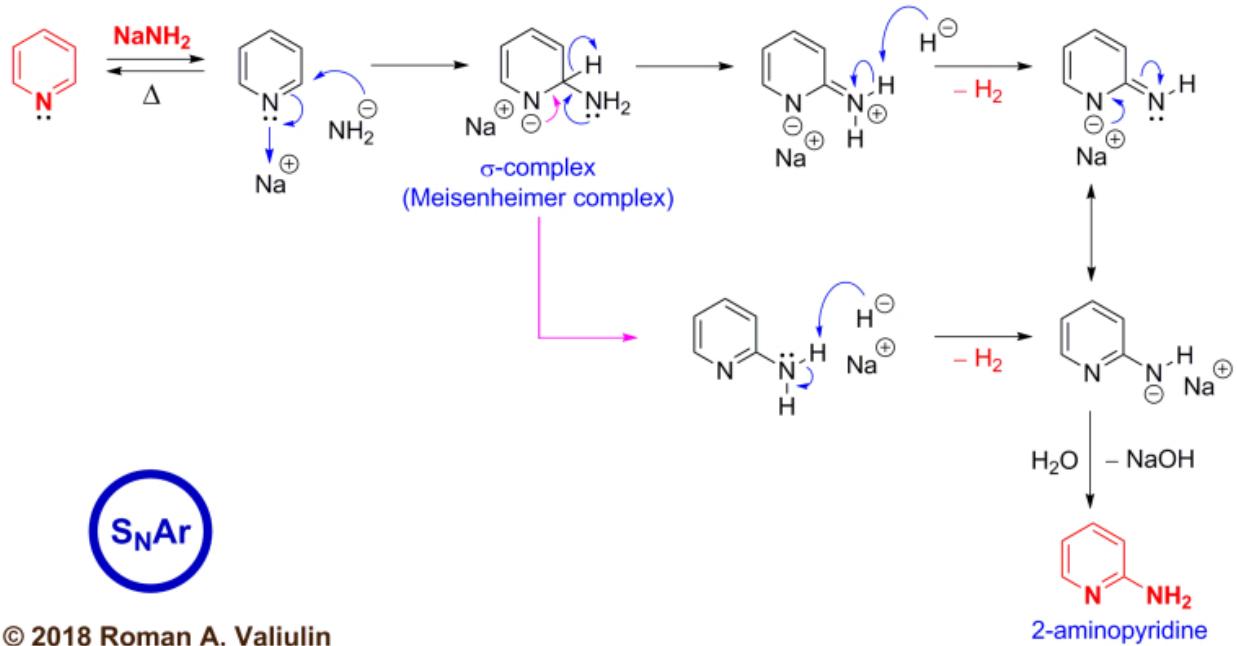


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## 66. Chichibabin Amination 1914

### Chichibabin Amination

[1914]

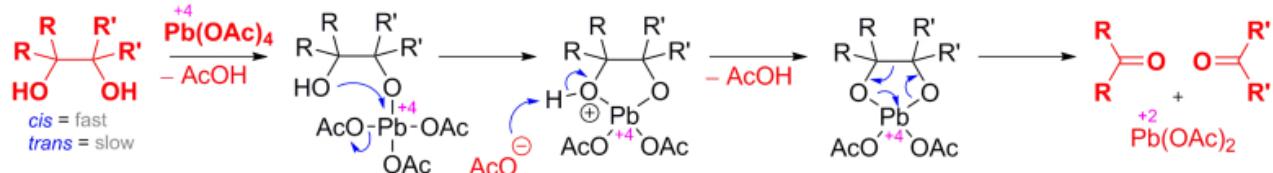


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## 67. Criegee Oxidation 1931 – Malaprade Oxidation 1934

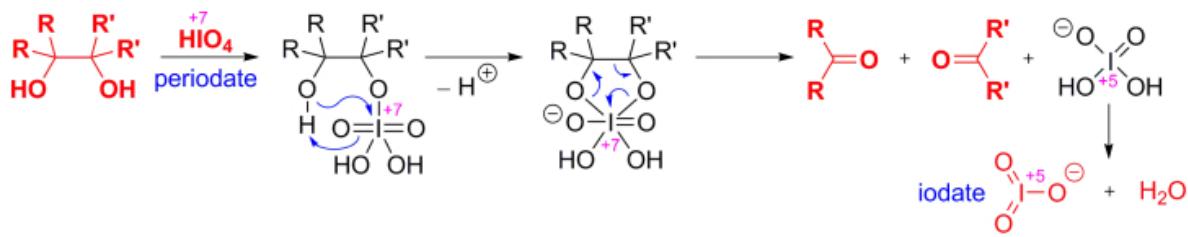
### Criegee Oxidation

[1931]



### Malaprade Oxidation

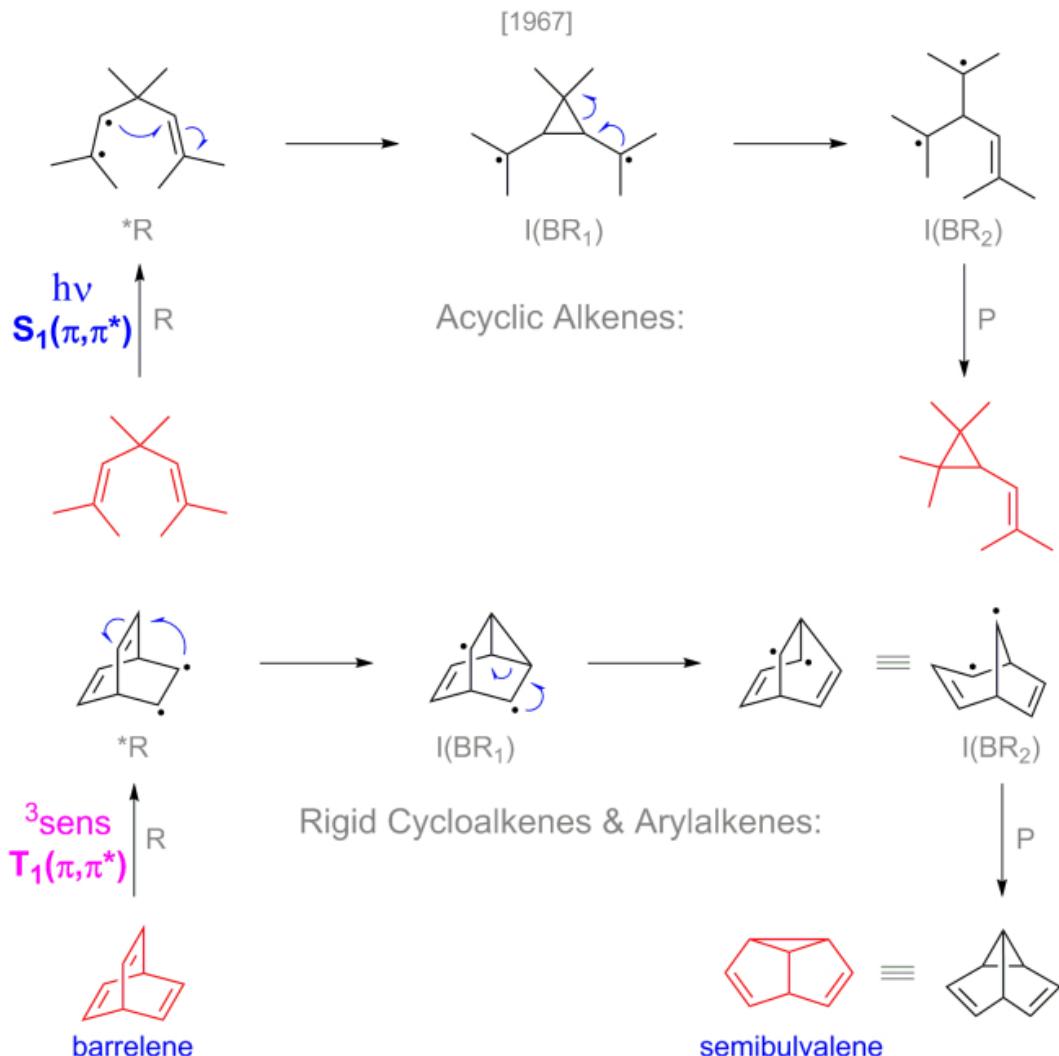
[1934]



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## 68. Di-pi-Methane (DPM) Rearrangement (Zimmerman Reaction) 1967

### Di- $\pi$ -Methane (DPM) Rearrangement (Zimmerman Reaction)

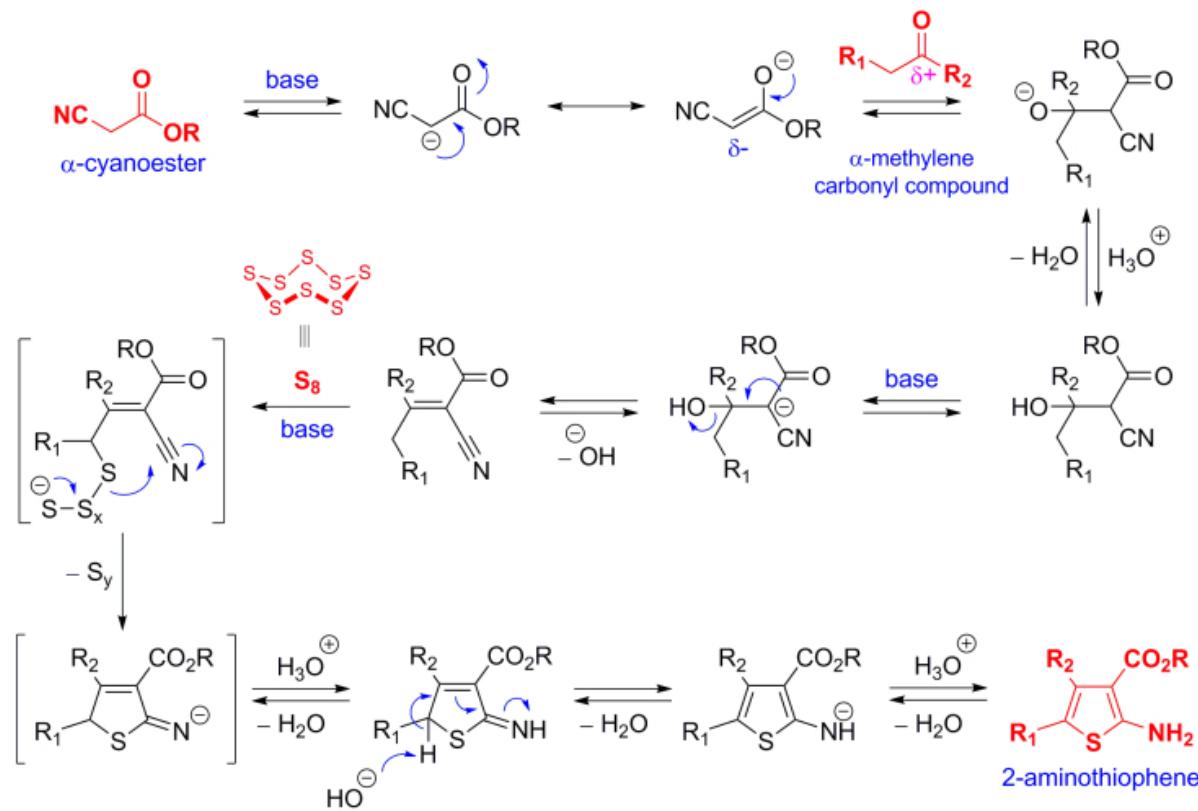


## 69. Gewald Reaction 1966

### Gewald Reaction

[1966]

Knoevenagel Condensation

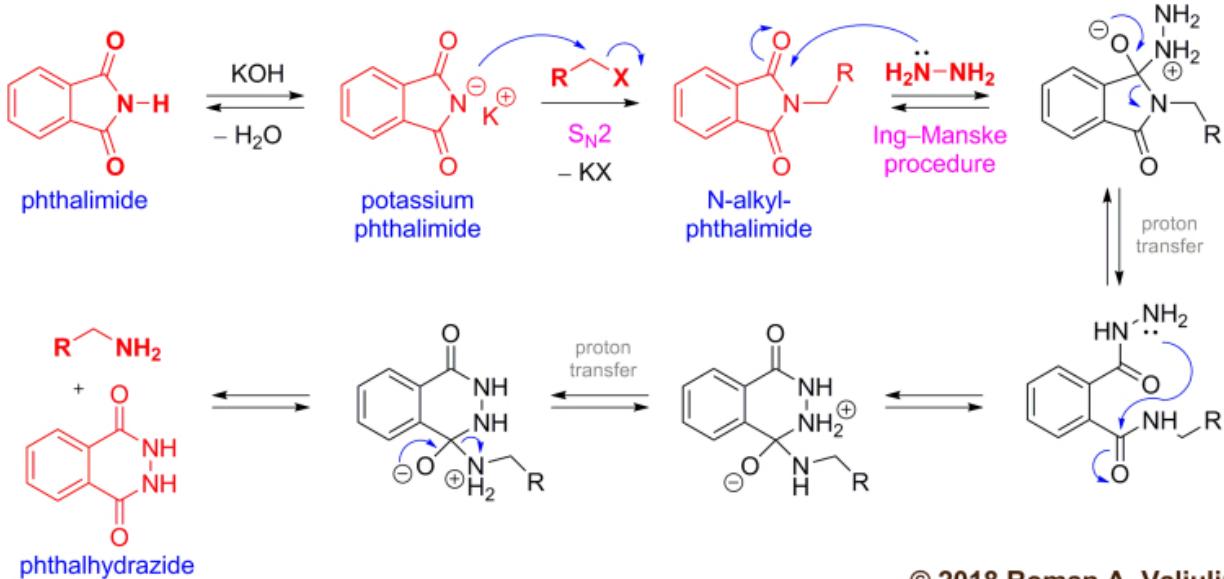


© 2018 Roman A. Valiulin

## 70. Gabriel Synthesis 1887

### Gabriel Synthesis

[1887]

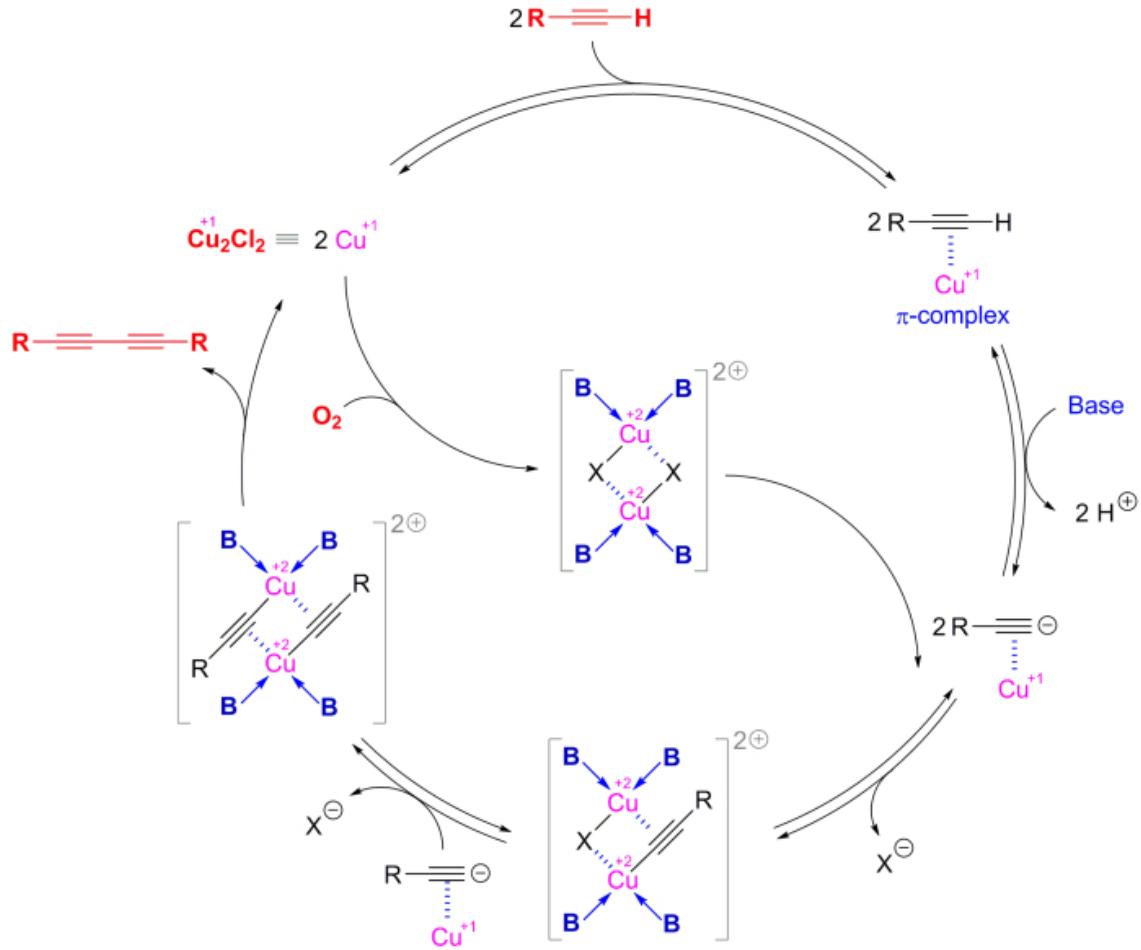


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# 71. Glaser-Hay Coupling 1869

## Glaser-Hay Coupling

[1869]

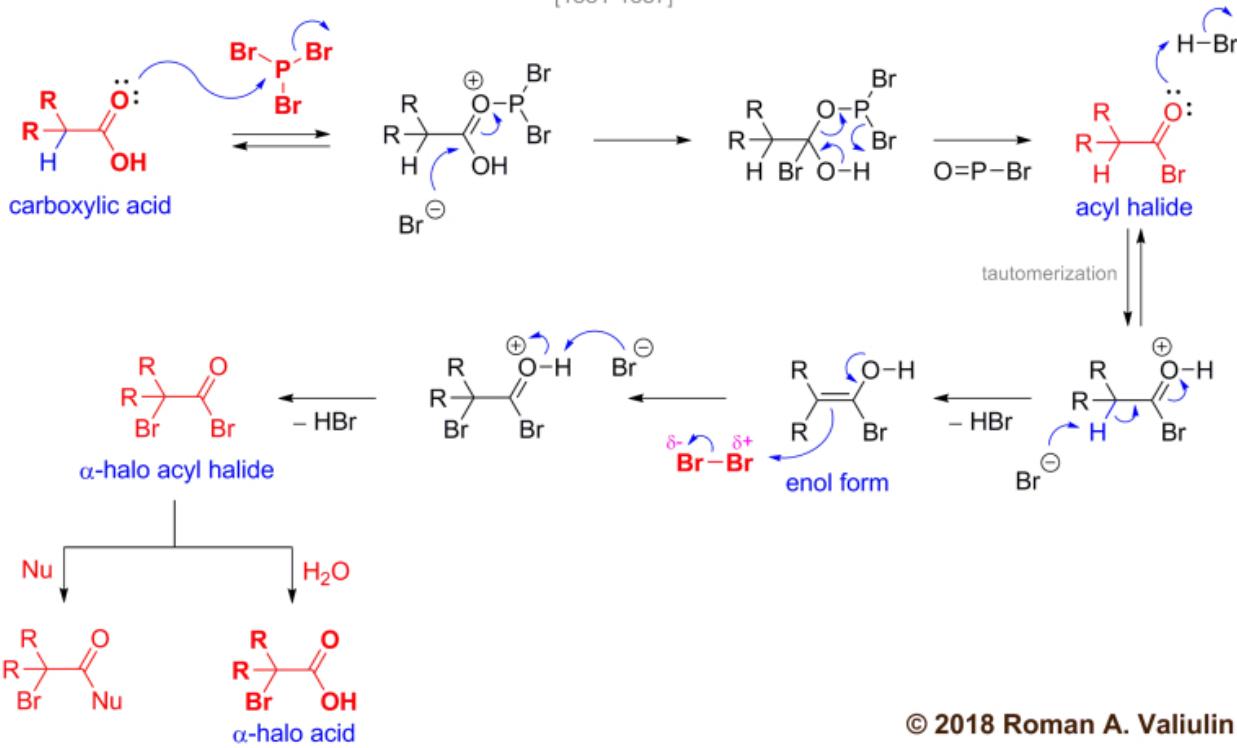


© 2018 Roman A. Valiulin

## 72. Hell-Volhard-Zelinsky Reaction 1881-1887

### Hell-Volhard-Zelinsky Reaction

[1881-1887]

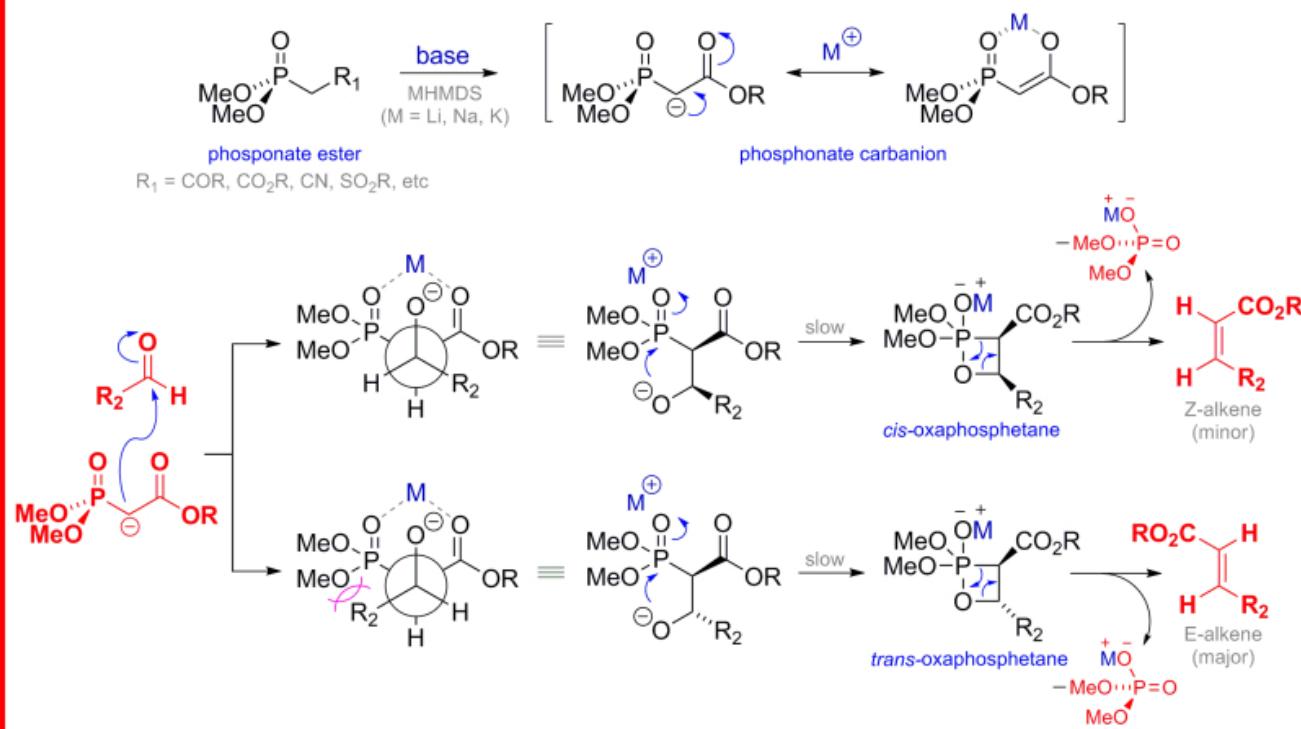


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## 73. Horner-Wadsworth-Emmons (HWE) Olefination 1958

### Horner-Wadsworth-Emmons (HWE) Olefination

[1958]

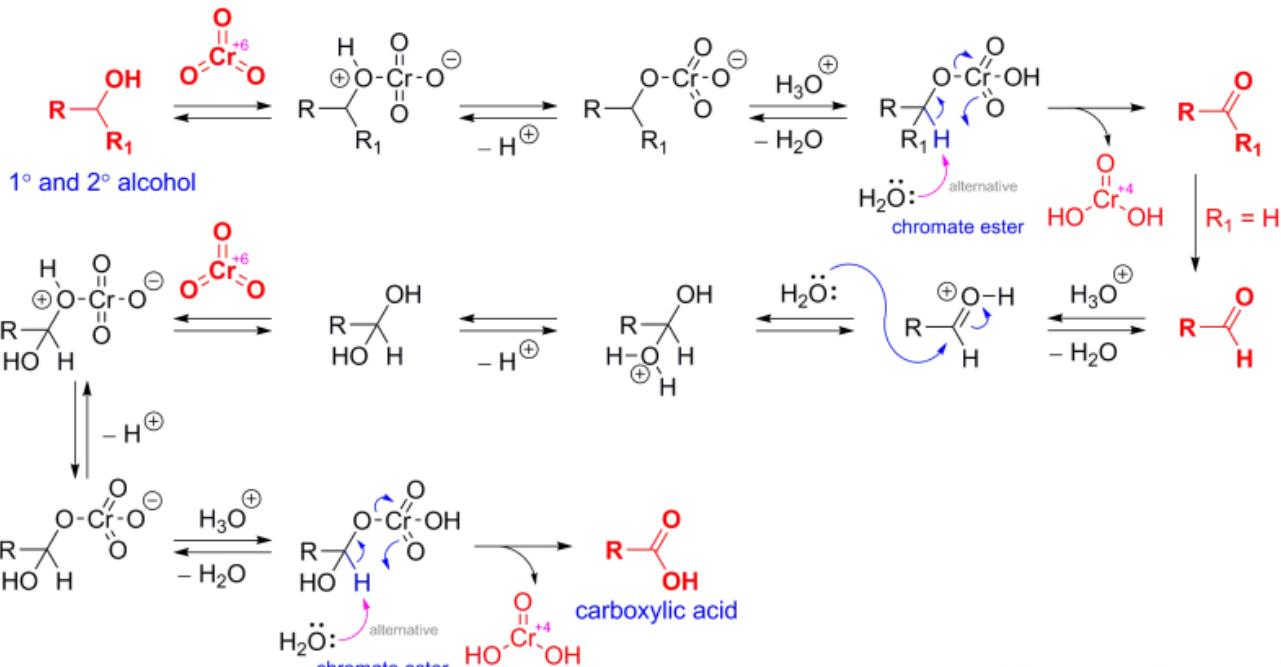
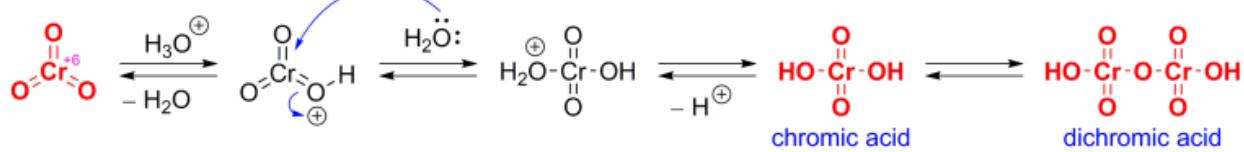


© 2018 Roman A. Valiulin

## 74. Jones Oxidation 1946

### Jones Oxidation

[1946]

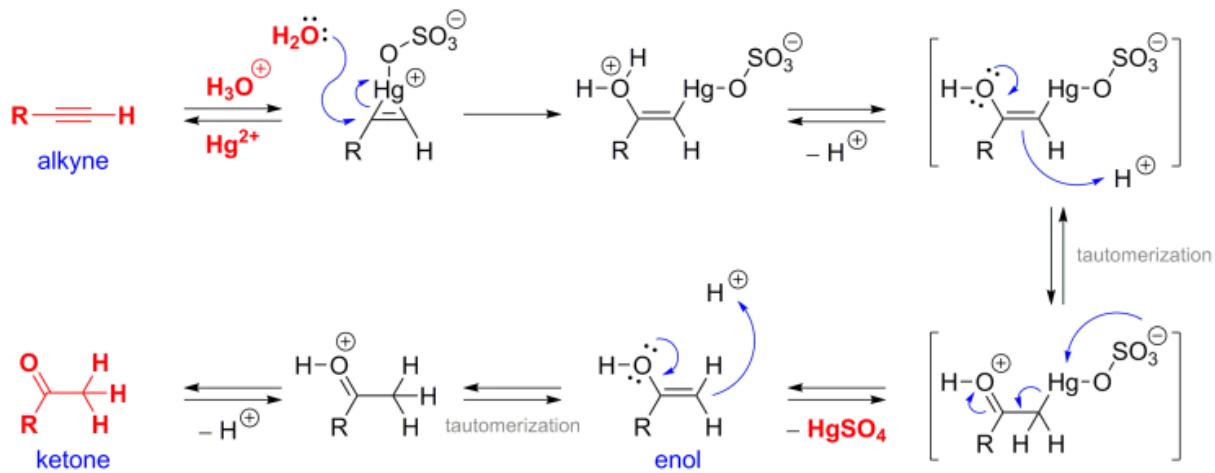


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## 75. Kucherov Reaction 1881

### Kucherov Reaction

[1881]

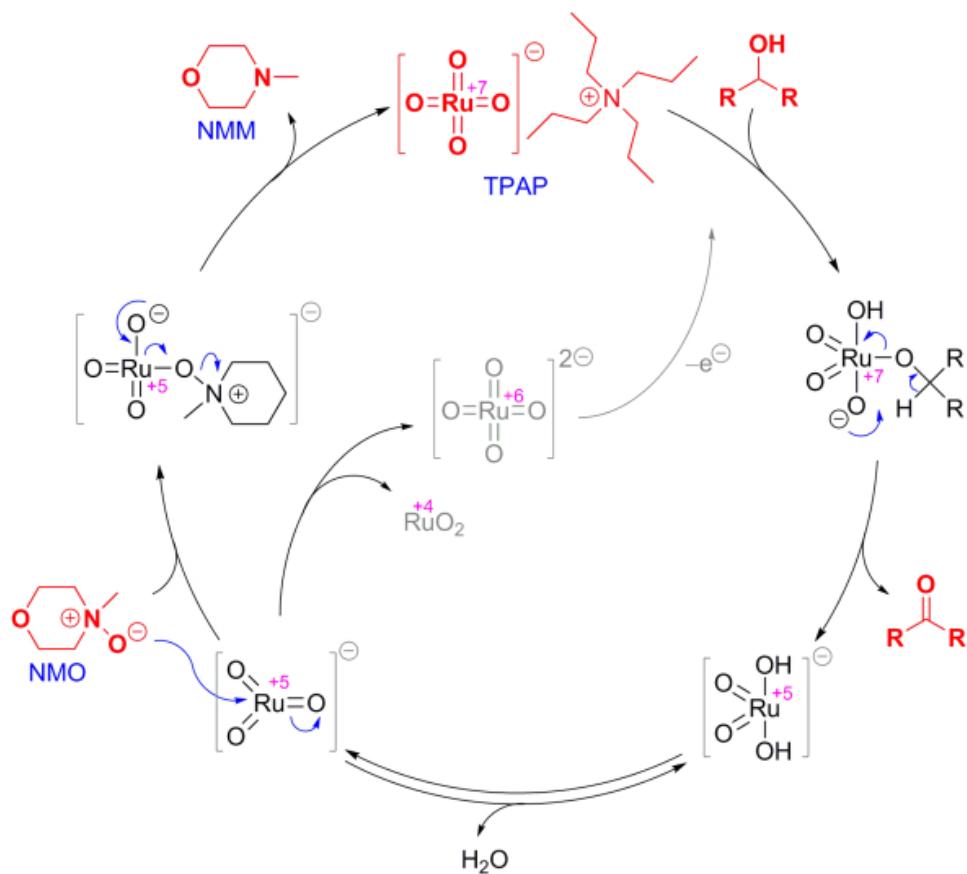


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## 76. Ley-Griffith Oxidation 1987

### Ley-Griffith Oxidation

[1987]

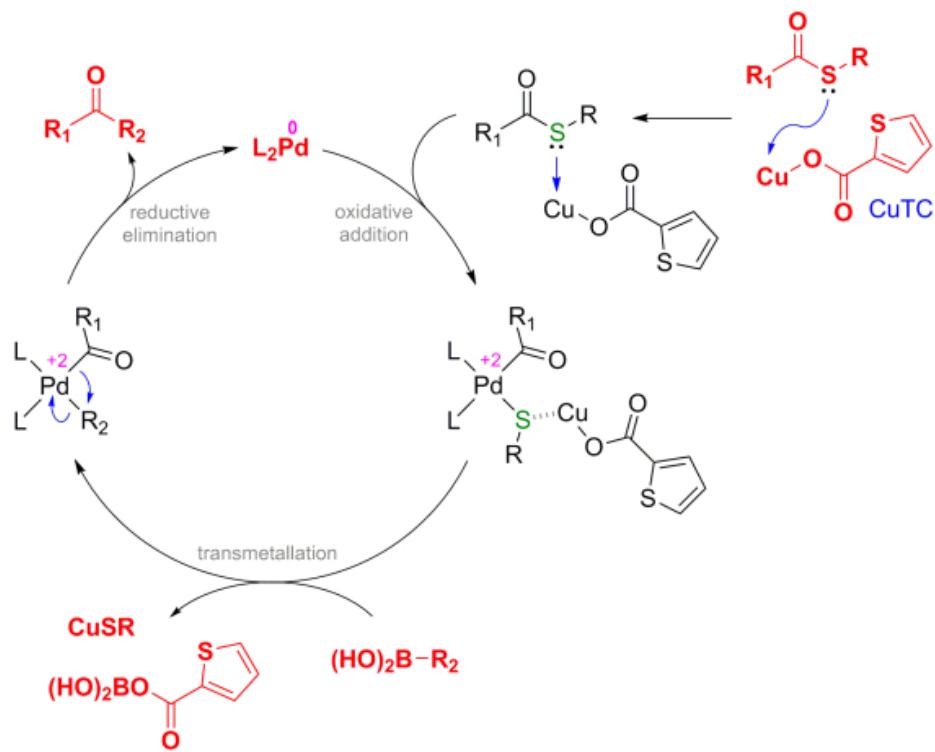


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## 77. Liebeskind-Srogl Coupling 2000

### Liebeskind-Srogl Coupling

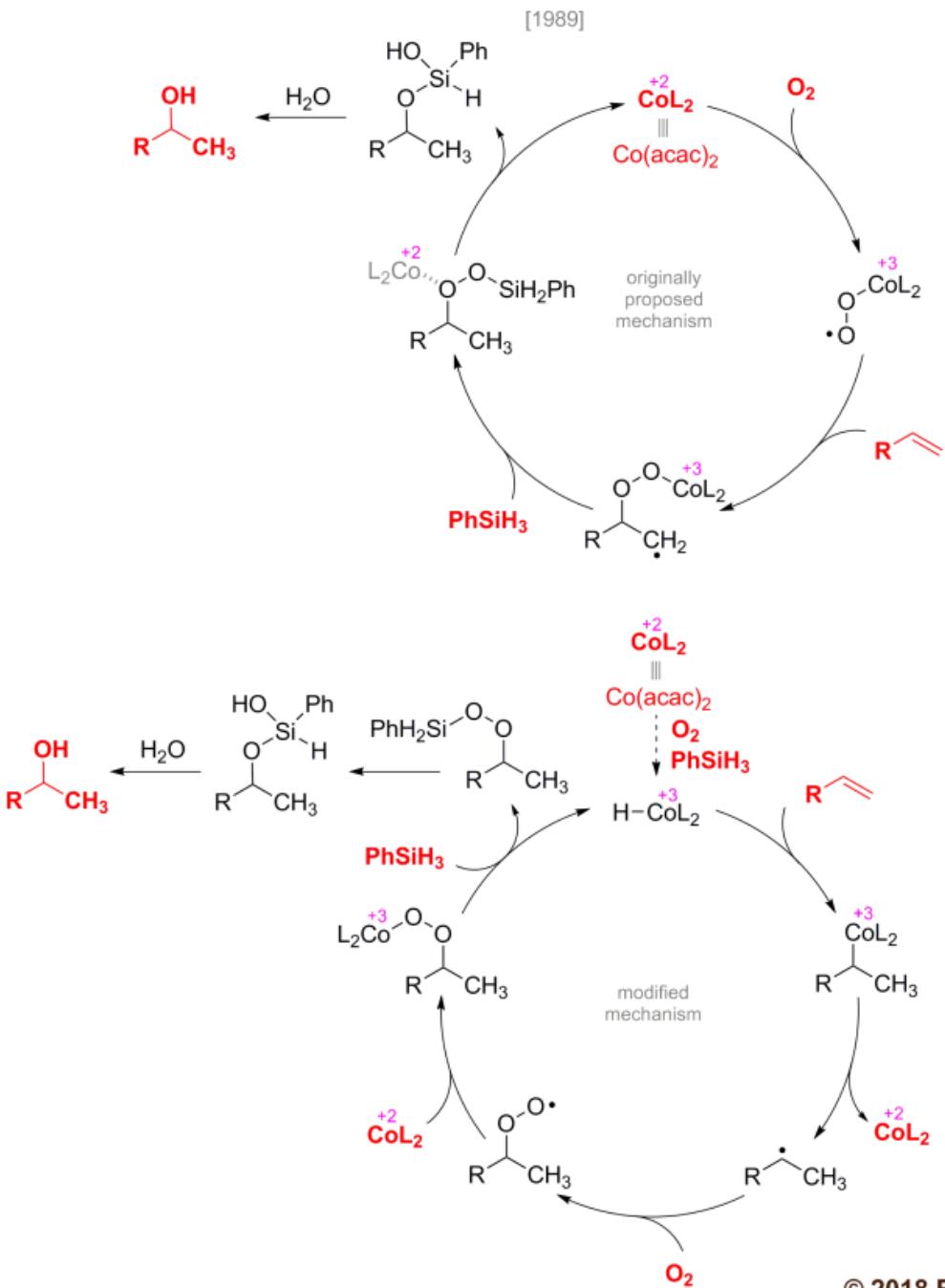
[2000]



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## 78. Mukaiyama Hydration 1989

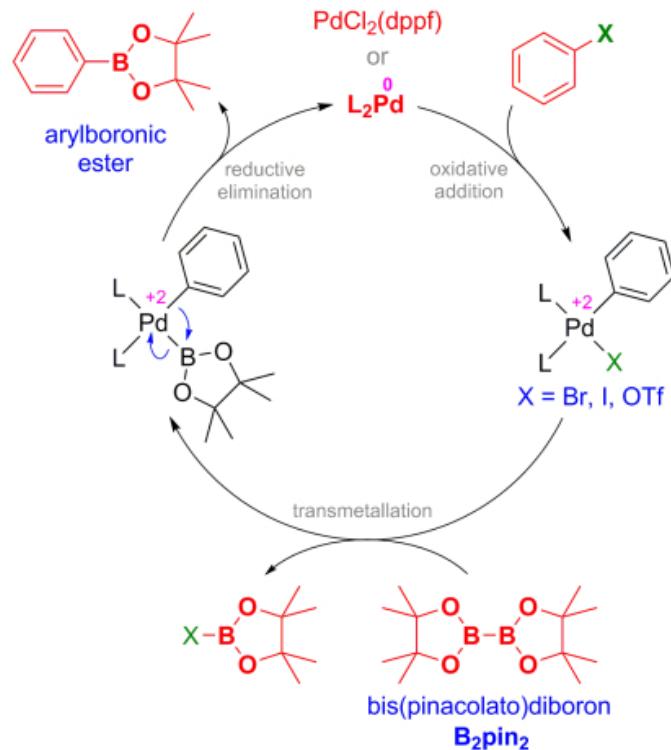
### Mukaiyama Hydration



## 79. Miyaura Borylation 1995

### Miyaura Borylation

[1995]

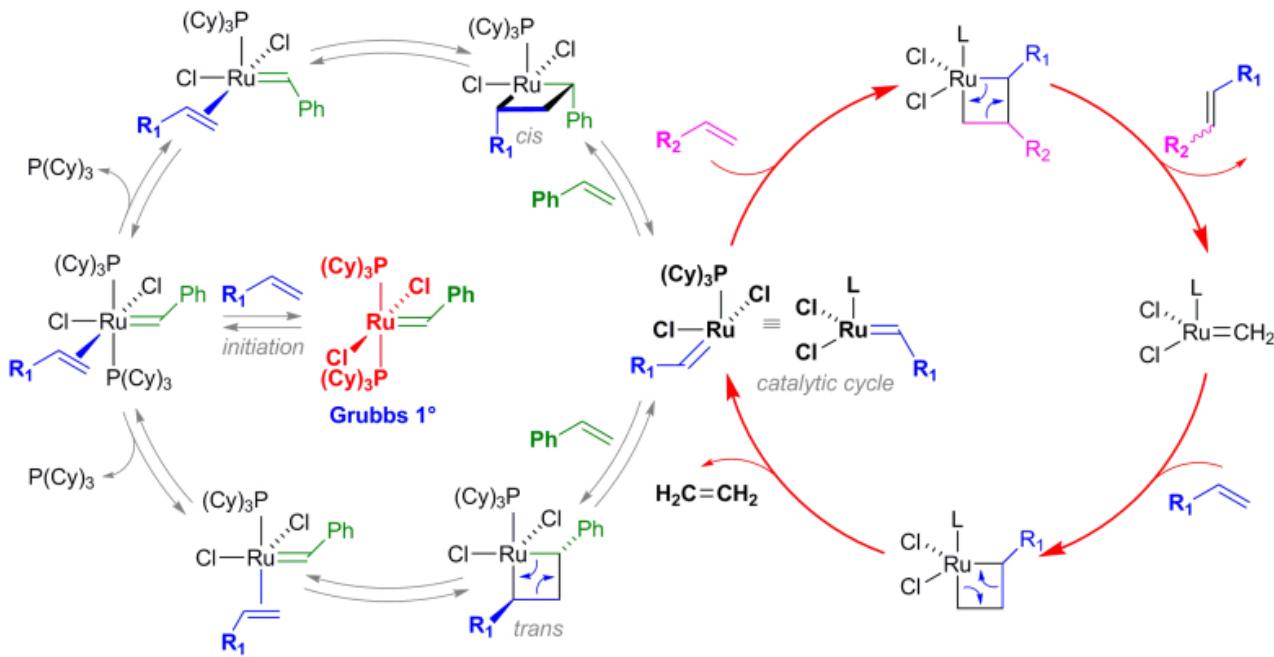


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## 80. Olefin (Alkene) Metathesis 1955

### Olefin (Alkene) Metathesis

[1955]

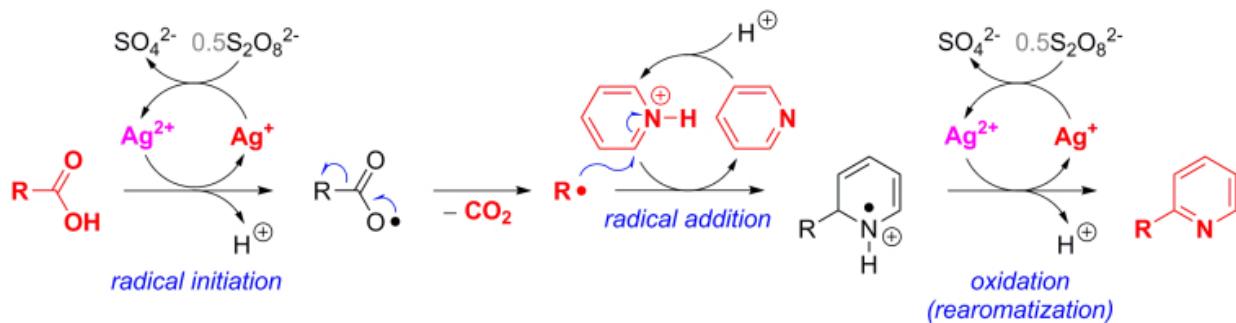


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## 81. Minisci Reaction 1968

### Minisci Reaction

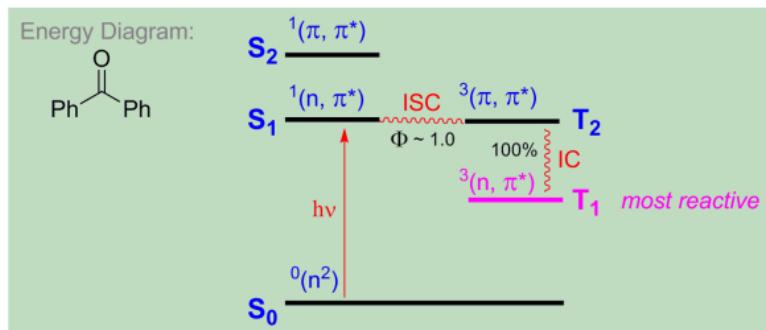
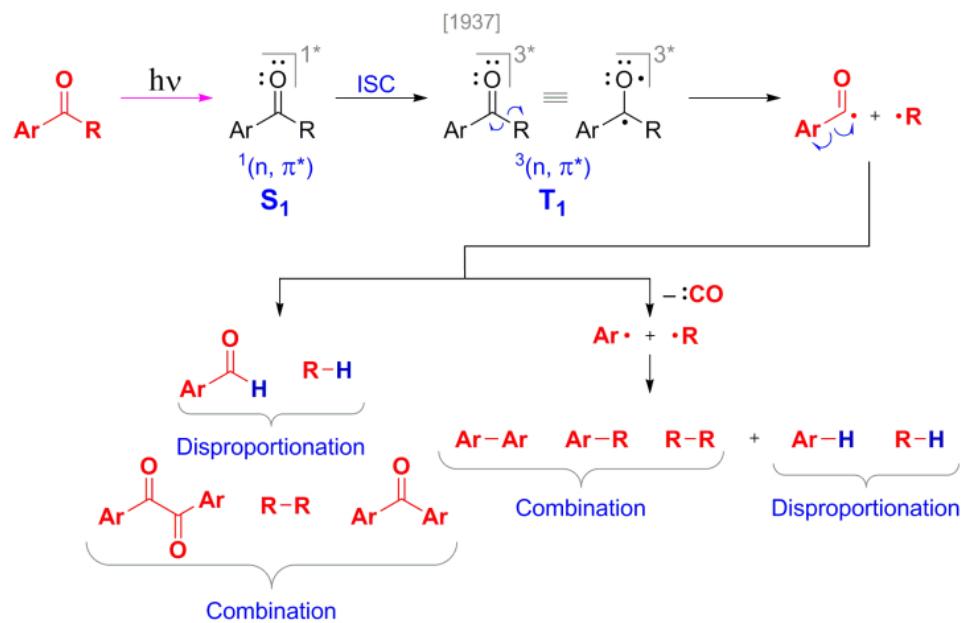
[1968]



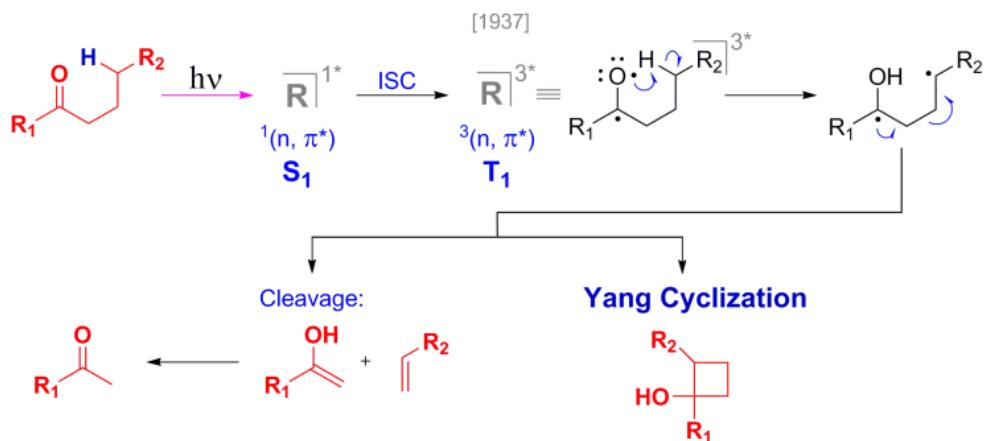
© 2018 Roman A. Valiulin

## 82. Norrish Type I and II Fragmentation 1937

### Norrish Type I Fragmentation



### Norrish Type II Fragmentation

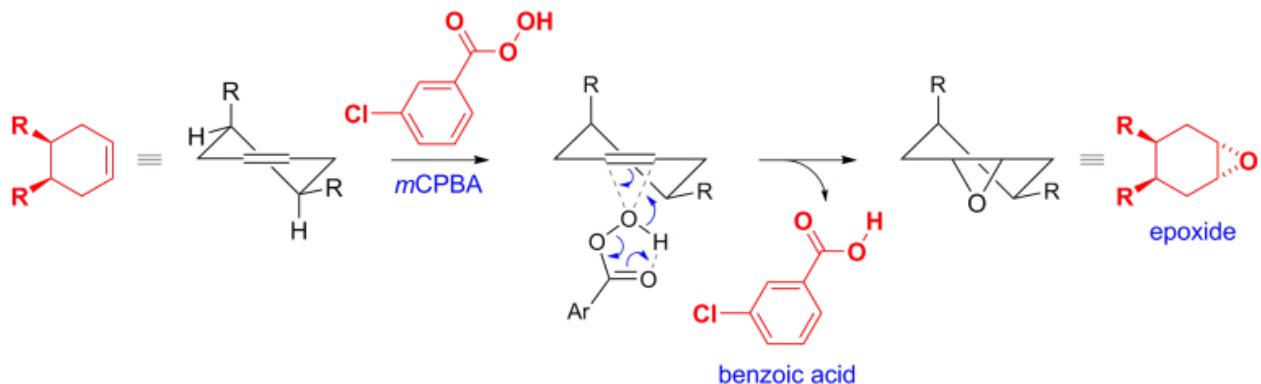


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### 83. Prilezhaev Epoxidation 1909

#### Prilezhaev Epoxidation

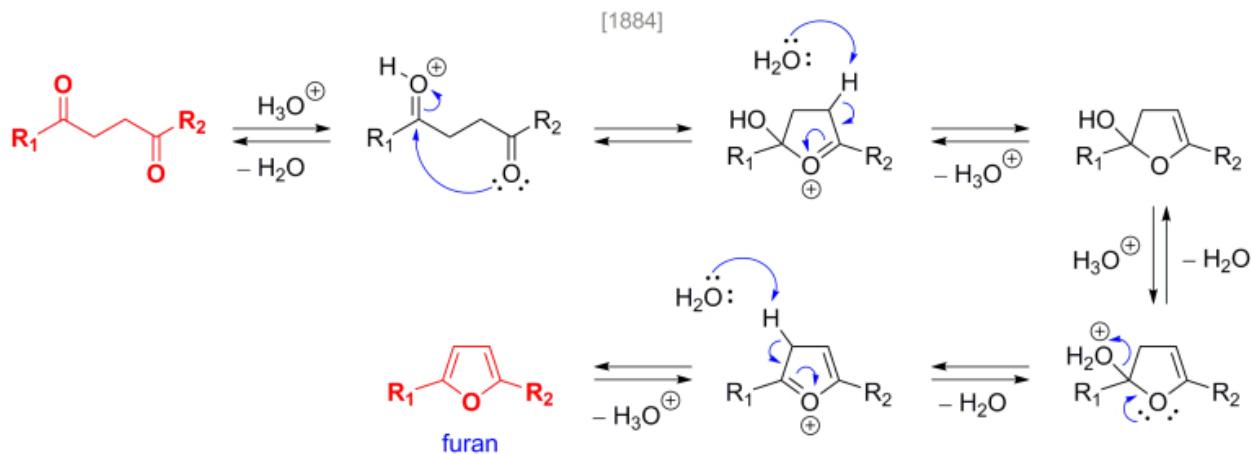
[1909]



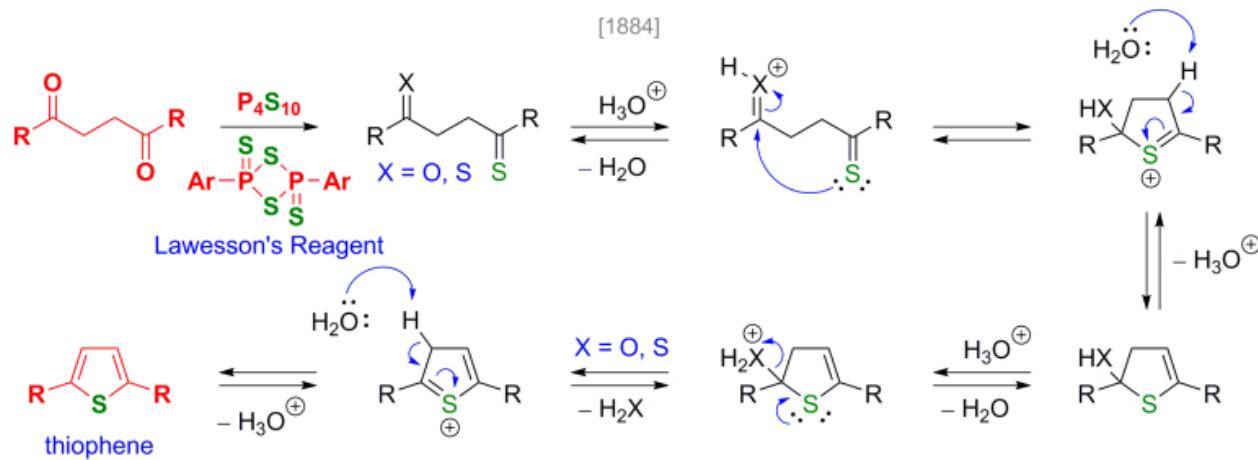
© 2018 Roman A. Valiulin

## 84. Paal-Knorr Syntheses 1884

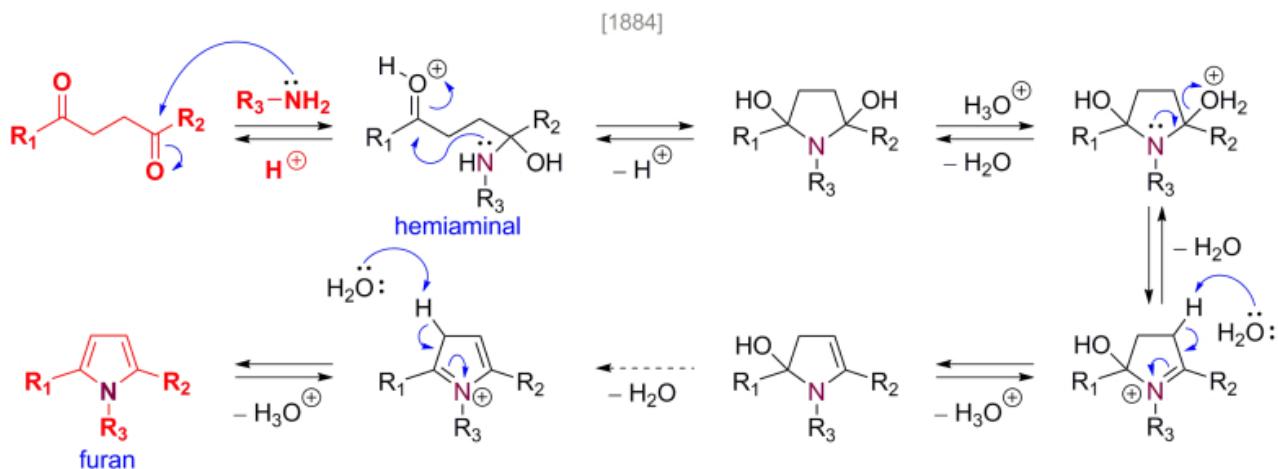
### Paal-Knorr Furan Synthesis



### Paal-Knorr Thiophene Synthesis



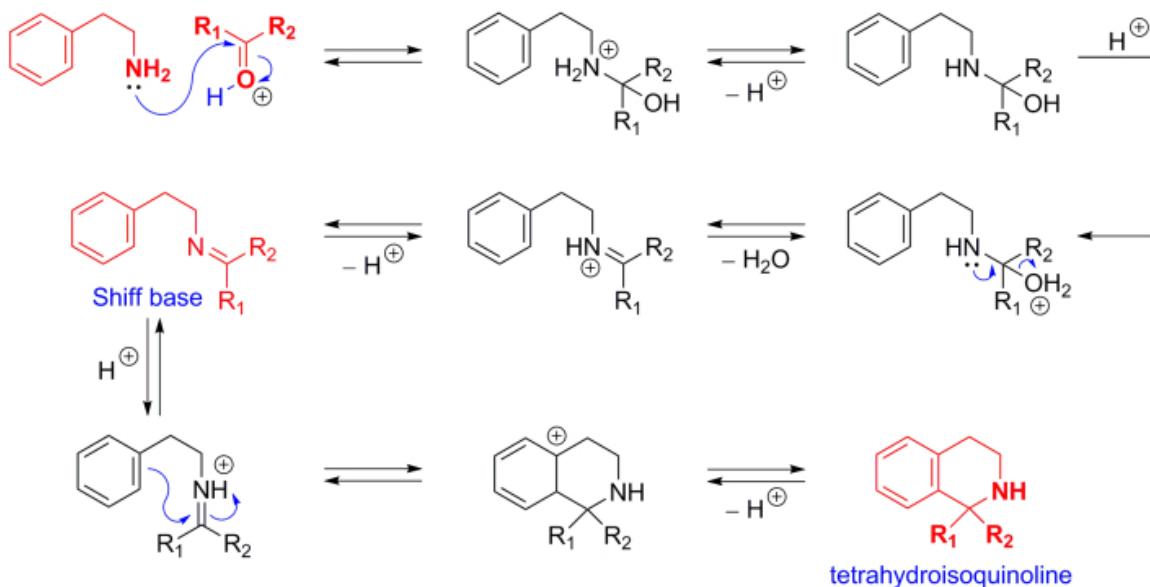
### Paal-Knorr Pyrrole Synthesis



## 85. Pictet-Spengler Reaction 1911

### Pictet-Spengler Reaction

[1911]



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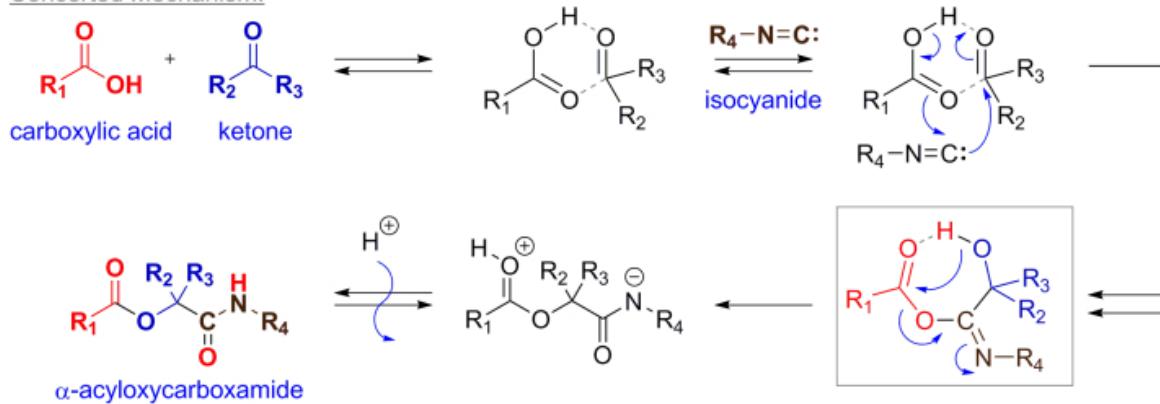
## 86. Passerini Three-Component Reaction 1921

### Passerini Reaction

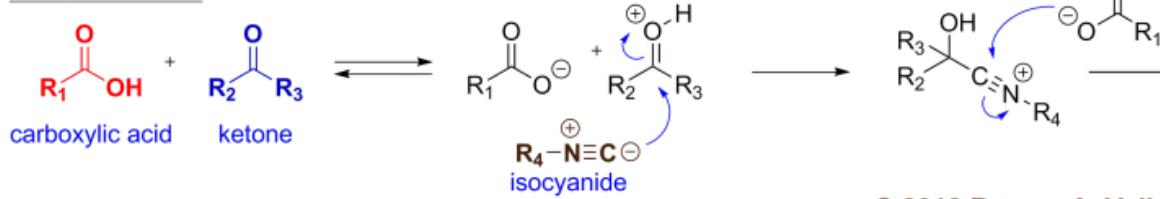
3-Component Reaction (3-CR)

[1921]

Concerted Mechanism:



Ionic Mechanism:

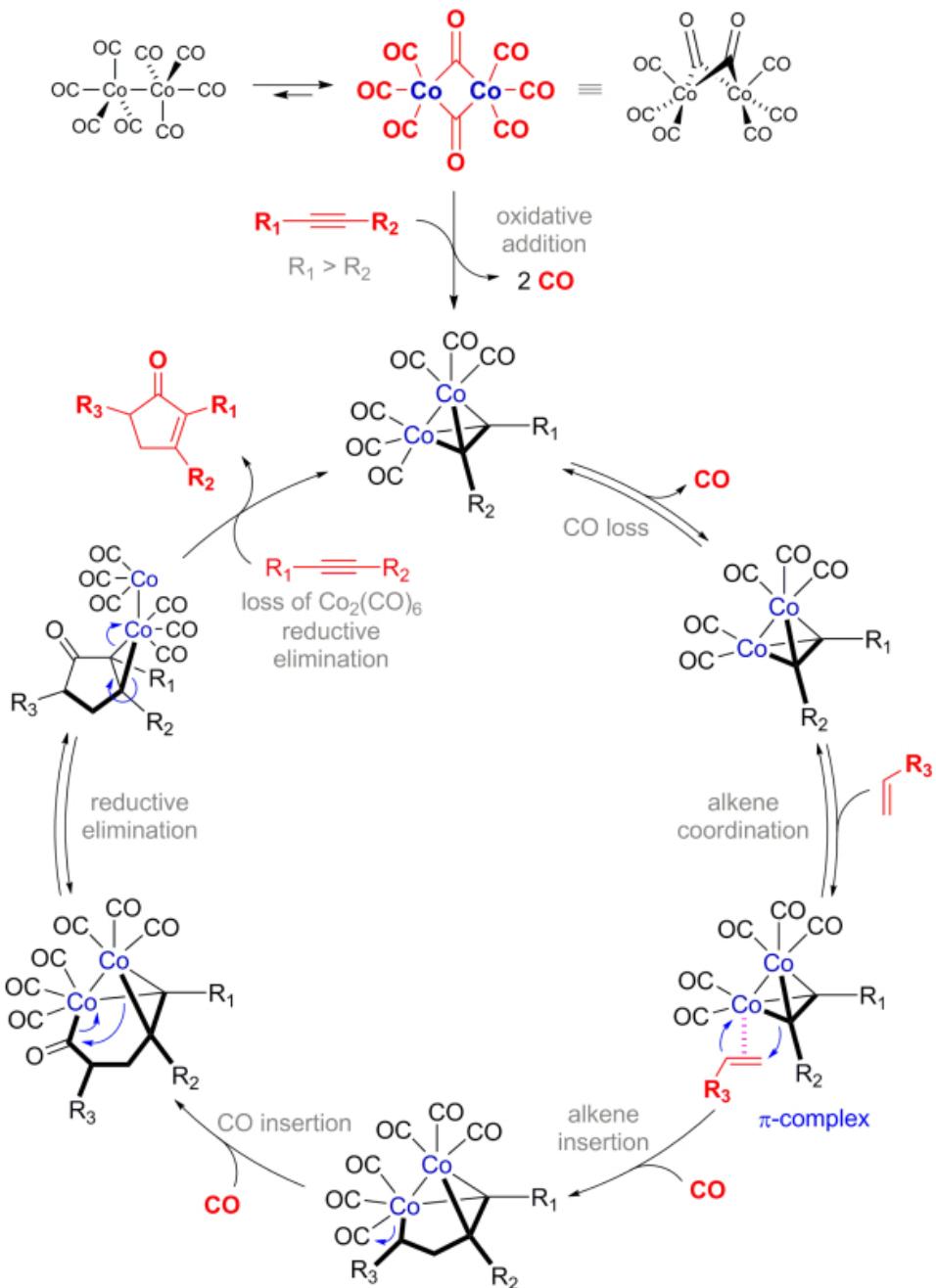


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## 87. Pauson–Khand Reaction 1977

### Pauson–Khand Reaction

[1977]



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## 88. Nucleophilic Substitution

### Nucleophilic Substitution

(see Finkelstein Reaction)

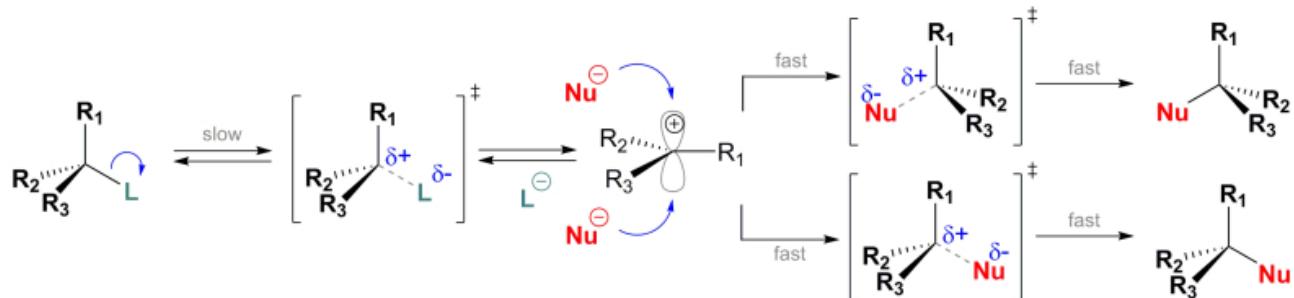
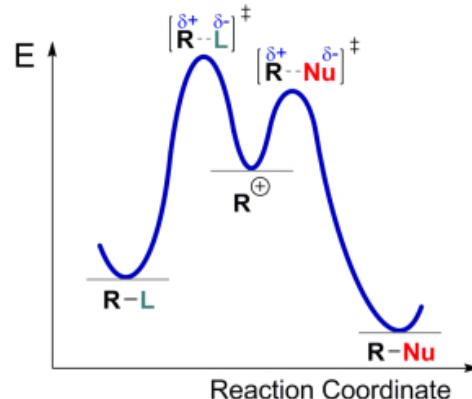


Unimolecular Nucleophilic Substitution

$$\text{rate} = k[\mathbf{R}-\mathbf{L}]$$

$\mathbf{L}$  = Cl, Br, I, OSO<sub>2</sub>R', OTf, OMs, OTs, OBs, ONs

$3^\circ > 2^\circ > 1^\circ$

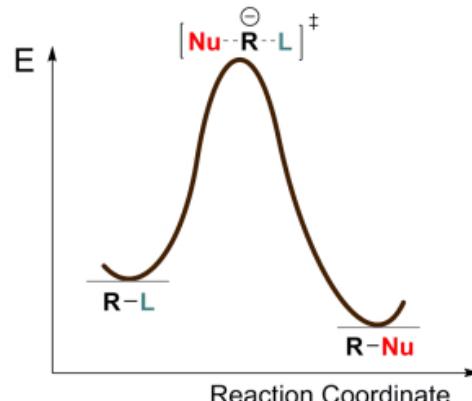


Bimolecular Nucleophilic Substitution

$$\text{rate} = k[\mathbf{Nu}^-][\mathbf{R}-\mathbf{L}]$$

$\mathbf{L}$  = Cl, Br, I, OSO<sub>2</sub>R', OTf, OMs, OTs, OBs, ONs

$1^\circ > 2^\circ > 3^\circ$

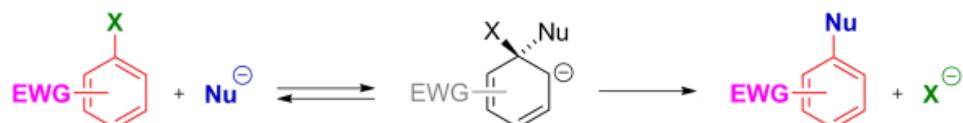


## 89. Nucleophilic Aromatic Substitution

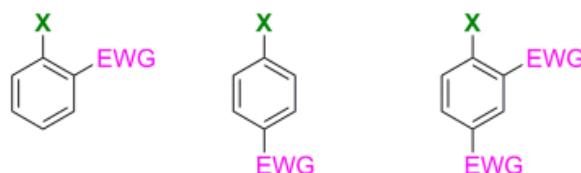
### Nucleophilic Aromatic Substitution

Bimolecular Nucleophilic Aromatic Substitution  
(addition-elimination)

$$\text{rate} = k[\text{Nu}][\text{ArX}]$$



$\sigma$ -complex  
(Meisenheimer complex)



Electron Withdrawing Group  
 $\text{NO}_2, \text{SO}_2\text{R}, \text{CN}, \text{N}_2^+$

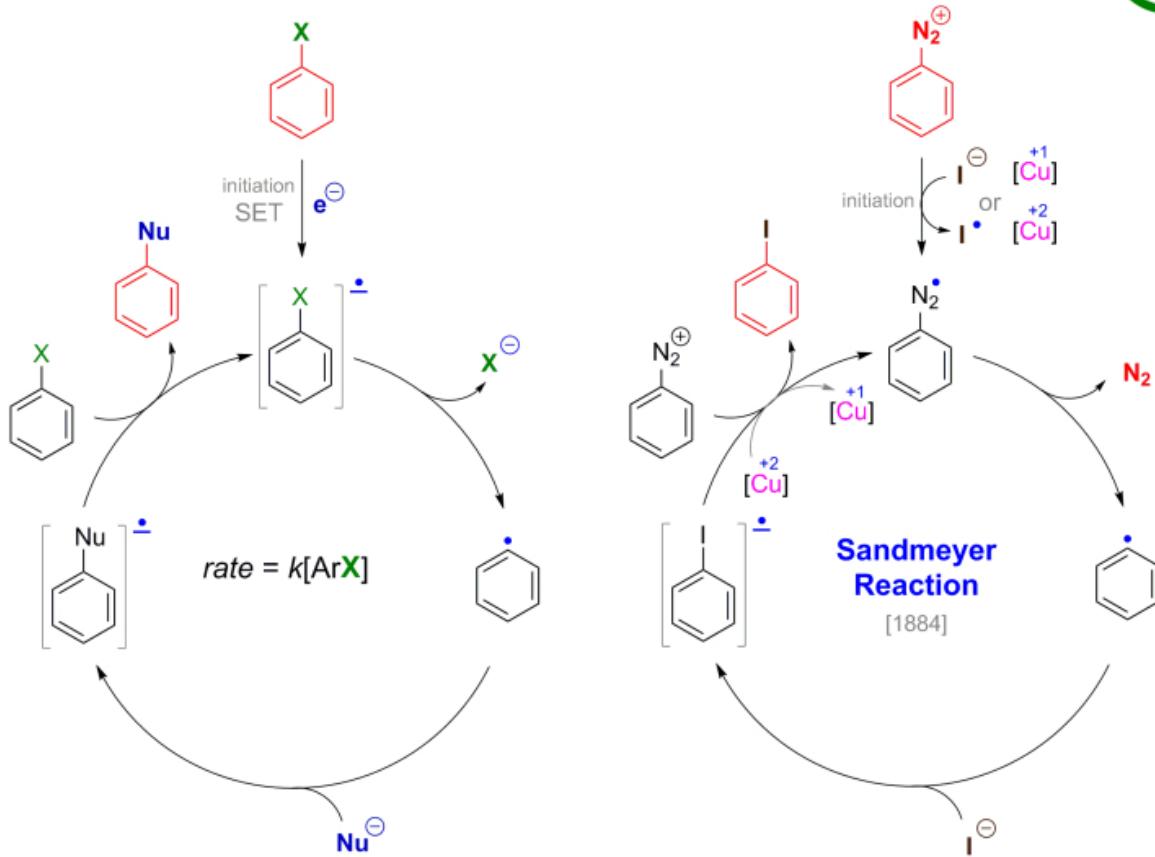
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## 90. Radical Nucleophilic Aromatic Substitution 1970

### Radical Nucleophilic Aromatic Substitution

[1970]

S<sub>RN1</sub>

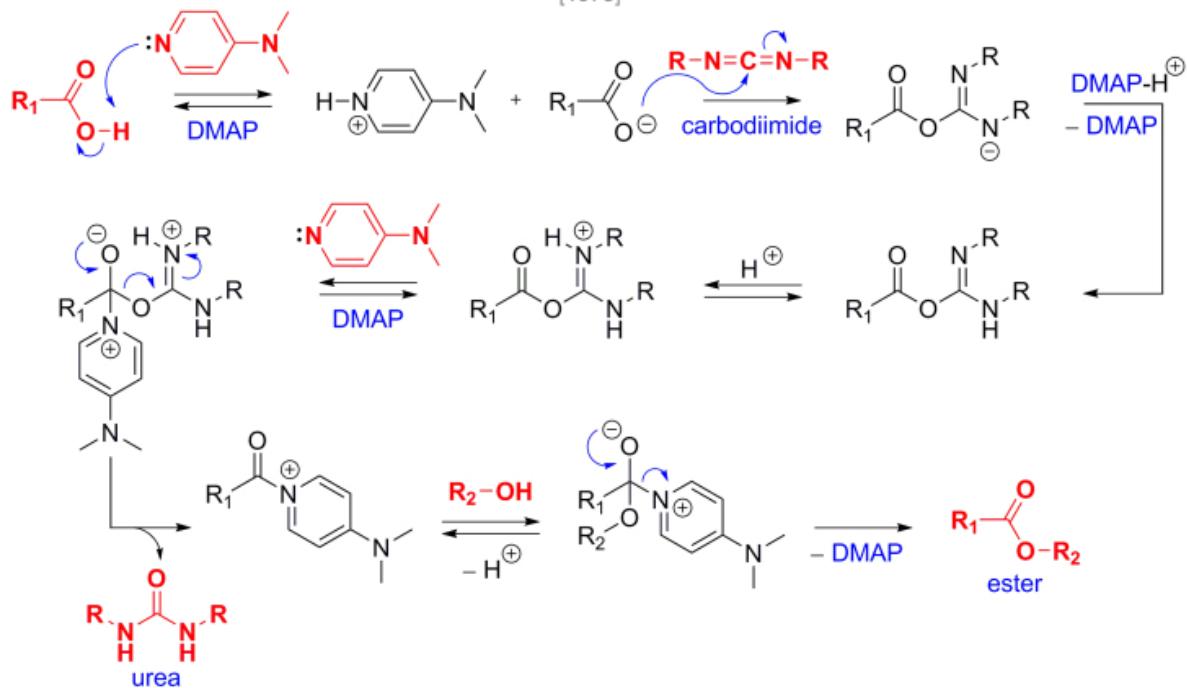


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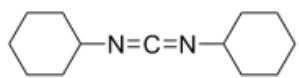
## 91. Steglich Esterification 1978

### Steglich Esterification

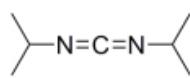
[1978]



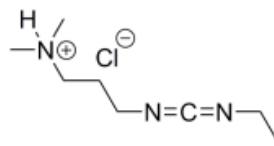
Carbodiimide reagent:



DCC



DIC



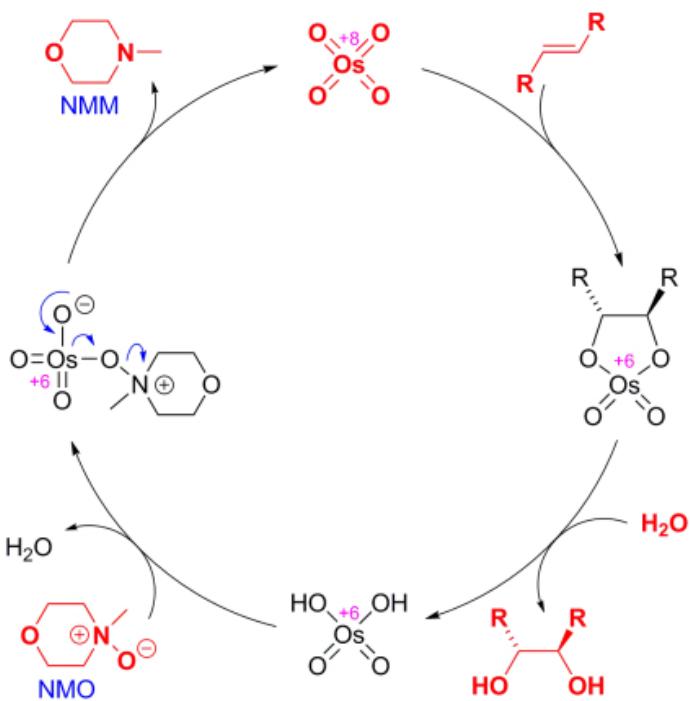
EDC

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## 92. Upjohn Dihydroxylation 1976

### Upjohn Dihydroxylation

[1976]



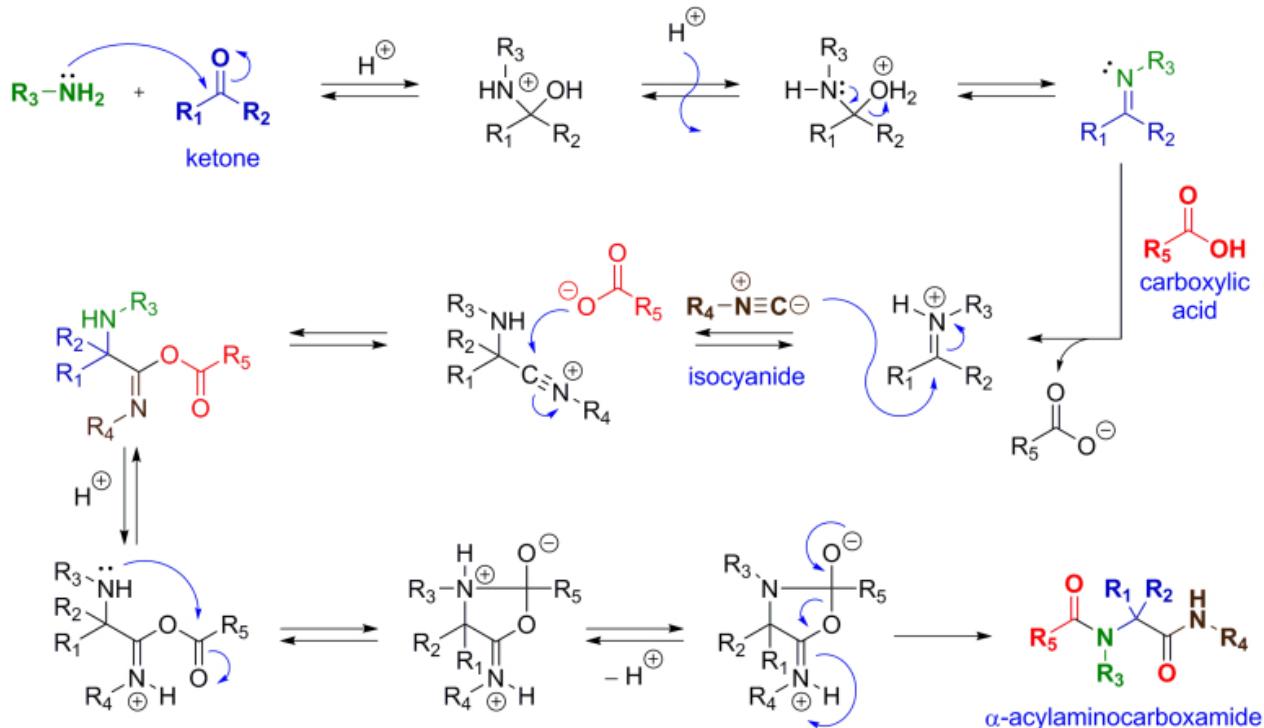
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## 93. Ugi Reaction 1959

### Ugi Reaction

4-Component Reaction (4-CR)

[1959]

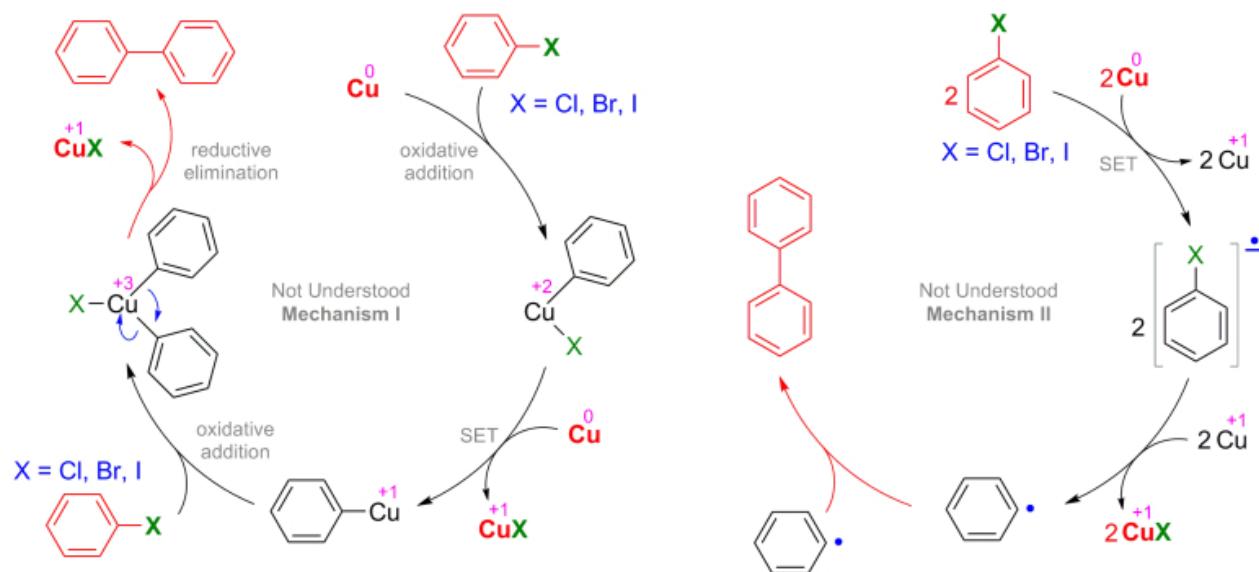


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## 94. Ullmann Aryl-Aryl Coupling 1901

### Ullmann Aryl-Aryl Coupling

[1901]

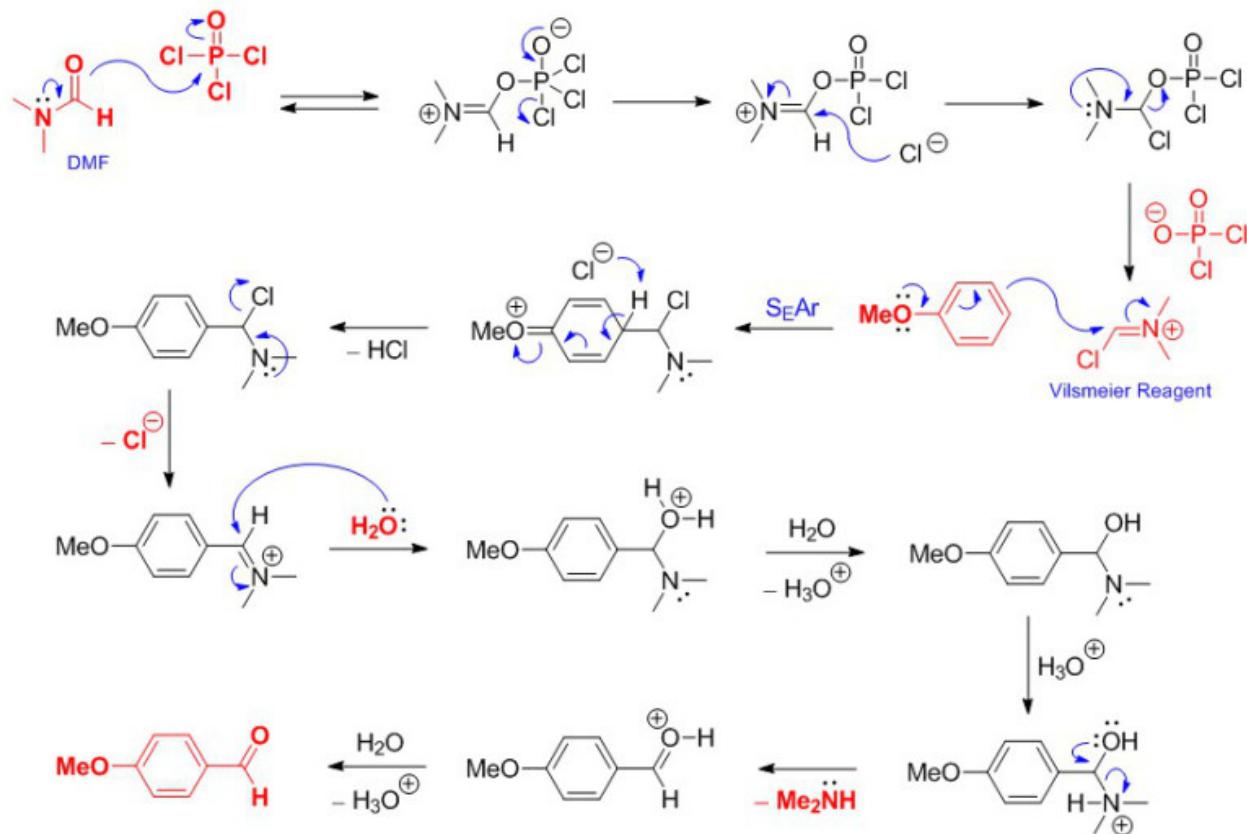


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## 95. Vilsmeier-Haak Formylation 1927

### Vilsmeier-Haak Formylation

[1927]

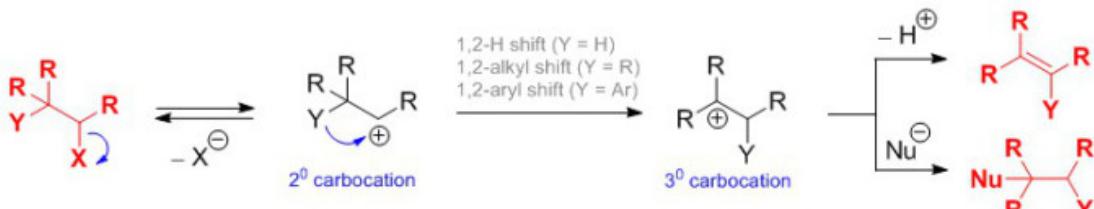


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## 96. Wagner-Meerwein Rearrangement (1899–1914)

### Wagner-Meerwein Rearrangement

[1899-1914]



Example:

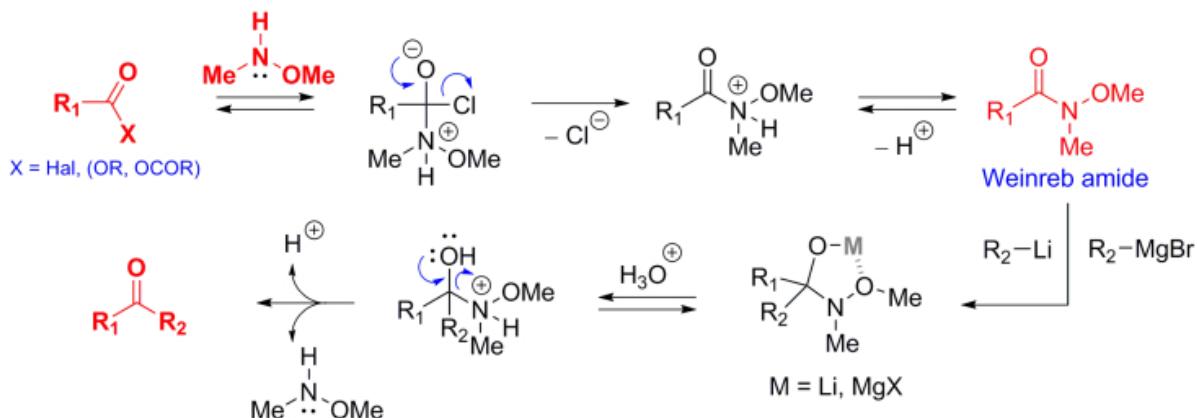


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## 97. Weinreb Ketone Synthesis 1981

### Weinreb Ketone Synthesis

[1981]

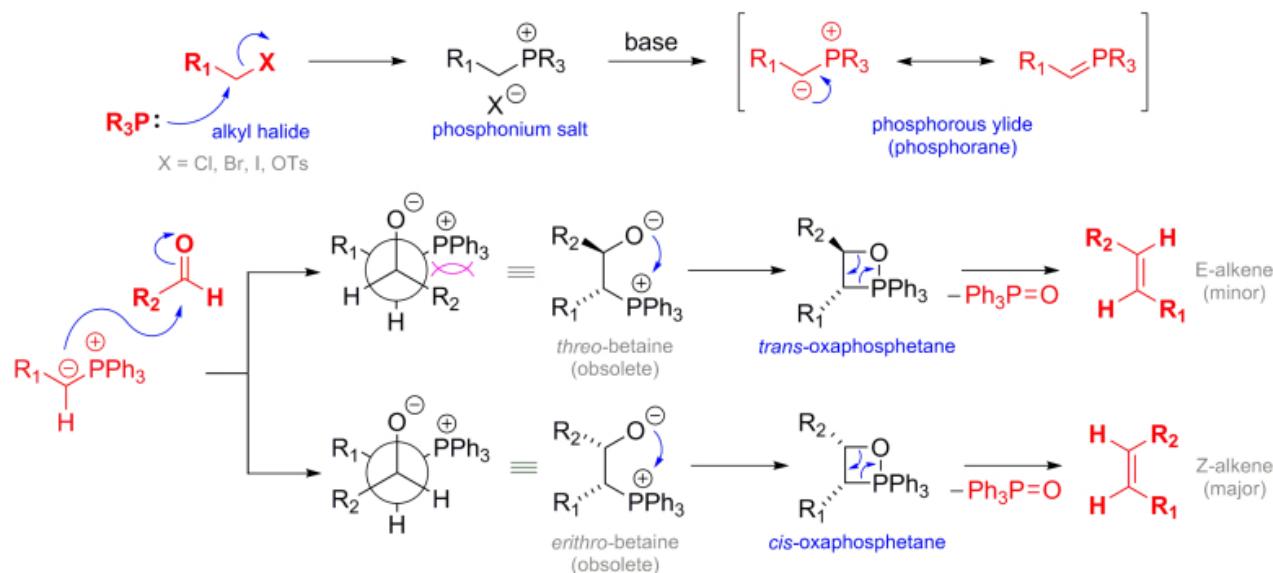


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## 98. Wittig Reaction 1954

### Wittig Reaction

[1954]

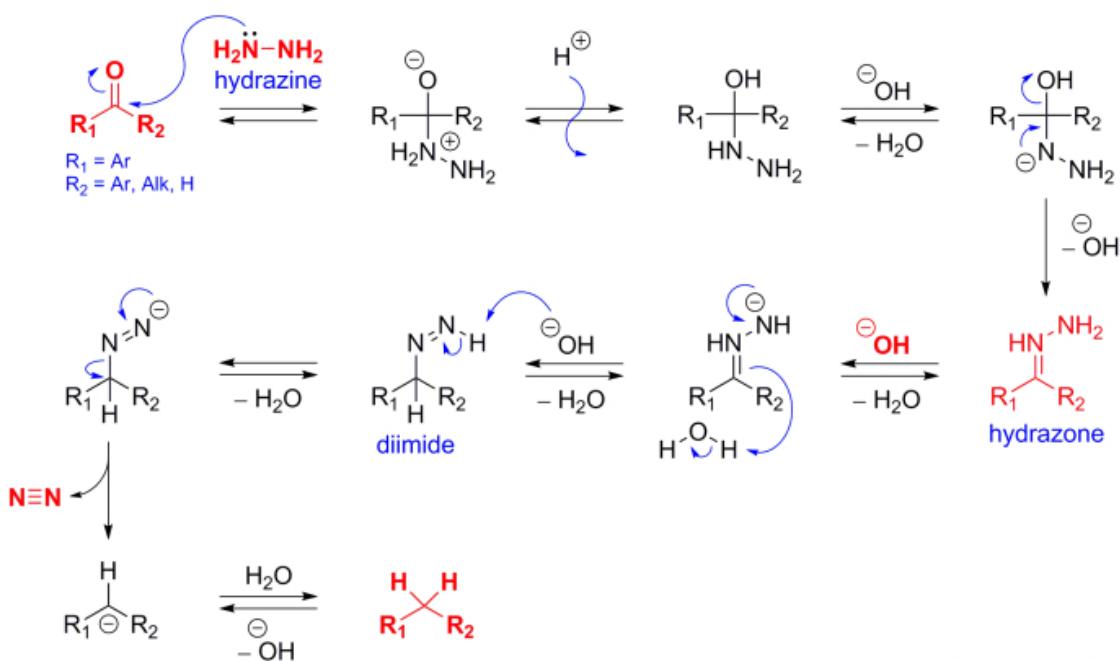


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## 99. Wolff-Kishner Reduction 1911

### Wolff-Kishner Reduction

[1911]

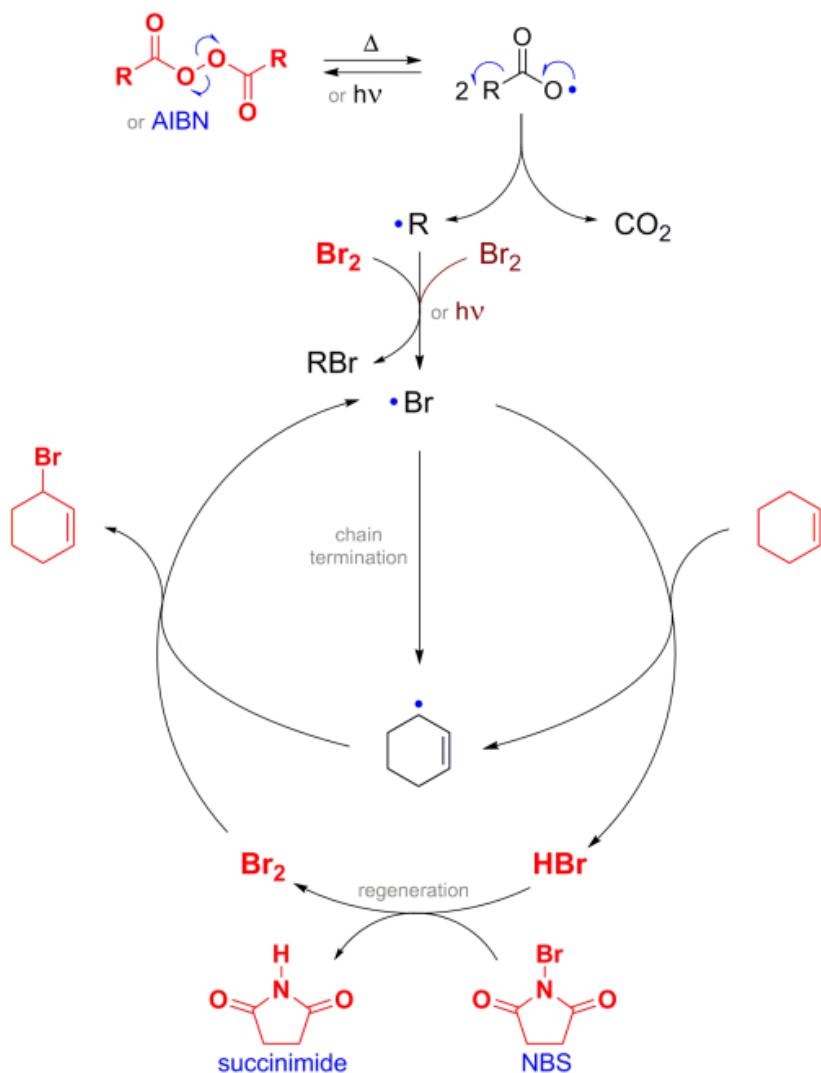


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# 100. Wohl-Ziegler Reaction (1919–1942)

## Wohl-Ziegler Reaction

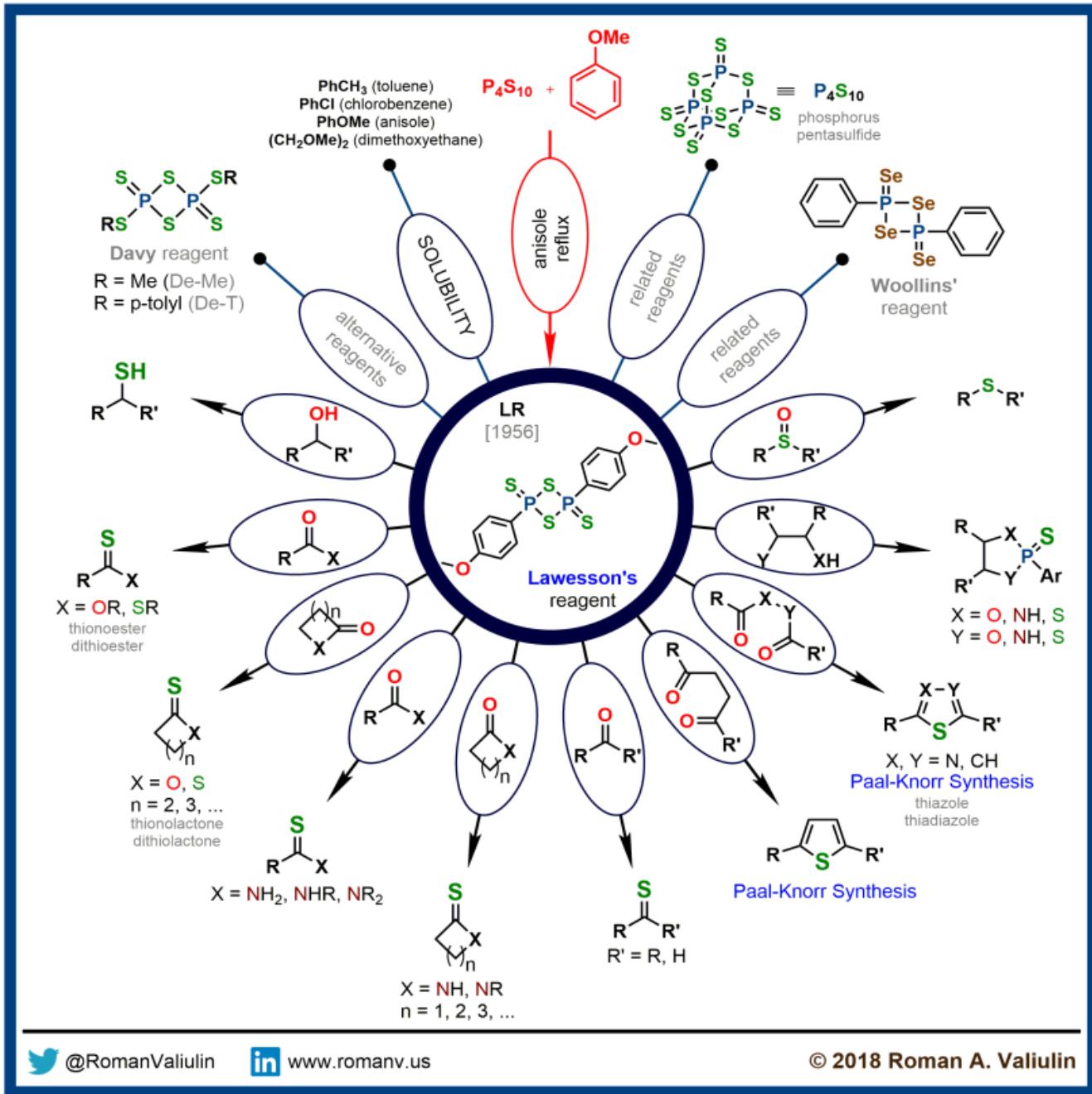
[1919–1942]



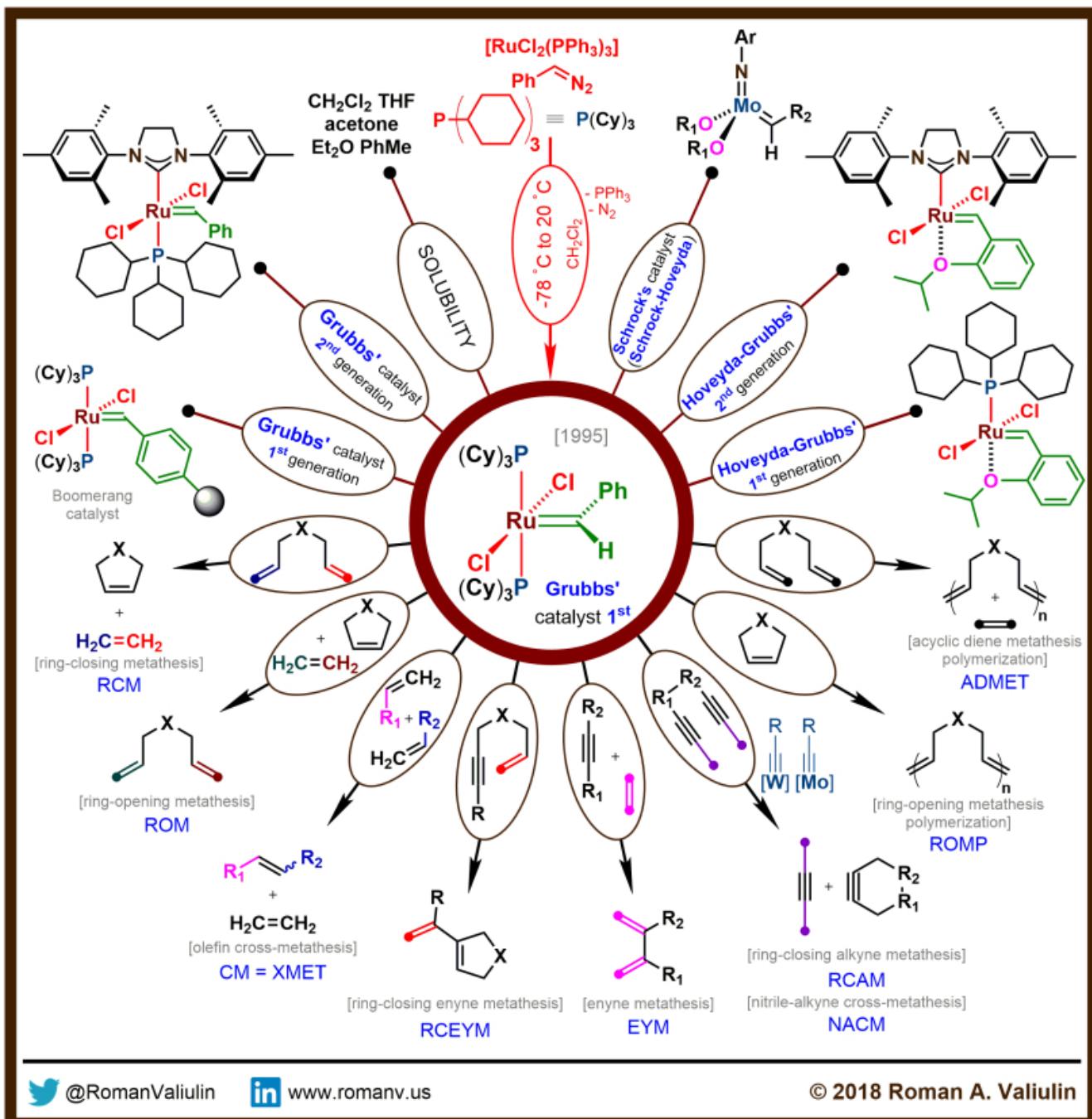
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## II. 100 Must Know Reagents

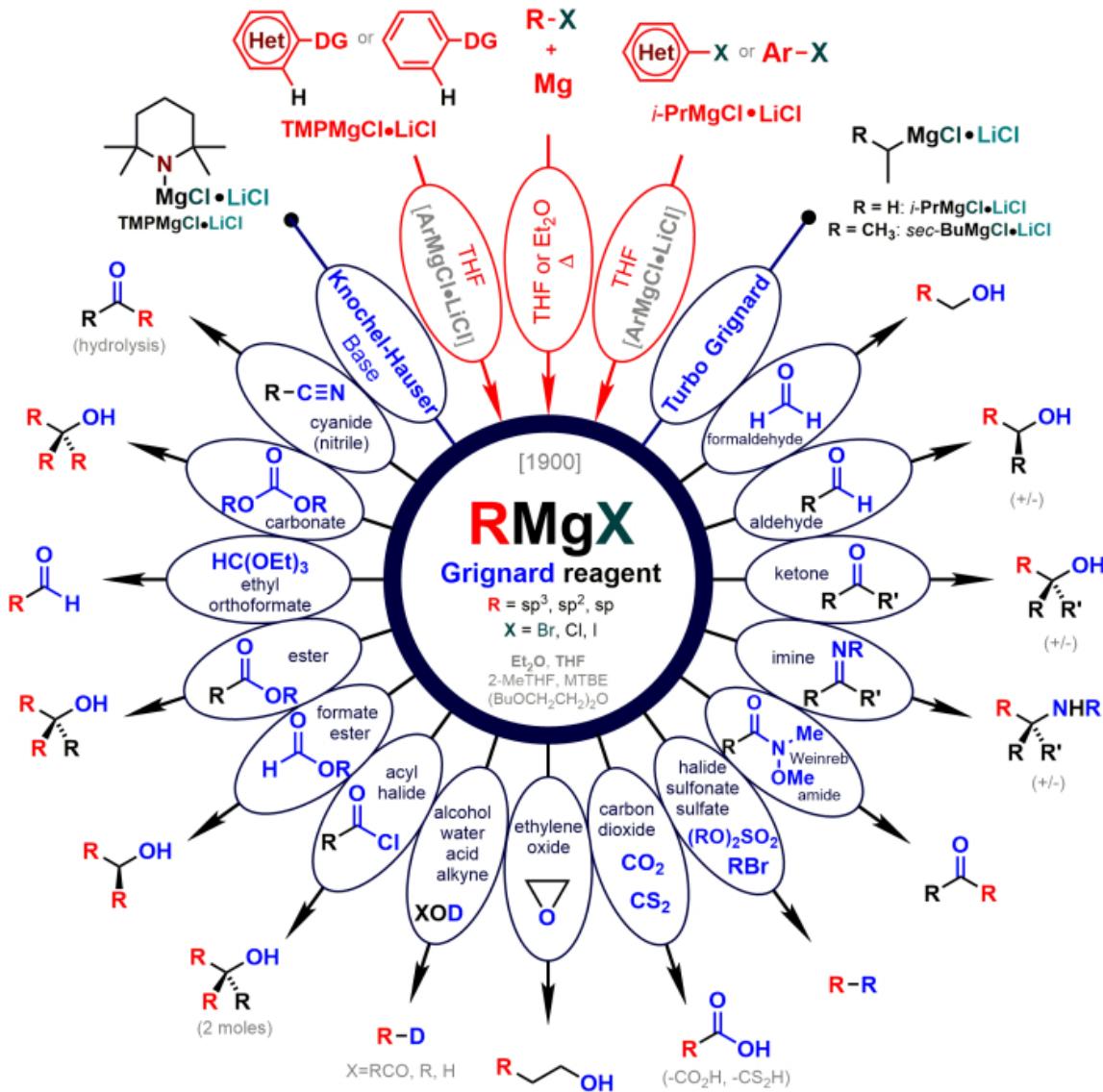
## 1. Lawesson's Reagent 1956



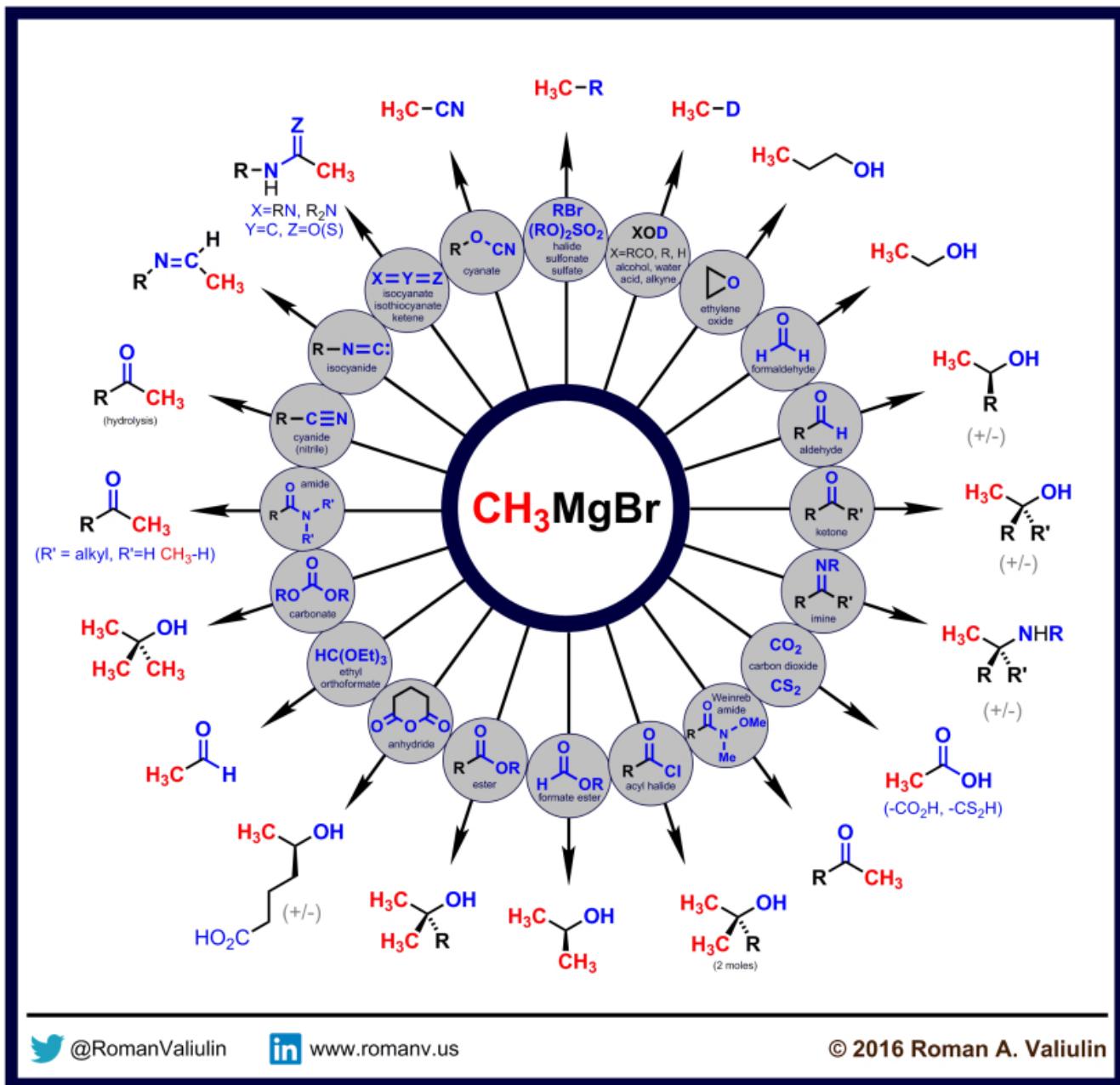
## 2. Grubbs' Catalyst First Generation 1995



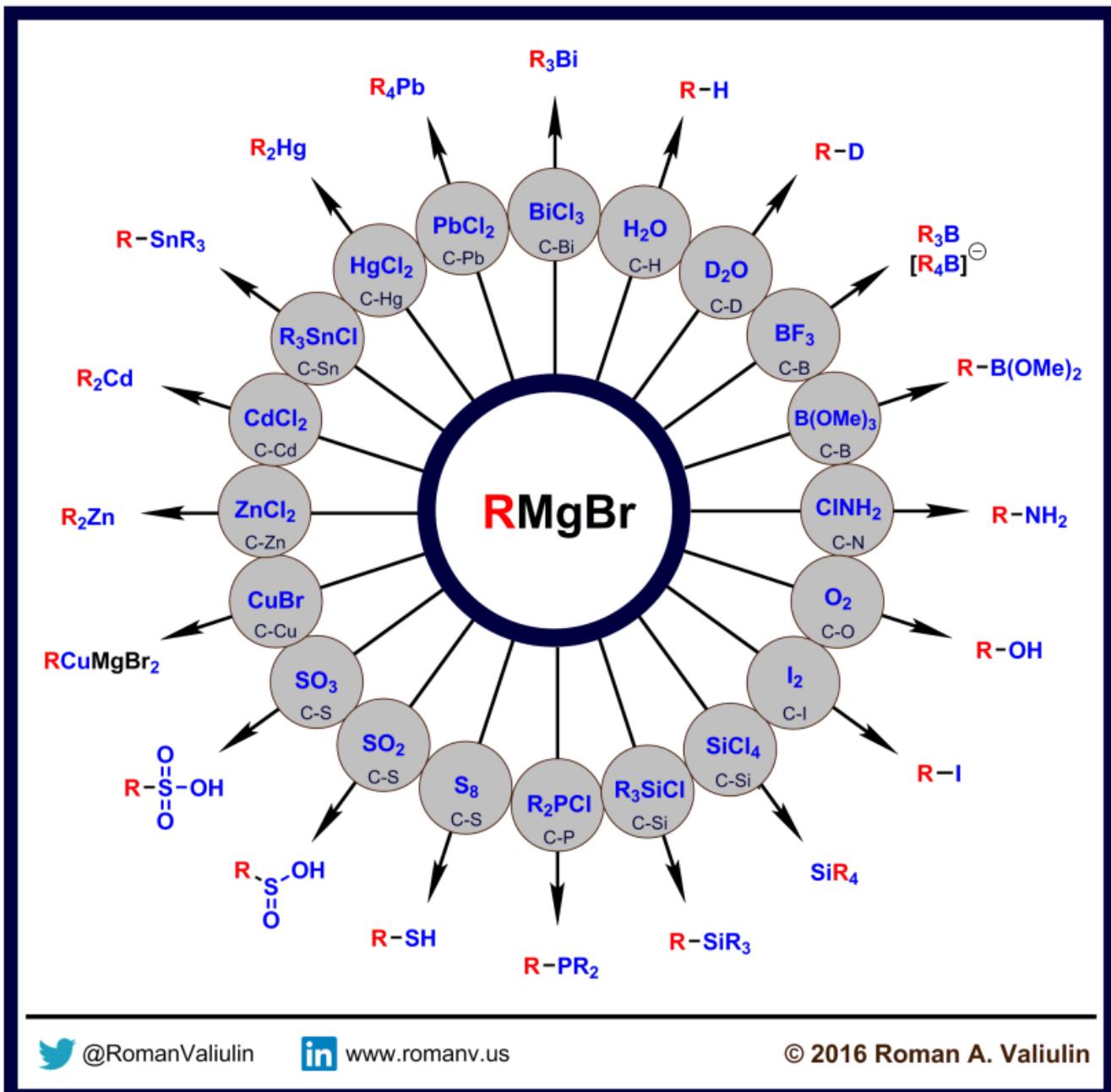
### 3. Grignard Reagent 1900



# Grignard Reagent C-C Bond



## Grignard Reagent C-X Bond



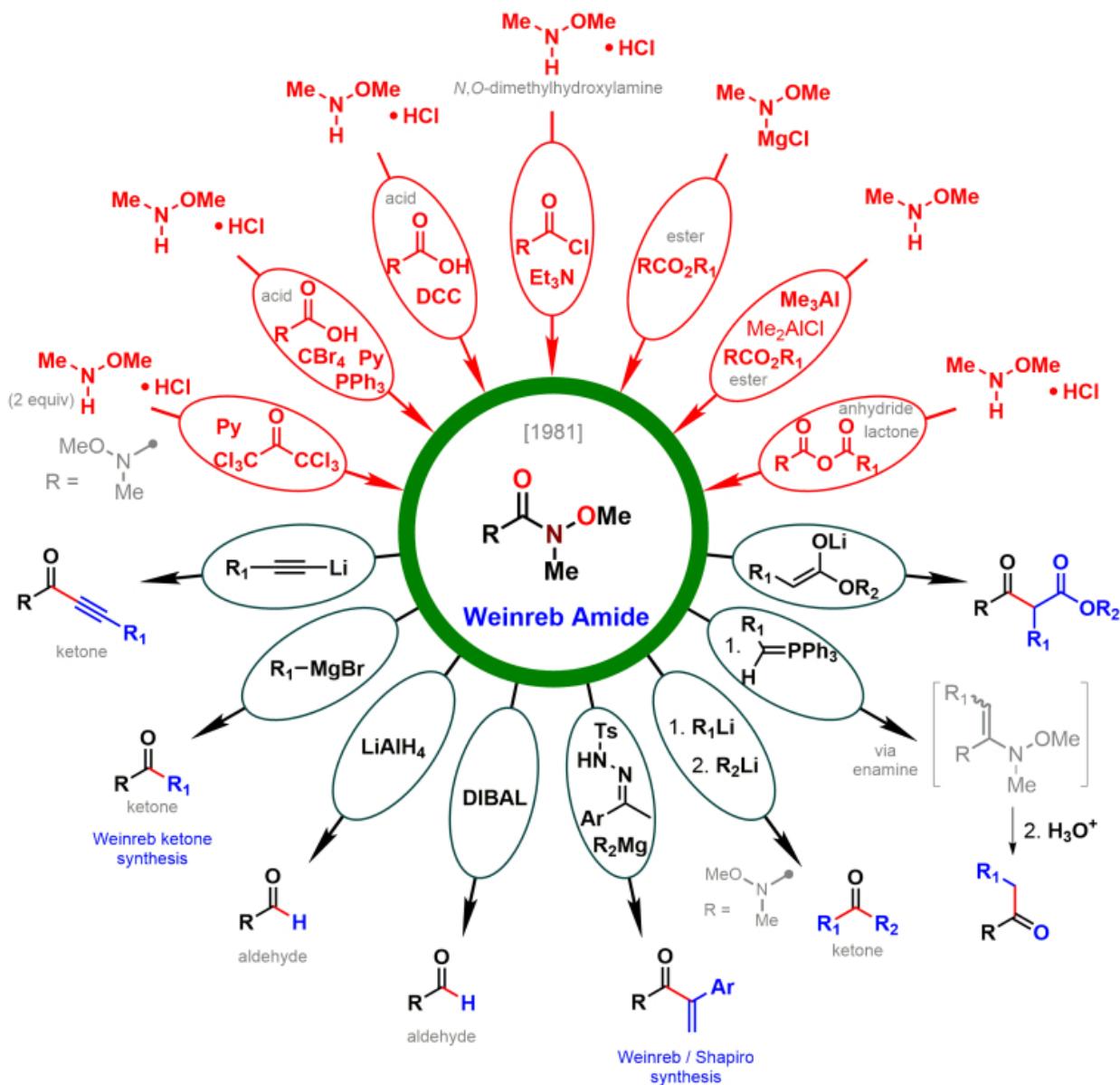
@RomanValiulin



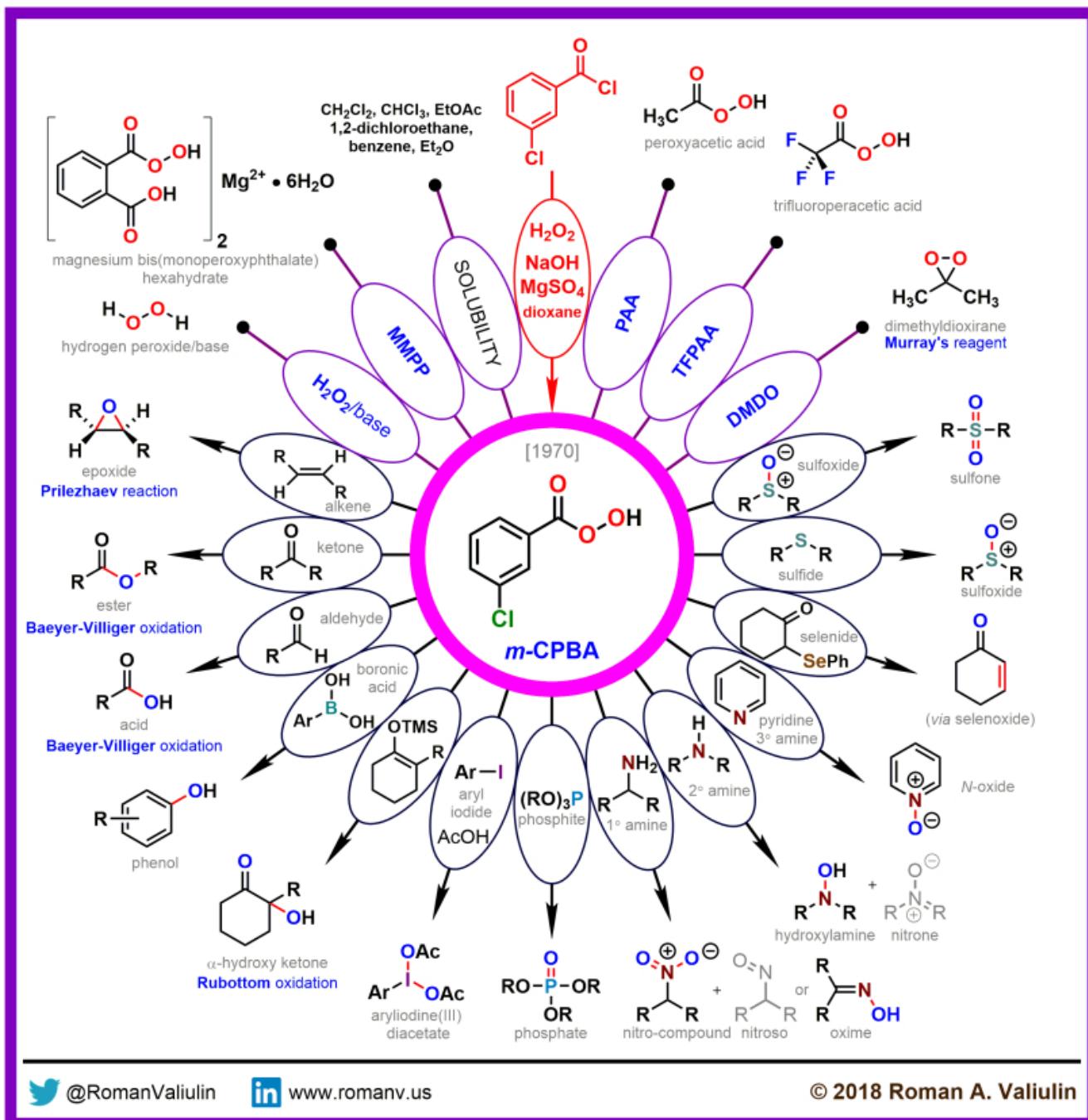
[www.romanv.us](http://www.romanv.us)

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## 4. Weinreb Amide 1981

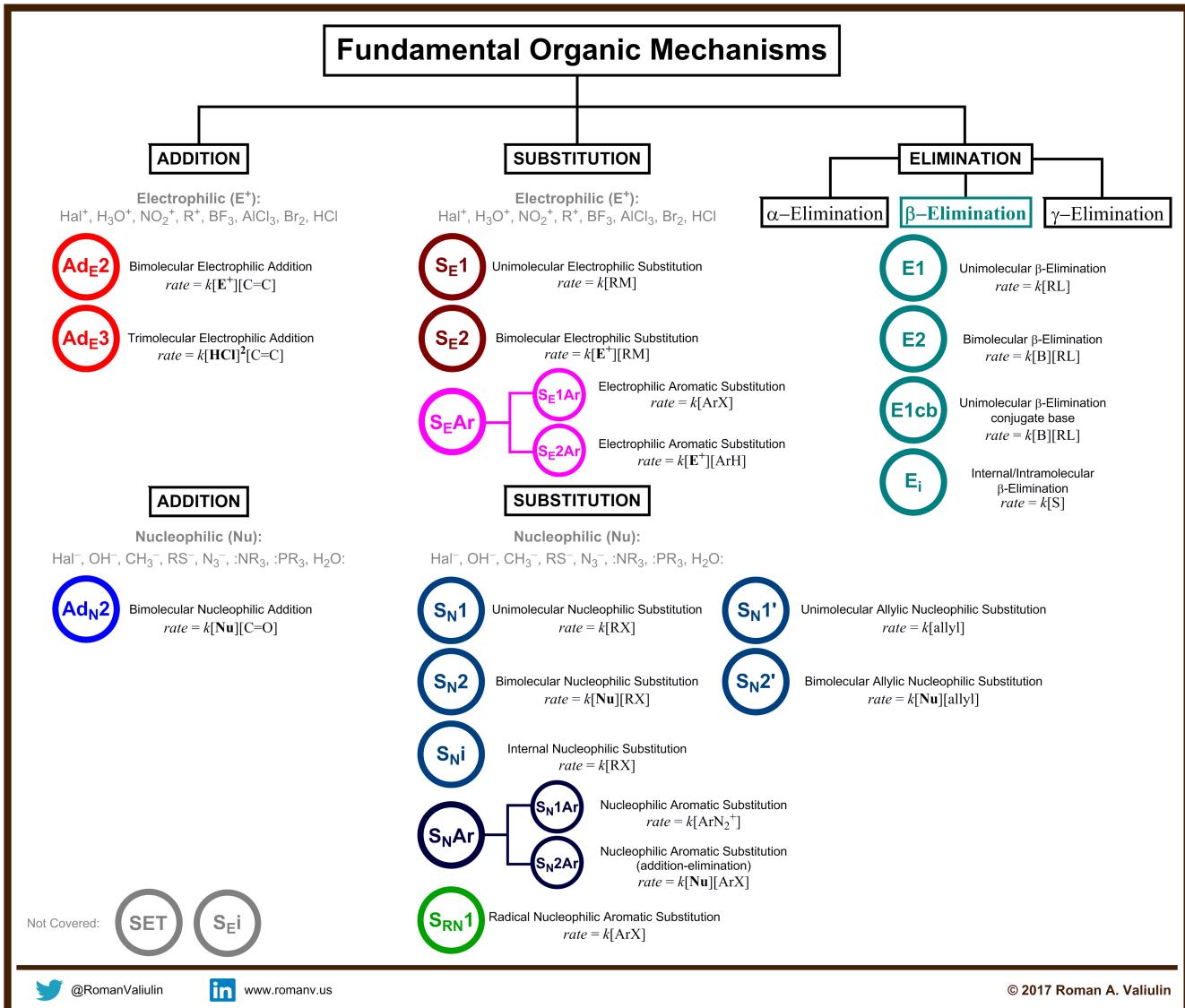


## 5. 3-Chloroperoxybenzoic Acid – mCPBA 1970

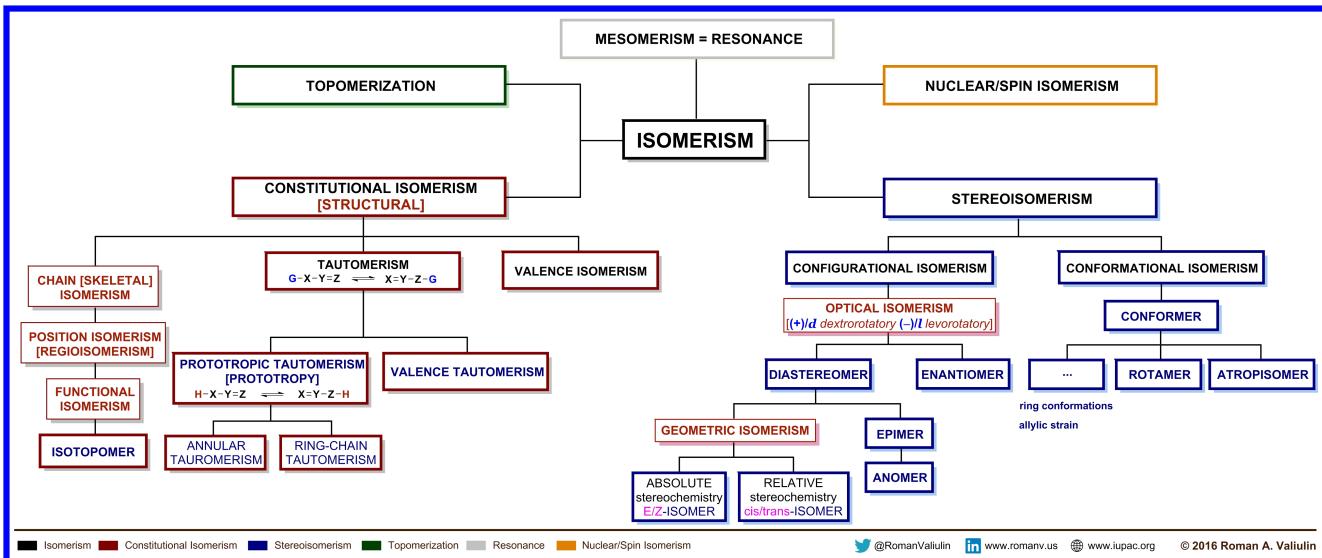


### III. Misc

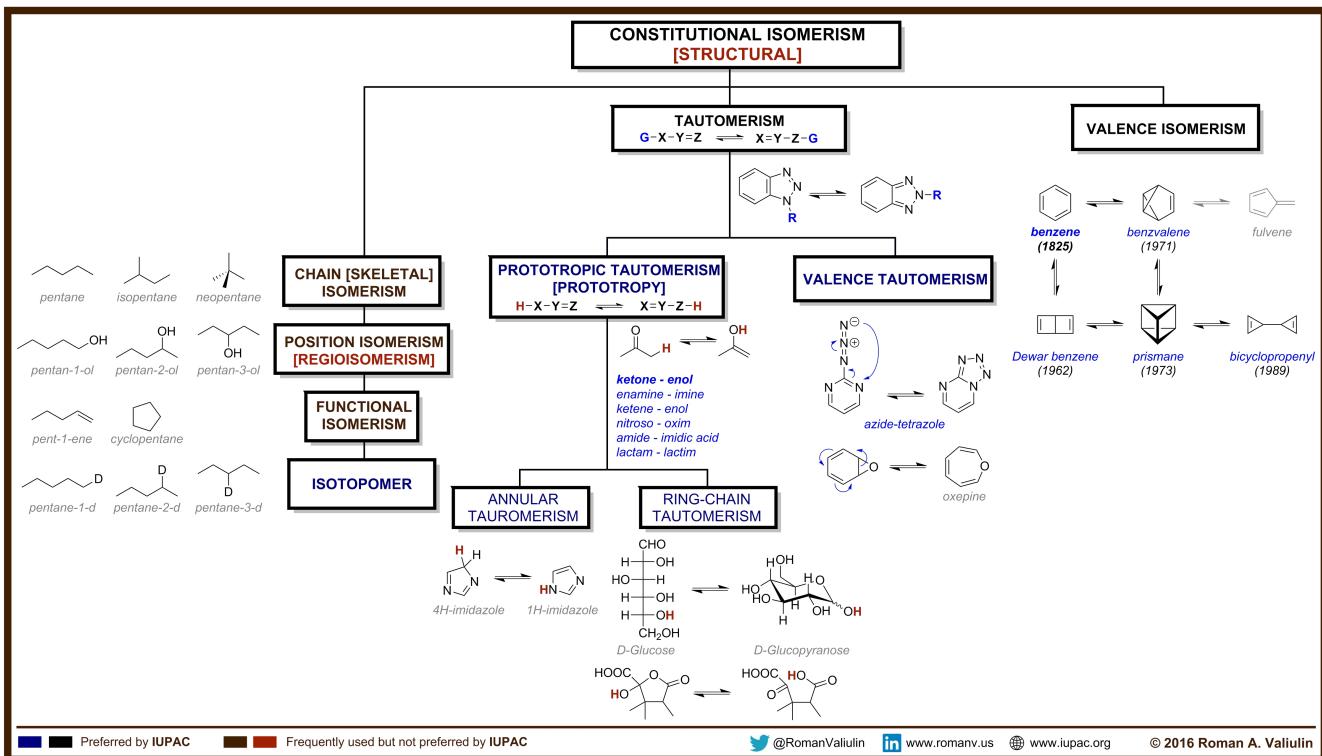
#### 1. Fundamental Organic Mechanisms



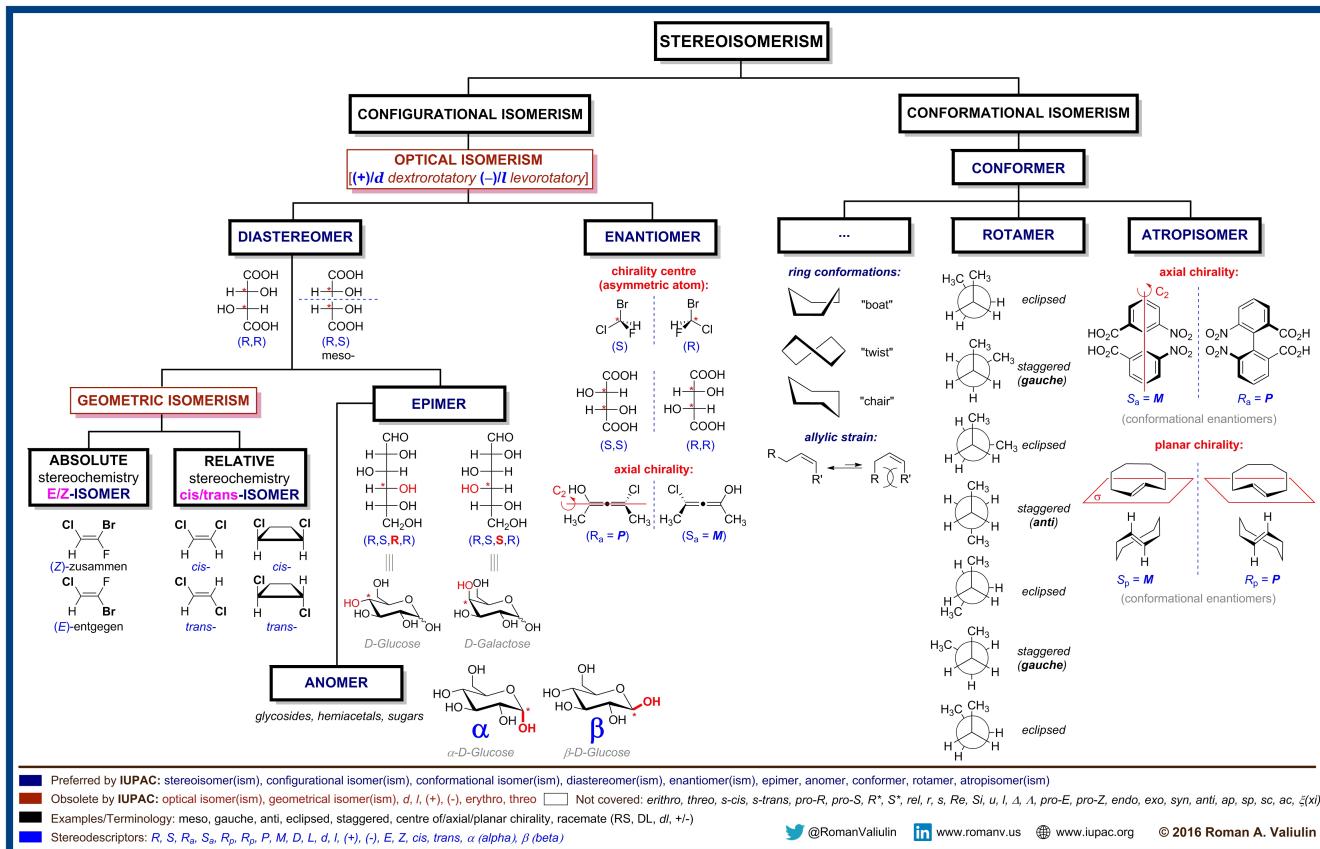
## 2. Isomerism



## 3. Constitutional Isomerism



# 4. Stereoisomerism



Preferred by IUPAC: stereoisomer(ism), configurational isomer(ism), conformational isomer(ism), diastereomer(ism), enantiomer(ism), epimer, anomer, conformer, rotamer, atropisomer(ism)

Obsolete by IUPAC: optical isomer(ism), geometrical isomer(ism), *d*, *l*, (+), (-), erythro, threo Not covered: erithro, threo, *s*-cis, *s*-trans, pro-*R*, pro-*S*, *R*\*, *S*\*, rel, *r*, *s*, *Re*, *Si*, *u*, *I*,  $\Delta$ ,  $\Lambda$ , pro-*E*, pro-*Z*, endo, exo, syn, anti, ap, sp, sc, ac,  $\zeta$ (xi)

Examples/Terminology: meso, gauche, anti, eclipsed, staggered, centre of axial/planar chirality, racemate (RS, DL, dl, +/−)

Stereodescriptors: *R*, *S*, *R*<sub>a</sub>, *S*<sub>a</sub>, *R*<sub>p</sub>, *P*, *M*, *D*, *L*, *d*, *l*, (+), (-), *E*, *Z*, *cis*, *trans*,  $\alpha$  (alpha),  $\beta$  (beta)



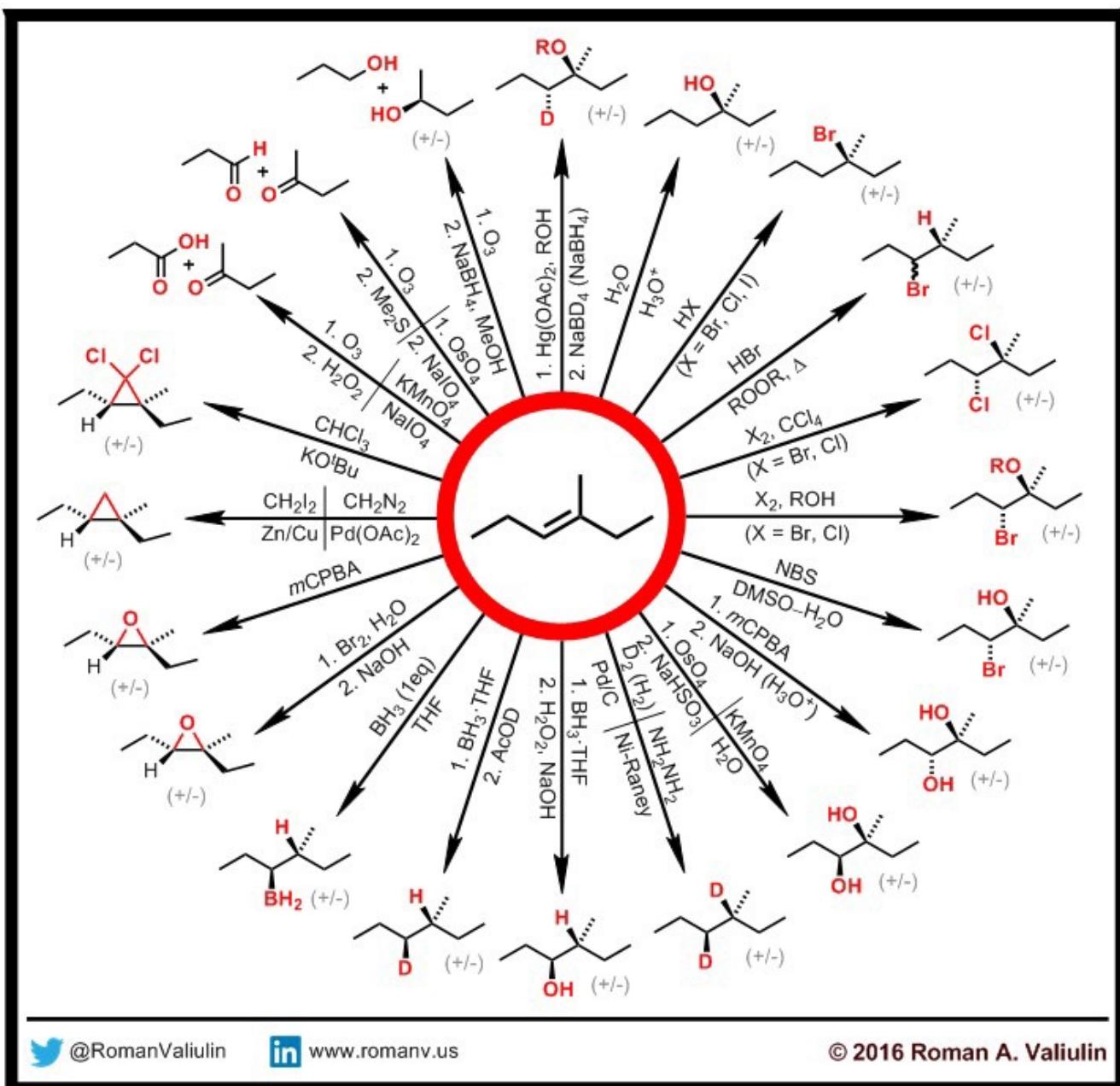
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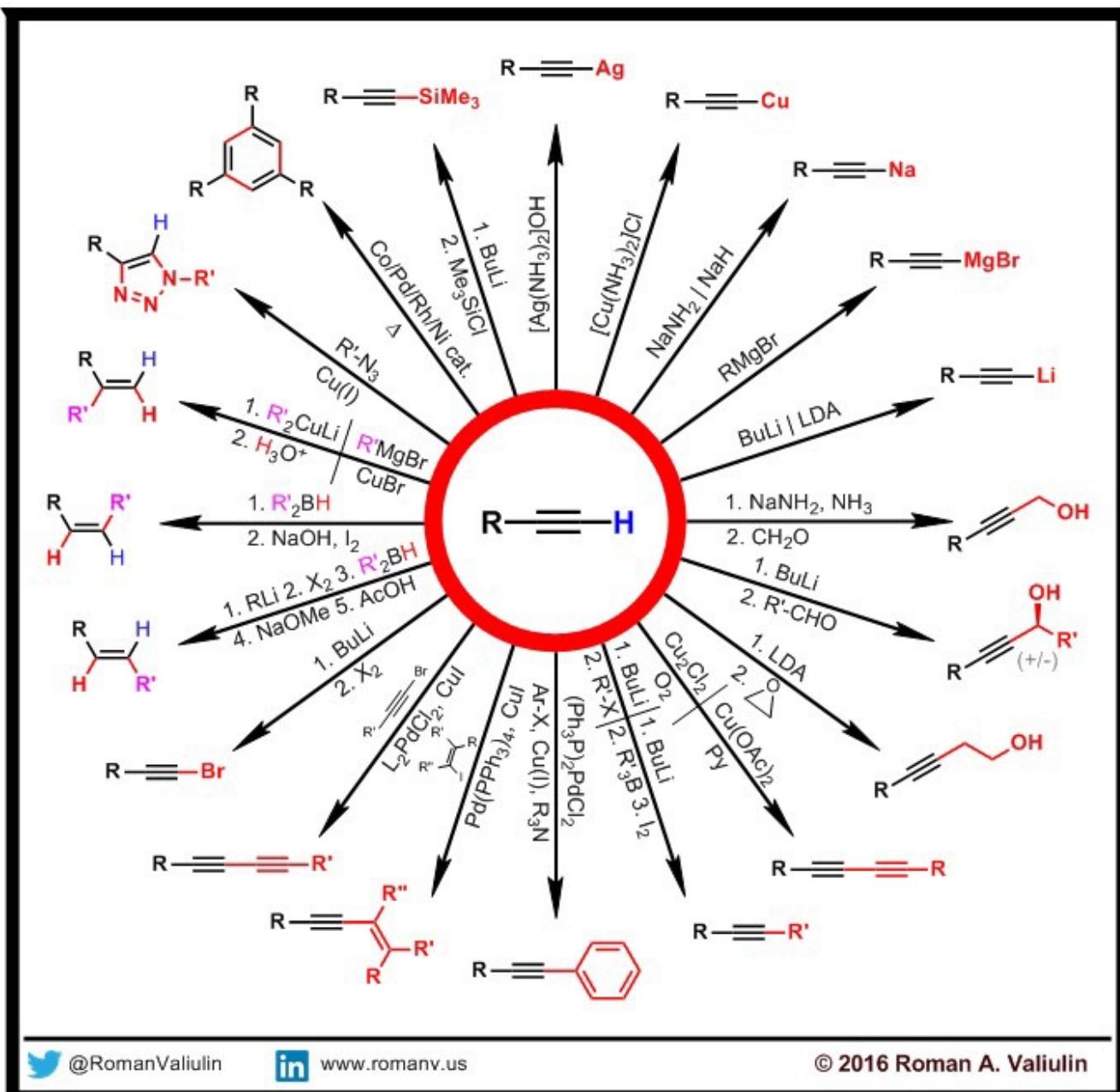
www.iupac.org

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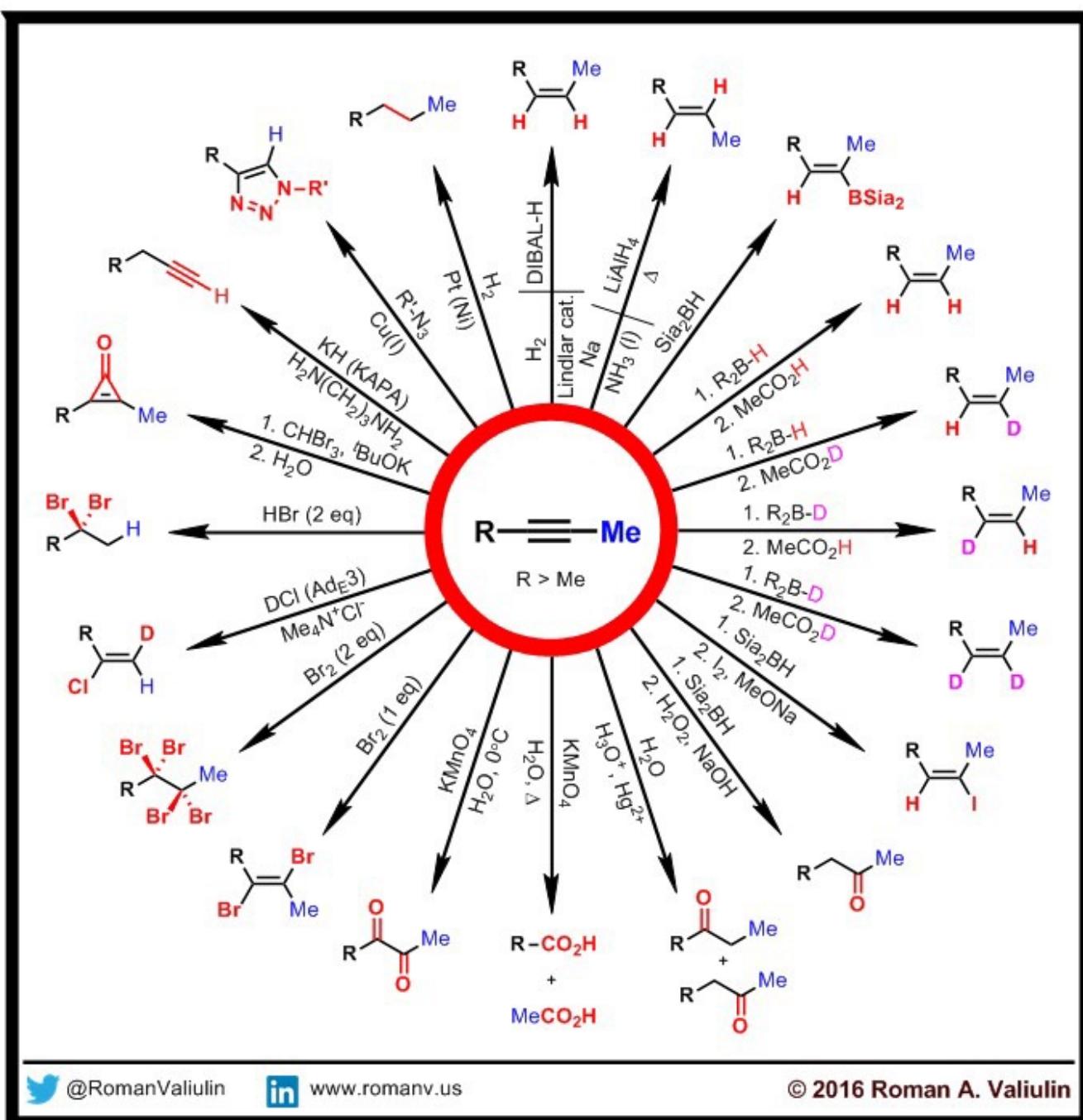
## 5. Alkenes



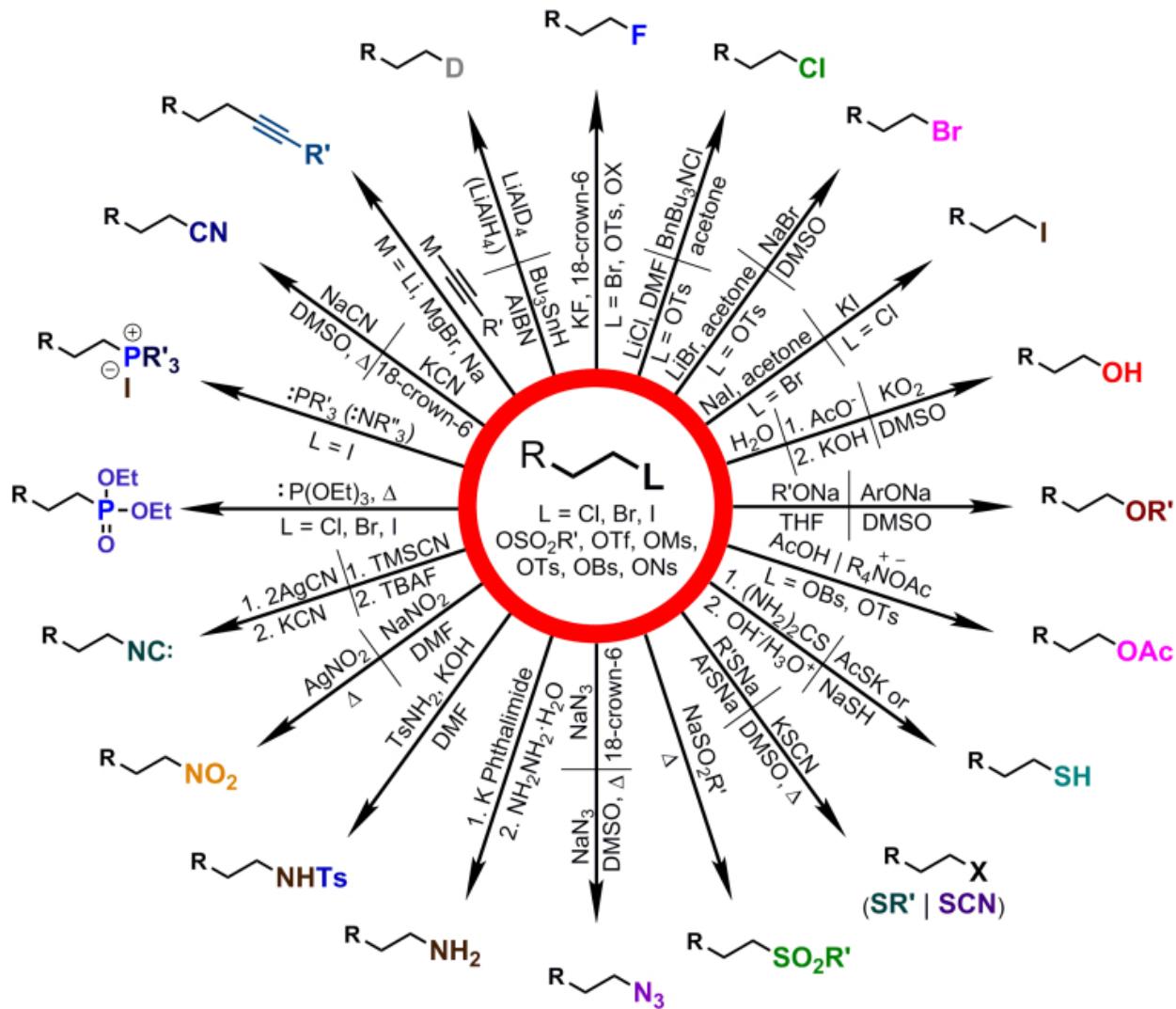
## 6. Terminal Alkynes



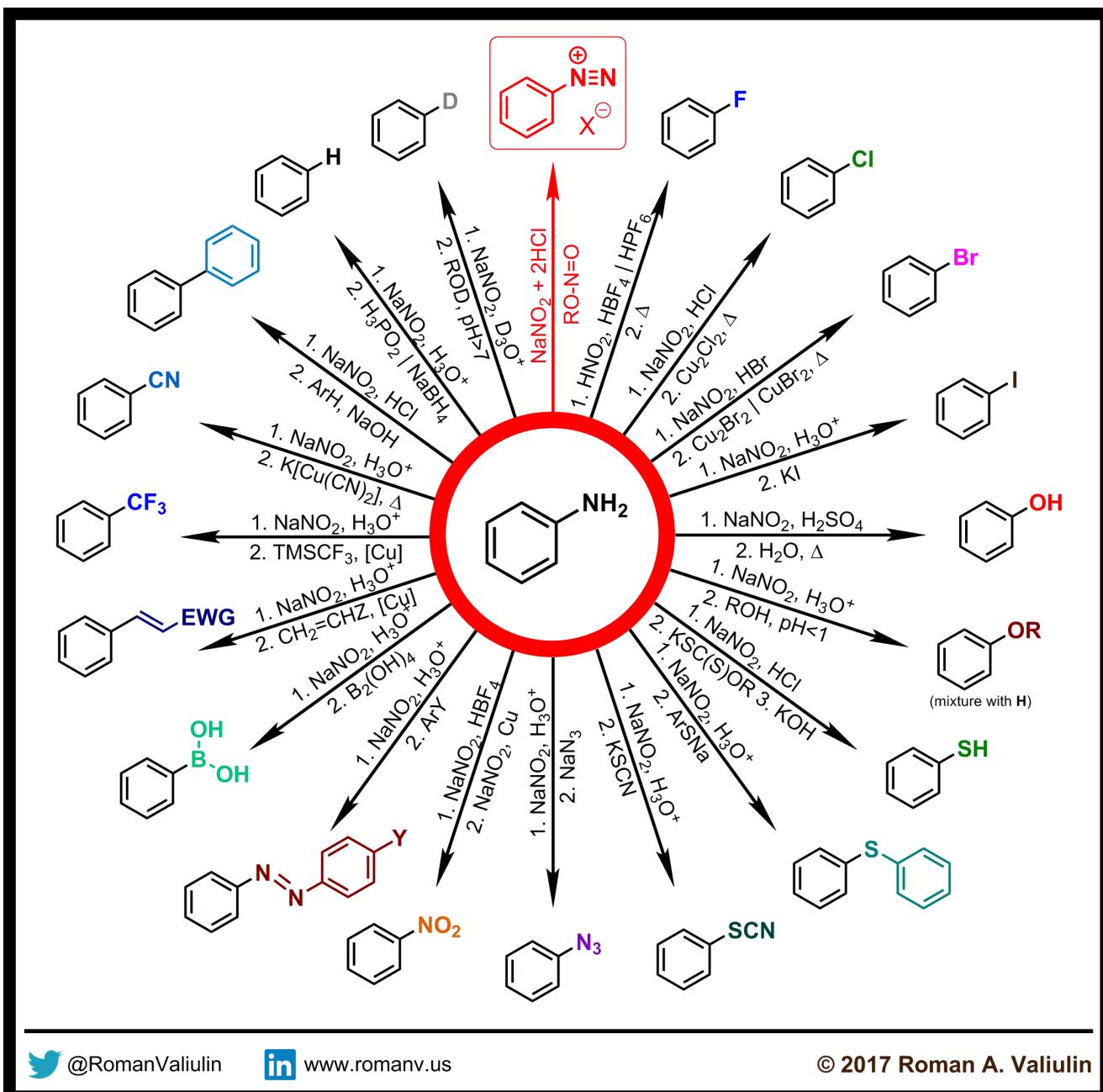
## 7. Internal Alkynes



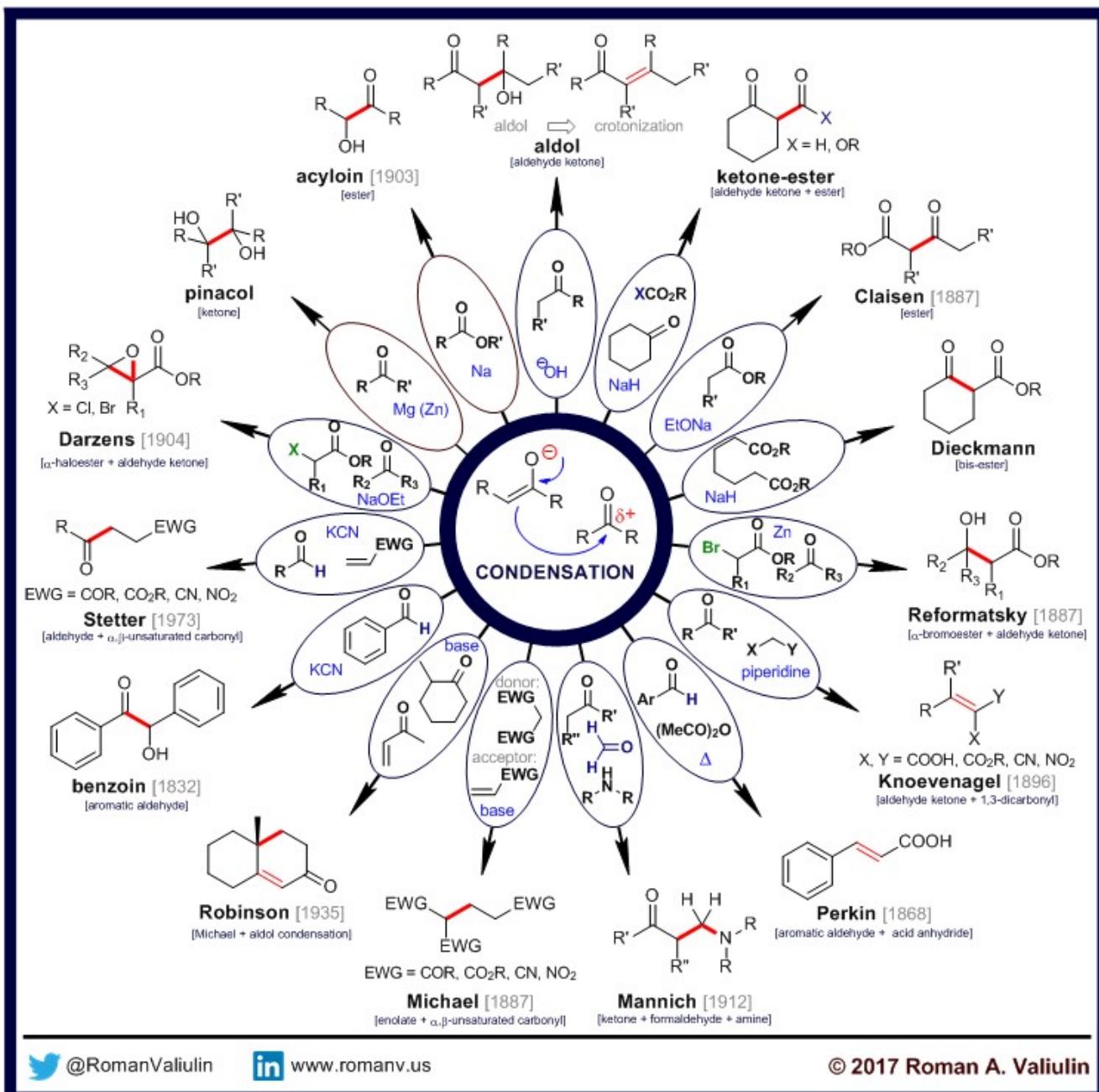
## 8. Nucleophytic Substitution



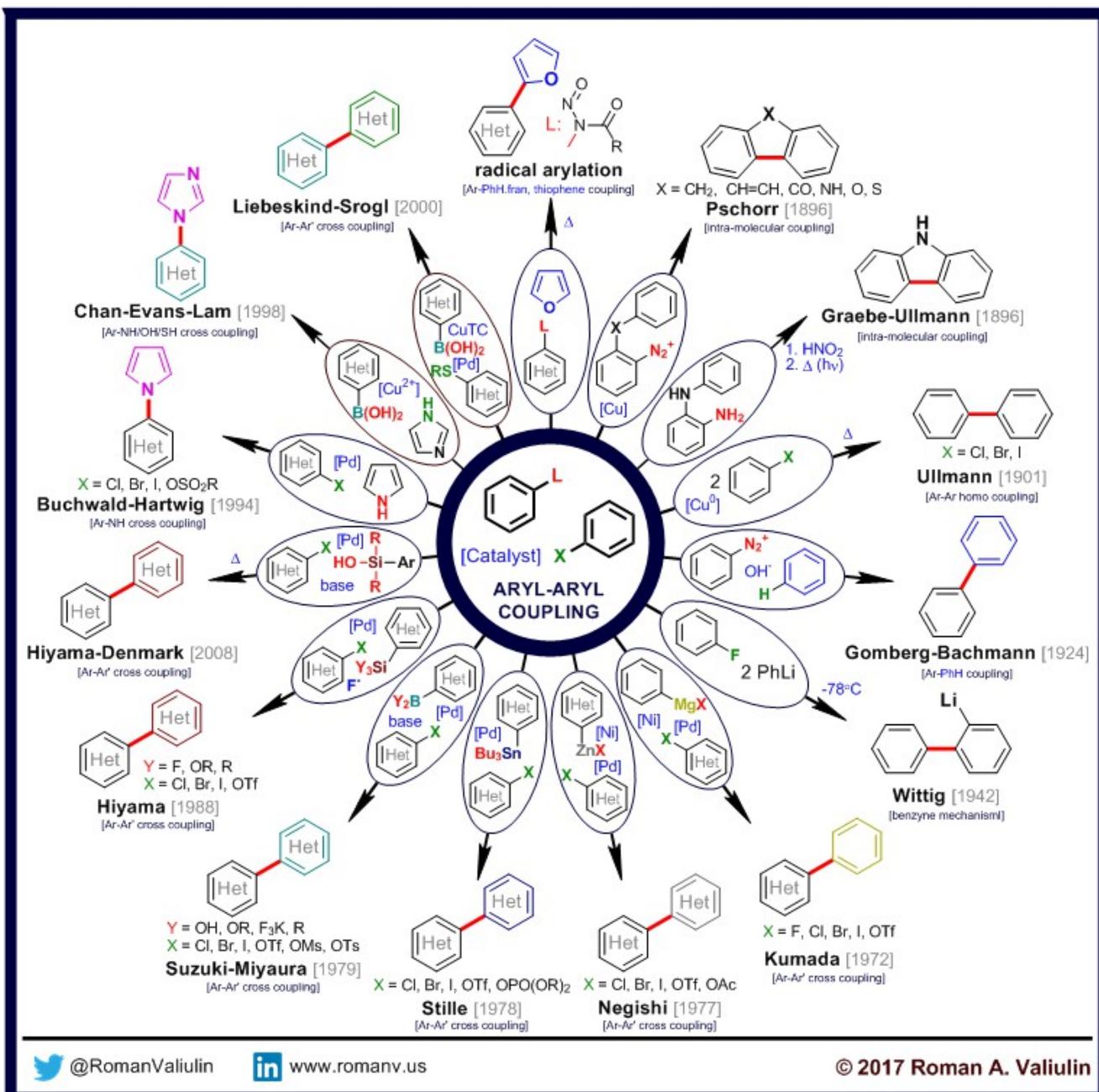
## 9. Diazonium Chemistry



# 10. Condensation



# 11. Aryl-Aryl Coupling



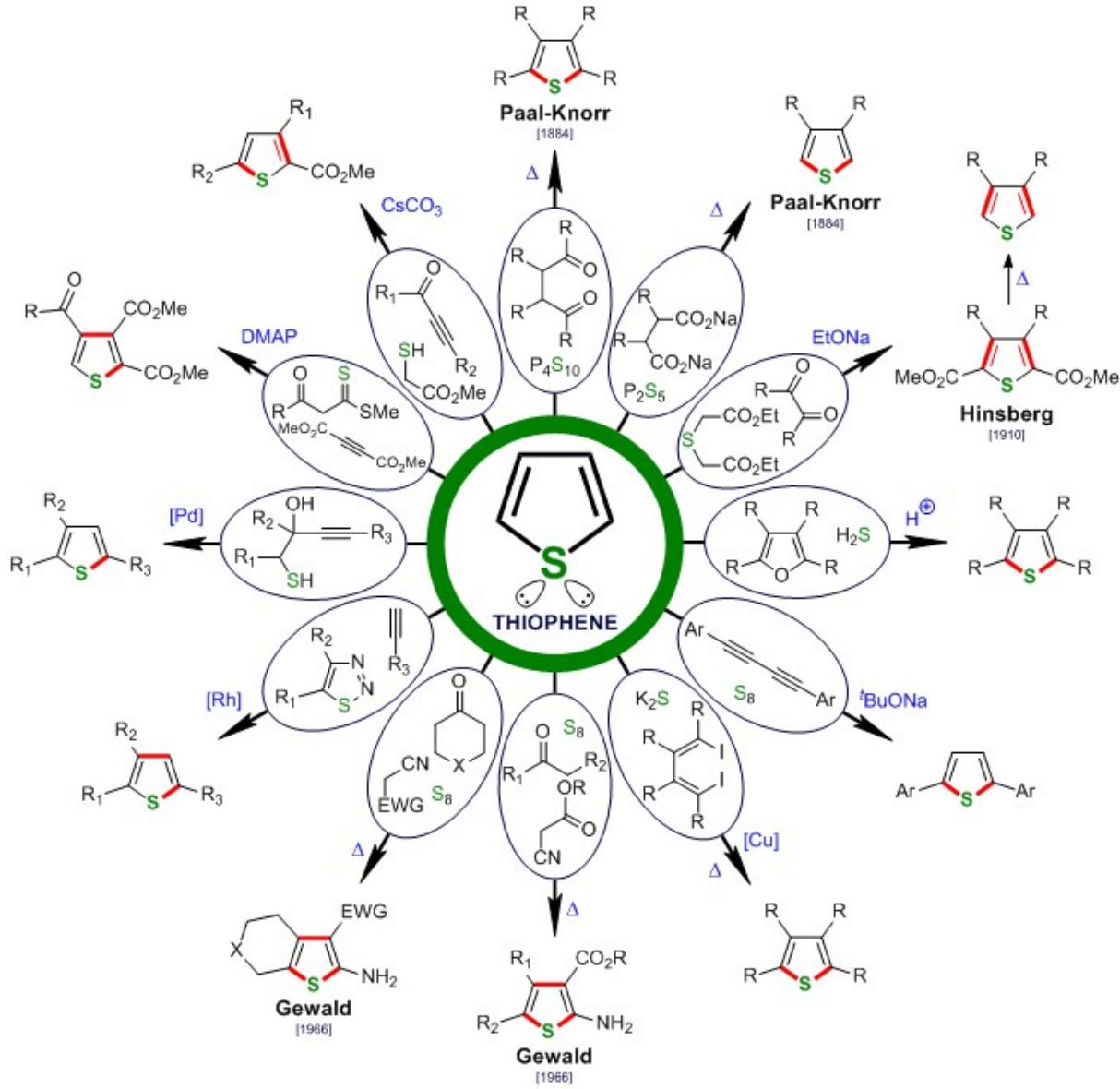
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## 12. Thiophene Synthesis A



## 13. Thiophene Synthesis B

