Angewandte Chemie International
1995 Year in Review

Stephen Harwood

Baran Group Meeting
11/4/17

News:
Oklahoma City Bombing
Michael Jordan returns to the NBA
Quebec Referendum (Canada)
DOW breaks 5000
Space Shuttle Atlantis
OJ found Innocent

Technology
Windows 95
DVD is announced
Ebay

Top 5 Songs
1. Gangsta's Paradise- Coolio
2. Waterfalls- TLC
3. Creep- TLC
4. Kiss from a Rose- Seal
5. On Bended Knee- Boyz II Men

Top 5 Grossing Movies
1. Toy Story (First fully animated picture)
2. Batman Forever
3. Apollo 13
4. Pocahontas
5. Ace Ventura: When Nature Calls

Sports
Superbowl XXIX: SF 49er's beat SD Chargers
World Series: Atlanta Braves beat Cleveland Indians
NBA Finals: Rockets win 4-0 over Magic
Stanley Cup- Devils win 4-0 over Red Wings

Nobel Prizes
Chemistry: Rowland, Molina, Crutzen "For their work in atmosphereic chemistry concerning the formation and decomposition of Ozone."
Physics: Perl (Discovery of tau lepton) **and Reines** (Detection of the neutrino)
Physiology and Medicine: Wieschaus, Lewis, Nüsslein-Volhard
"Discoveries concerning the genetic control of emryonic development

Bill Clintion- President durring 1995

ACIEE 1995 General Stats

Total Articles: 684
TSRI: 11 articles, 2nd most of any institution
Nicolaou 3, Ghadiri 2, Wong 2, Sharpless 1. Janda 1, Reymond 1, Siuzdak 1

Top Performers
1) Wolfgang Herrmann (7 publications
1) Peter Jones (7 Publications)
1) David Williams (7 publications)
4) Stephan Menzer (6 Publications)
4) Hans Greorg Von Schnering (6 Publications)

Top 5 Articles (excluding reviews)

1) A Series of Well-Defined Metathesis Catalysts—Synthesis of $[RuCl_2(=CHR')(PR_3)_2]$ and Its Reactions
by Grubbs et al. **2039 (828 Citations)**

2) Synthesis of Hexagonally Packed Mesoporous TiO_2 by a Modified Sol- Gel Method
by Ying et al. 2014 **(674 Citations)**

3) A Simple Catalytic Method for the Conversion of Aryl Bromides to Arylamines
by Buchwald et al. 1348 **(638 Citations)**

4) Metal Complexes of N-Heterocyclic Carbenes— A New Structural Principle for Catalysts in Homogeneous Catalysis
by Herrmann et al. 2371 **(531 Citations)**

5) Palladacycles as Efficient Catalysts for Aryl Coupling Reactions
by Beller, Herrmann et al. 1844 **(492 Citations)**

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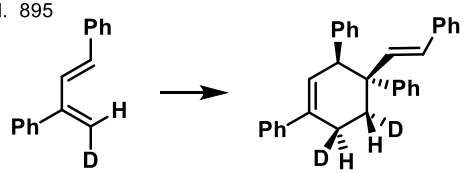
Physical Organic Mechanisms

The Cope Rearrangement Transition Structure Is Not Diradicaloid, but Is It Aromatic?

Schleyer et al. 334

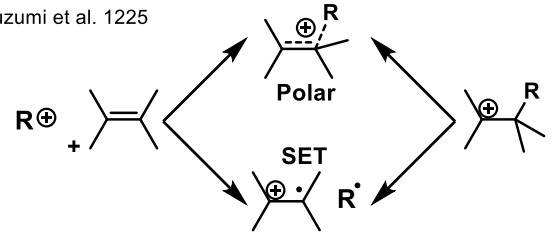
The Dimerization of (E)-1,3-Diphenyl-1,3-butadiene Proceeds Suprafacially with Respect to Both Components: Evidence for a Concerted [4+ 2] Cycloaddition

Mulzer et al. 895



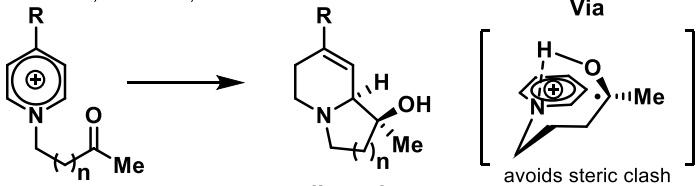
Reactions of Carbocations with π Nucleophiles Polar Mechanism and No Outer Sphere Electron Transfer

Fukuzumi et al. 1225



Diastereoselective Cathodic Cyclization of 1-(4- and 1-(3-Oxoalkyl)pyridinium Salts to Quinolizidine and Indolizidine Derivatives

Schafter, Fröehlich, et al. 2007



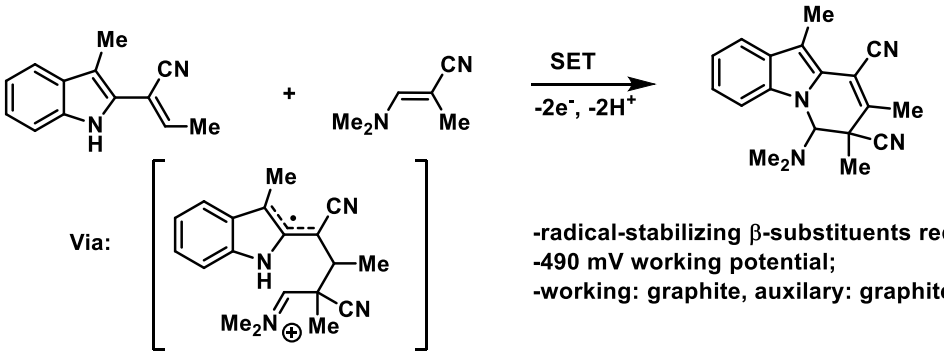
n= 1, 2, 3

+ alkene isomers
+ carbonyl reduction

avoids steric clash of methyl

Radical Cation [4+2] Cycloadditions with 2-Vinylindoles

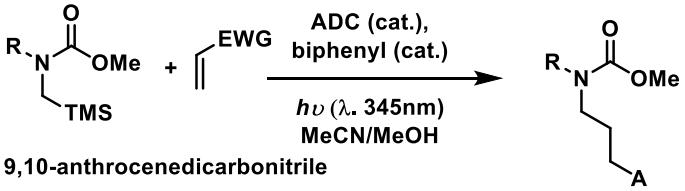
Blechert, Steckhan et al. 1900



-radical-stabilizing β-substituents required
-490 mV working potential;
-working: graphite, auxilary: graphite

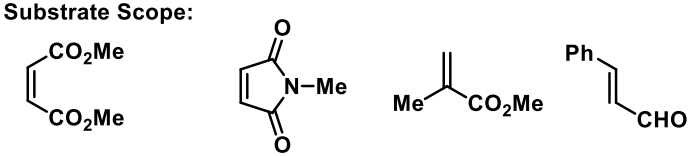
Radical C-C Bond Formation by Photoinduced Electron Transfer Addition of α-Silyl Carbamates to Acceptor-Subsituted Alkenes

Steckhan et al. 2137



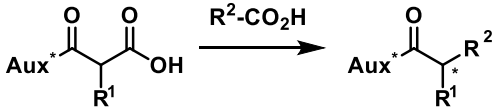
ADC= 9,10-anthrocenedicarbonitrile

Substrate Scope:



Diastereoselctive Coupling of Anodically Generated Radicals Bearing Chiral Amide Groups

Schäfer, Fröehlich et al. 189



Yield: 13-69%
de: 20-86%

R^2= alkyl, 1 example of an ether

conditions:
5-10 eq. R_2-CO_2H
Steel Cathode; Platinum anode
Current Density: 600mAcm^{-2},
35 °C

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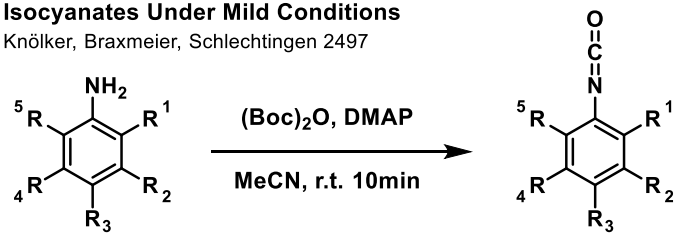
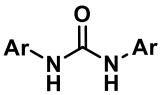
A Novel Method for the synthesis of Isocyanates Under Mild Conditions

Knölker, Braxmeier, Schlechtingen 2497



Sterically hindered alkyl amines also work

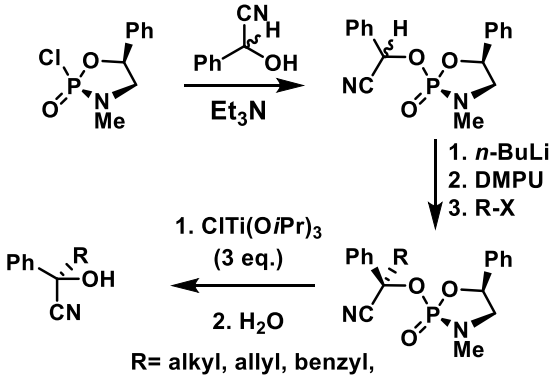
When using bis(4-nitrophenyl) carbonate Ureas were the major product:



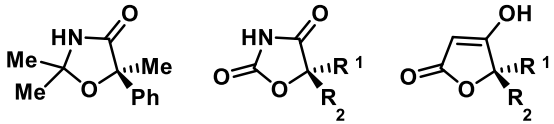
Mild alternative to traditional isocyanate formation

A Chiral Cyanohydrin Phosphate for Carbonyl Umpolung—Stereoselective Synthesis of Tertiary Cyanohydrins

Thomas Schrader 917



R= alkyl, allyl, benzyl,
de= 82-94%
after hydrolysis and recrystalization
ee= >96%

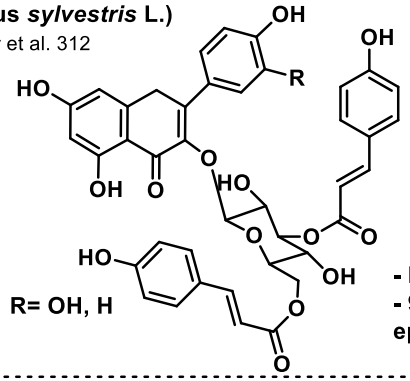


-First method for tertiary cyanohydrin synthesis
-Cyanohydrin phosphates can be used as chiral nucleophiles for Michael Reactions

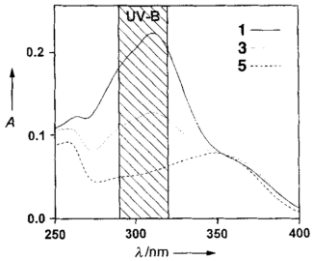
Schrader Eur. J. Chem 1997, 3, 8, 1273.

Structures of UV-B Induced Sunscreen Pigments of the Scots Pine (Pinus *sylvestris* L.)

Heller et al. 312



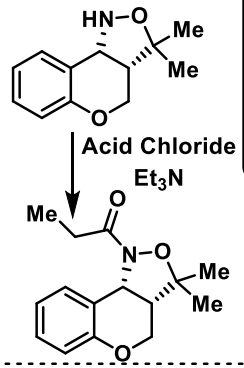
R= OH, H



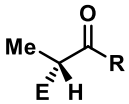
- Isolated from pine needles
- 94% of the compound exists in epidermis of the needles.

Benxopyranoisoxazolidines as Chiral Auxiliaries for Asymmetric Synthesis

Masamune et al. 793

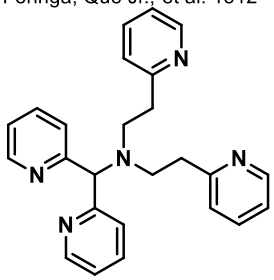


Electrophile	Yield	dr
$PhCH_2Br$	93	99:1
$CH_2{=}CHCH_2Br$	96	98:2
$CH_2{=}C(CH_3)CH_2Br$	78	96:4
$n\text{-}C_5H_{11}I$	93	98:2
$C_6H_{11}CH_2OTf$	90	98:2

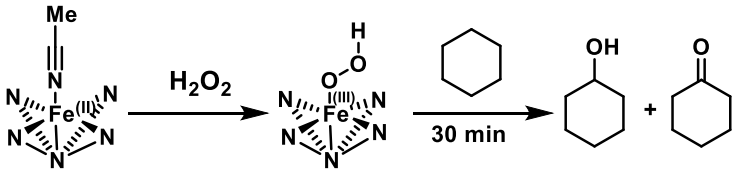


Nonheme Iron Centers in Oxygen Activation: Characterization of an Iron(III) Hydroperoxide Intermediate

Feringa, Que Jr., et al. 1512



N4Py



- First MS evidence of a synthetic hydroperoxoiron(III)
- 36 turnovers/hour
- 1000 eq. cyclohexane
-13 eq. hexanol and 5 eq. hexanone formed

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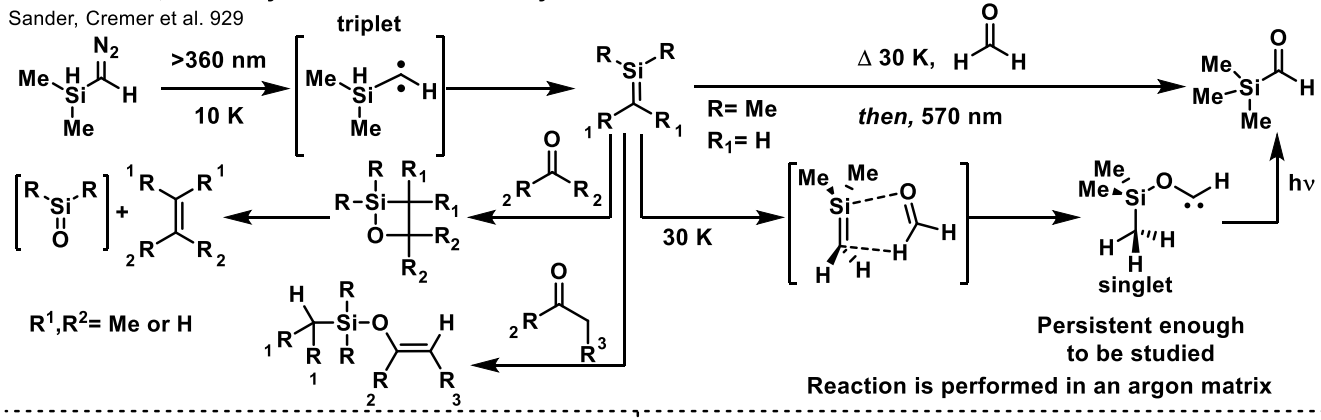
Reaction of 1,1-Dimethylsilene with Formaldehyde

Sander, Cremer et al. 929

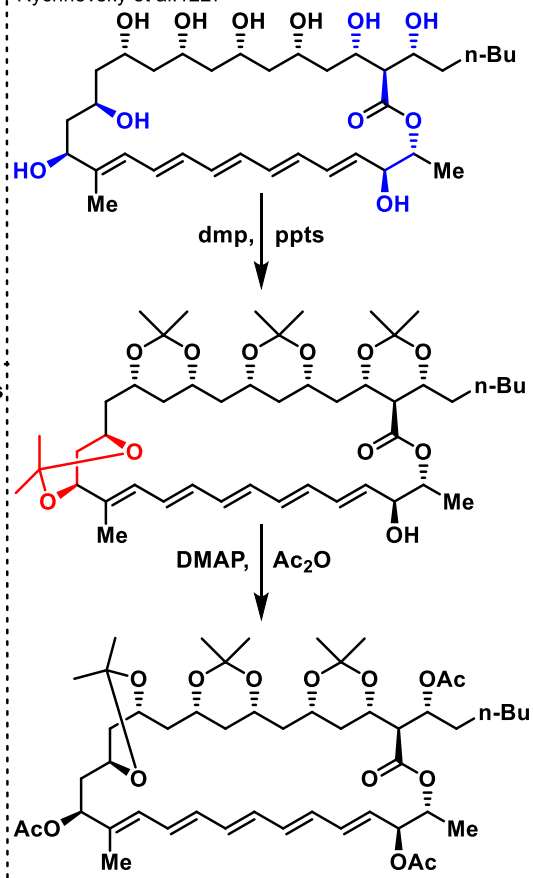


Persistent enough to be studied

Reaction is performed in an argon matrix

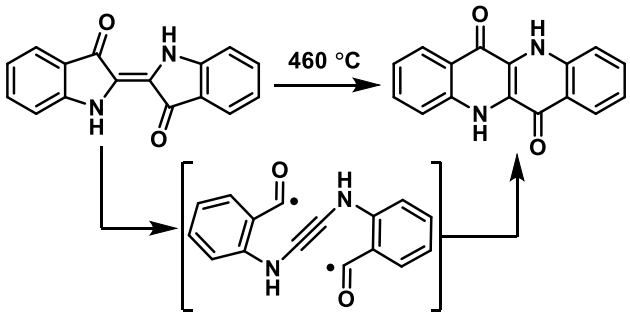
Relative and Absolute Configuration of Filipin III

Rychnovsky et al.1227



Thermal Isomerization of Indigo

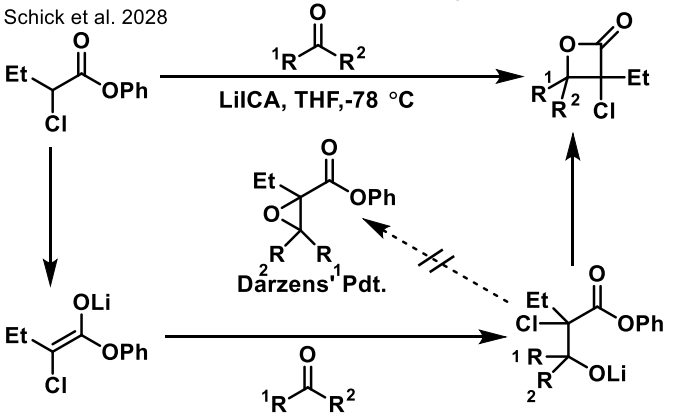
Haucke et al. 67



- Dyotrope rearrangment allowed if π-electrons included in the TS
- Calculations of E_a suggest stepwise mechanism

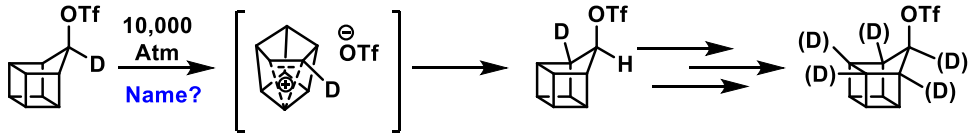
Unexpected Course of the Darzens Reaction of Phenyl esters of α–Chlorocarboxylic Acids with Carobonyl Compounds—A Novel One-Step Synthesis of α-Chloro-β-lactones

Schick et al. 2028



Fluxionality Induced by High Pressure: [9-D]9-Homocubyl Triflate, a Pressure-sensing Molecule

Spitz and Eaton, 2030



Statistical distribution acheived after 3 days.
No byproducts observed.

Effects of Pressure:
1) Le Chateliers principle in effect:
Favors product with decreased volume.
(Diels-Alder Transition state has negative volume of activation)
2) Electrostriction:
Polarization of solvent induced by ions causes the dielectric medium to pack more tightly and decrease its volume.

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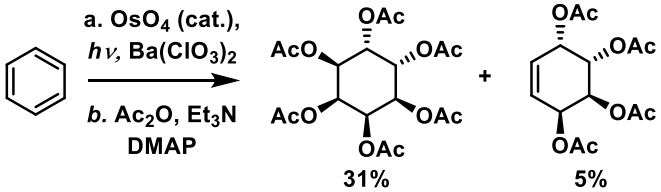
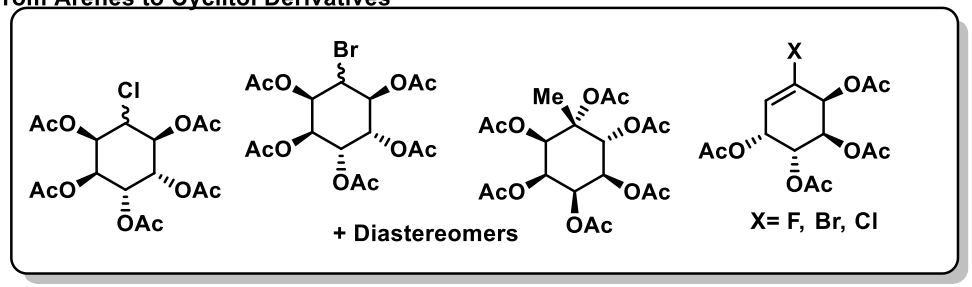
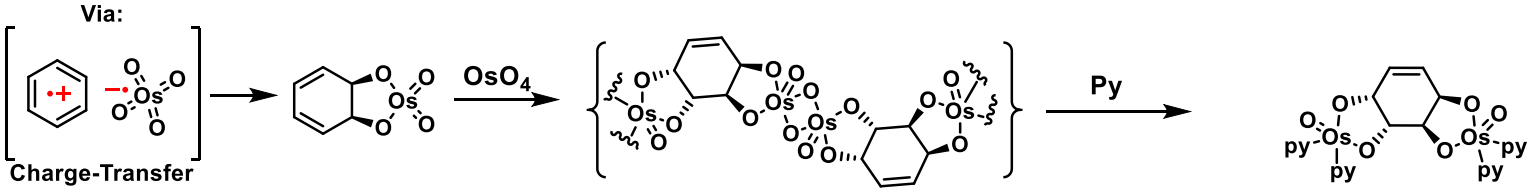
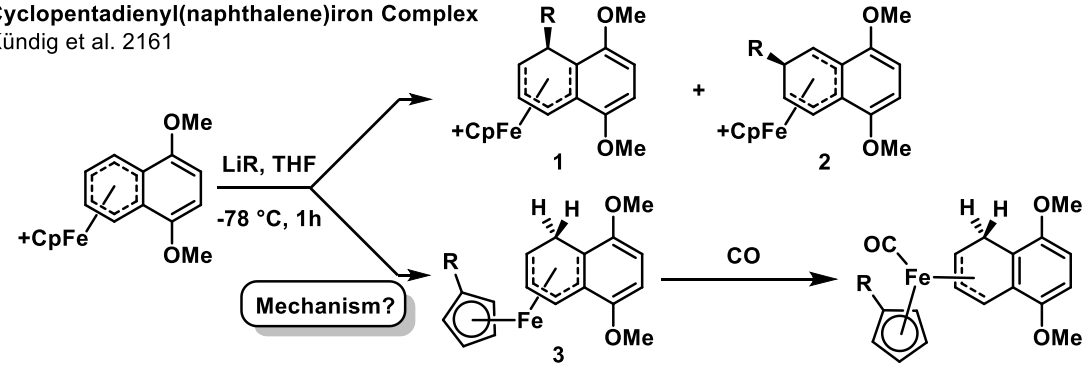
Catalytic Photoinduced Charge-Transfer Osmylation: A Novel Pathway from Arenes to Cyclitol Derivatives
Motherwell and Williams 20313



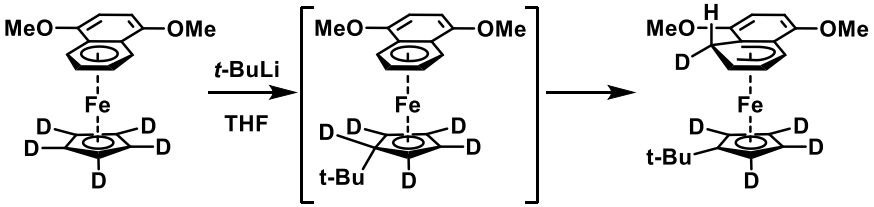




Additions of Carbanions to a Cationic Cyclopentadienyl(naphthalene)iron Complex
Kündig et al. 2161



Nucleophile	1	2	3	Yield
$LiCH_2CN$	91	9	0	85
$LiCH_2CO_2tBu$	80	20	0	97
tBuLi	0	0	100	77
$NaBH_4$	69	31	0	92
MeLi	72	17	11	91
PhLi	61	26	13	92
AllylLi	75	7	18	98
$LiCMe_2CN$	36	35	29	84
$LICHS(CH_2)_3S$	0	66	34	92



Cited by:
"Transition metals in organic synthesis. Highlights for the year 1995"
Louis Hegedus
Coordination Chemistry Reviews 1997, 129

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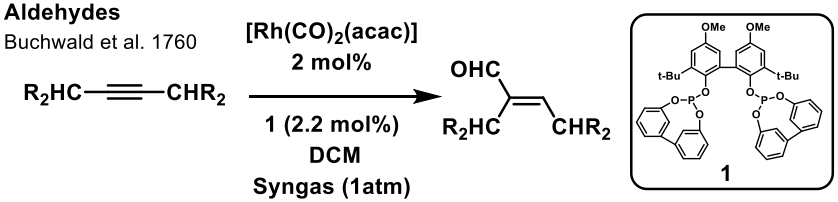
Rhodium-Catalyzed Hydroformylation of Internal Alkynes to α,β-Unsaturated Aldehydes

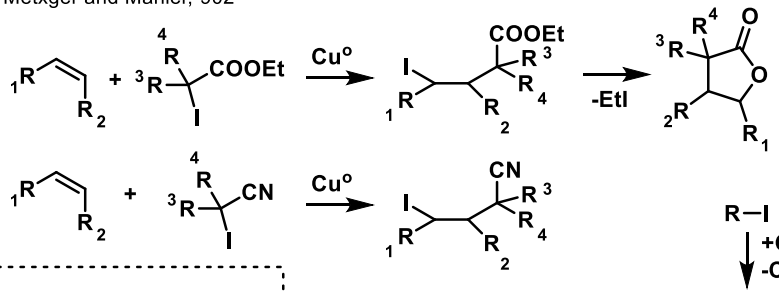
Buchwald et al. 1760

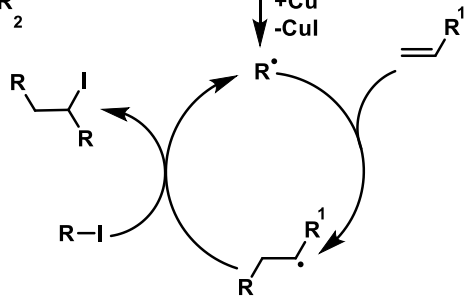


Regioselectivity: Insertion occurs on less sterically encumbered side.
Authors also note that electronics can also influence regioselectivity.

Radical Additions of Activated Haloalkanes to Alkenes Initiated by Electron Transfer from Copper in Solvent-Free System

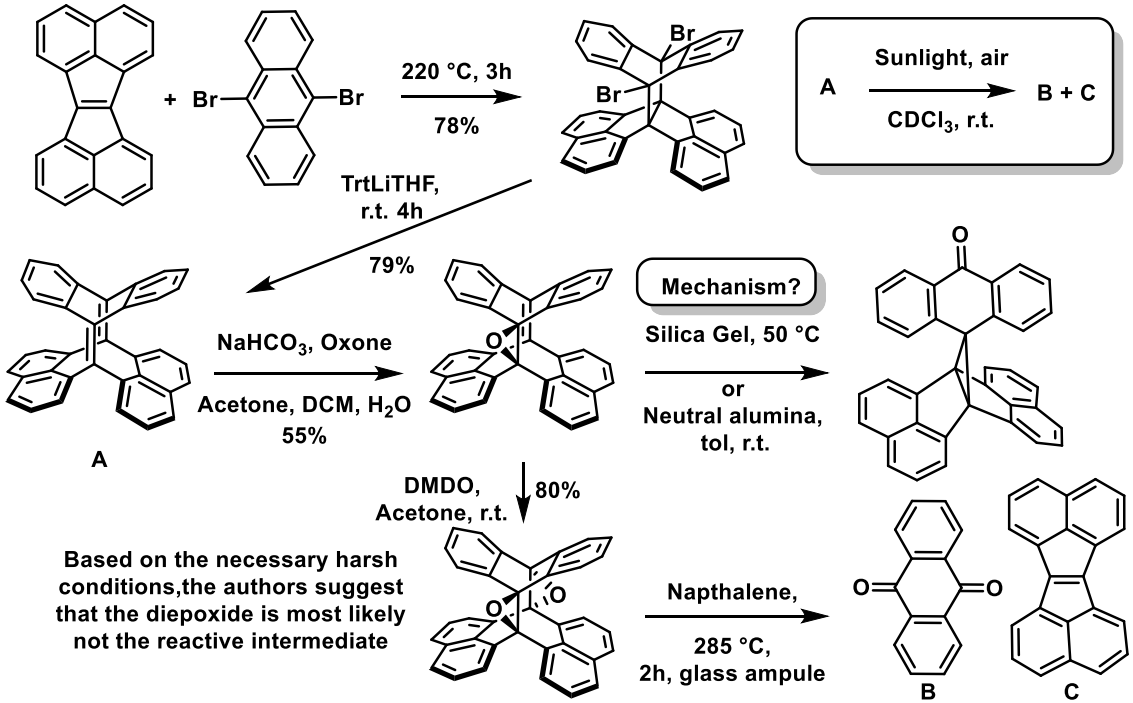
Metxger and Mahler, 902





Oxidative Transformations of a Pyrimidalized 1,5- Diene

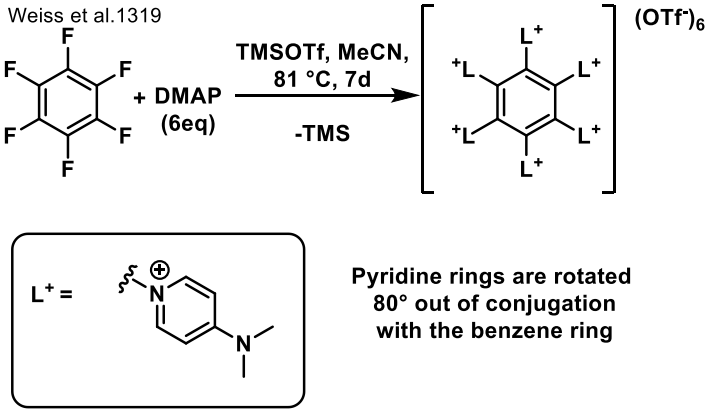
Dyker et al.2502



Based on the necessary harsh conditions,the authors suggest that the diepoxide is most likely not the reactive intermediate

First-Ever Per(onio) Subsitution of Benzene: The Role of the Counterion

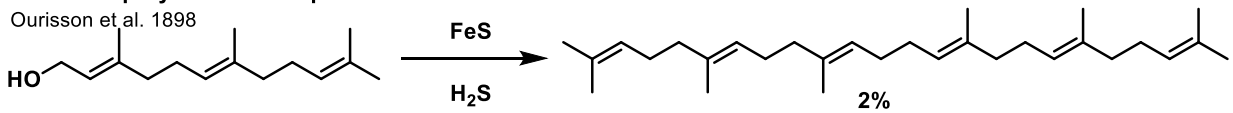
Weiss et al.1319



Pyridine rings are rotated 80° out of conjugation with the benzene ring

A One-Step Synthesis of Squalene From Farnesol under Prebiotic Conditions

Ourisson et al. 1898



Major product is Squalene monothiol

Prebiotic reductive coupling run in H_2O under Argon

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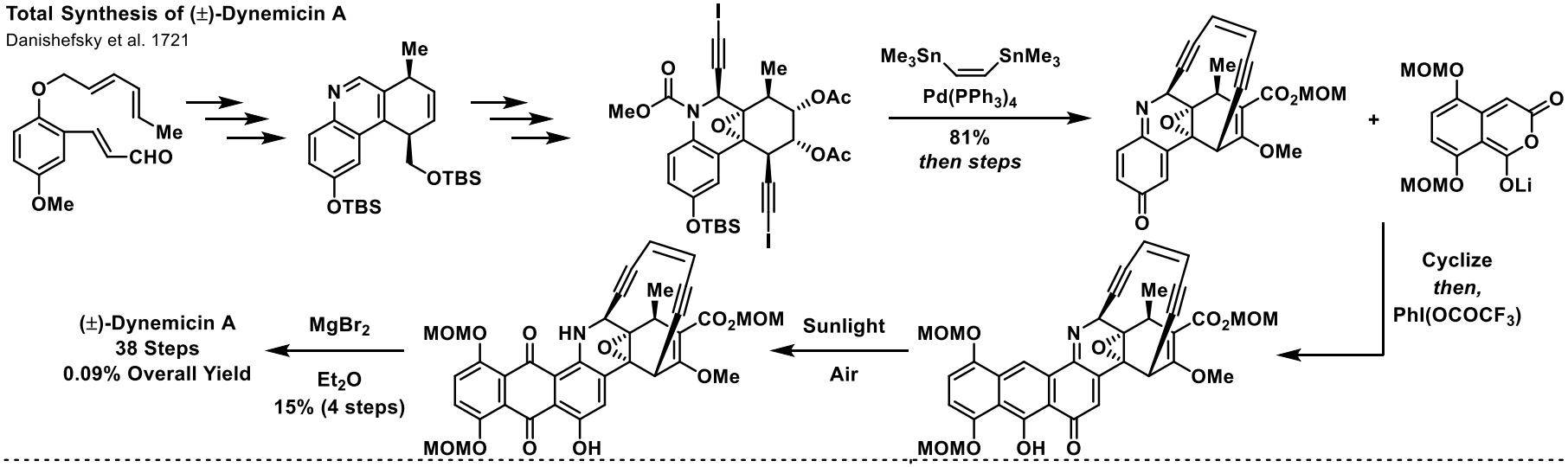
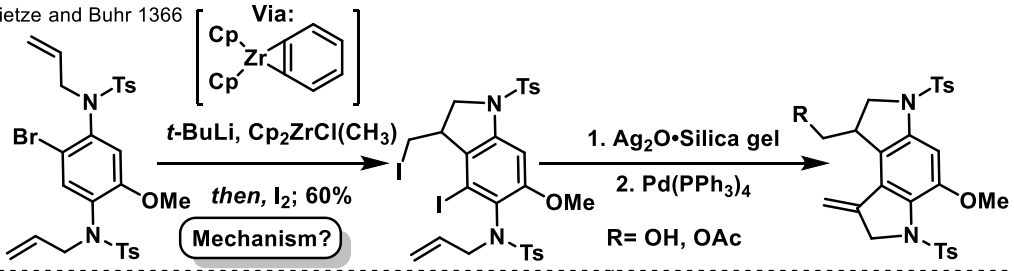
Total Synthesis of (±)-Dynemicin A

Danishefsky et al. 1721



Efficient Total Synthesis of the Pharmacophore of the Anticancer Antibiotic CC-1065 by Zirconocene- and Palladium-Initiated Cyclizations

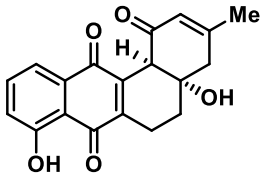
Tietze and Buhr 1366

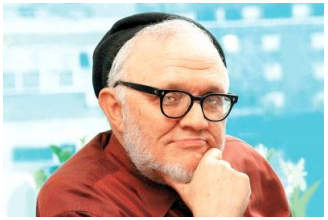


Total Synthesis Topics Not Covered

Total Synthesis of Natural (+)- SF2315A and Determination of the Absolute Configuration

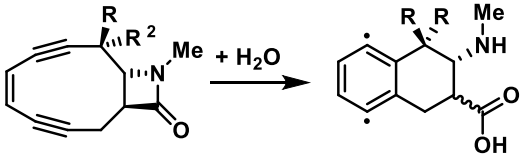
Sulikowski et al. 2396





Enediynes and the Bergman Cyclization
Lactendiynes: A New Class of Triggered Cyclic Enedieynes

Guanti et al. 2393



A Novel Intramolecualr Heck Reaction: Synthesis of a Cholersterol- Baccatin III hybrid

Danishefsky et al. 452

The Conquest of Taxol (a review)

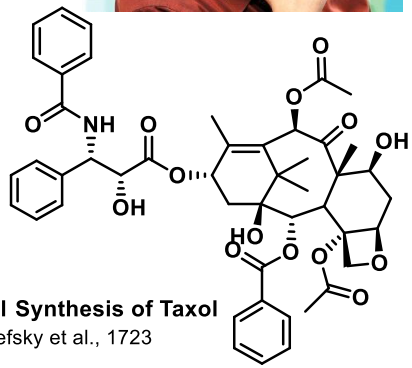
Nicolaou et al. 2079

Synthesis of a dynemicin A analog and its Bergman- type cycloaromatization

Takahashi et al. 1345

Activation of macrovyvlic biaryl-enediynes by metal ion coordination

Jones et al. 2502



A Total Synthesis of Taxol

Danishefsky et al., 1723

See Baran GM: Taxol (Wilde, 2012)