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Jie Jack Li

Name Reactions

A Collection
of Detailed Reaction Mechanisms

Springer

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Preface

What's in a name? That which we call a rose by any other name would smell as sweet.[a] On the other hand, *name reactions* in organic chemistry and the corresponding mechanisms are nevertheless fascinating for their far-reaching utility as well as their insight into organic reactions. Furthermore, understanding their mechanisms greatly enhances our ability to solve more complex chemical problems. As a matter of fact, some name reactions are the direct result of better understanding of the mechanisms, as exemplified by the Barton–McCombie reaction.[b] In addition, our knowledge of how reactions work can shed light on side reactions and by-products, or when a reaction does not give the "desired" product, the mechanism may provide clues to where the reaction has gone awry.

I started collecting named and unnamed organic reactions and their mechanisms while I was a graduate student. It occurred to me that many of my fellow practitioners are doing exactly the same, and that these efforts could be made easier through a monograph tabulating interesting and useful mechanisms of name reactions. To this end, I have updated my collection with many *contemporary* name reactions and added more recent references, especially up-to-date review articles. In reflecting the advent of asymmetric synthesis, relevant name reactions in this field have been included to the repertoire. Since the step-by-step mechanisms delineated within are mostly self-explanatory, detailed verbal explanations are not offered, although some important jargons entailing the types of transformations are highlighted. For some reactions, short descriptions are given as mnemonics rather than accurate definitions. With regard to the references, the first one is generally the original article, whereas the rest are articles and review articles. Readers interested in in-depth coverage of name reactions are encouraged to follow up with the references as well as the following five books covering the relevant topic:

1 Mundy, B. R.; Ellerd, M. G. *Name Reactions and Reagents in Organic Synthesis* John–Wiley & Sons, New York, **1988**.
2 Hassner, A.; Stumer, C. *Organic Synthesis Based on Named and Unnamed Reactions* Pergamon, **1994**.
3 Laue, L.; Plagens, A. *Named Organic Reactions* John–Wiley & Sons, New York, **1999**.
4 "*Organic Name Reactions*" section, *The Merck Index* (13th edition), **2001**
5 Smith, M. B.; March, J. "*Advanced Organic Chemistry*" (5th edition), Wiley, New York, **2001**.

I would like to express my grateful thanks to Dr. Brian J. Myers of Wayne Sate University, Profs. Jeffrey N. Johnston of Indiana University and Christian M. Rojas of Bernard College, who read the manuscript and offered many invaluable comments and suggestions. Special thanks are due to Profs. Gordon W. Gribble of Dartmouth College, Louis S. Hegedus of Colorado State University, and Thomas R. Hove of University of Minnesota for their critique of the drafts. In addi tion, I am very much indebted to Nadia M. Ahmad, John (Jack) Hodges, Michael D. Kaufman, Peter L Toogood, and Kim E. Werner for proofreading the manuscript. Any remaining errors are, of course, solely my own. I am also grateful to Ms. Ann Smith of Merck & Co., Inc. for her helpful communications and discussions. Last but not the least, I wish to thank my wife, Sherry Chun-hua Cai, for her understanding and support throughout the entire project.

Jack Li
Ann Arbor, Michigan
November, 2001

References

a. William Shakespeare, "*Romeo and Juliet*" Act II, Scene ii, **1594–1595**.
b. Derek H. R. Barton, "*Some Recollections of Gap Jumping*" American Chemical Society, Washington, DC, **1991**.

Table of Contents

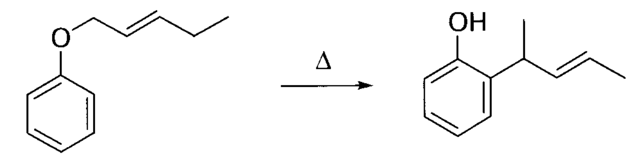
Abbreviations and Acronyms

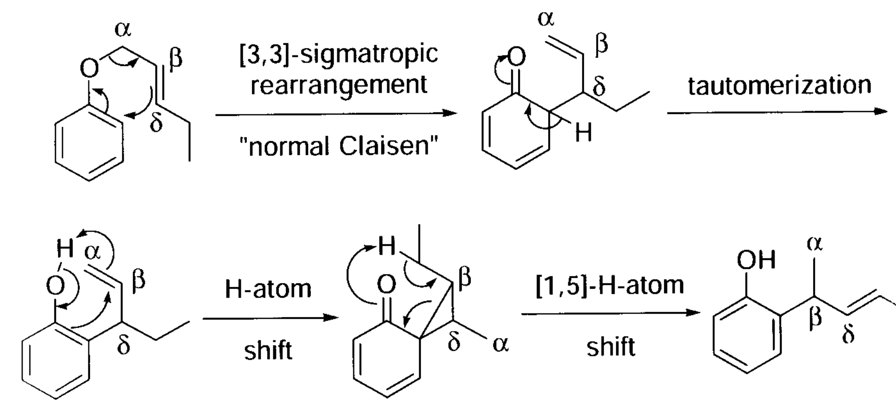
Ac	acetyl
AIBN	2,2'-azobisisobutyronitrile
Alpine-borane®	*B*-isopinocamphenyl-9-borabicyclo[3.3.1]-nonane
B:	generic base
9-BBN	9-borabicyclo[3.3.1]nonane
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Boc	*tert*-butyloxycarbonyl
t-Bu	*tert*-butyl
Cbz	benzyloxycarbonyl
m-CPBA	*m*-chloroperoxybenzoic acid
CuTC	copper thiophene-2-carboxylate
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	1,3-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
Δ	solvent heated under reflux
$(DHQ)_2$-PHAL	1,4-bis(9-*O*-dihydroquinine)-phthalazine
$(DHQD)_2$-PHAL	1,4-bis(9-*O*-dihydroquinidine)-phthalazine
DIBAL	diisobutylaluminum hydride
DMA	*N,N*-dimethylacetamide
DMAP	*N,N*-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMS	dimethylsulfide
DMSO	dimethylsulfoxide
DMSY	dimethylsulfoxonium methylide
DMT	dimethoxytrityl
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane
E1	unimolecular elimination
E2	bimolecular elimination
E1cb	2-step, base-induced β-elimination *via* carbanion
Eq	equivalent
HMPA	hexamethylphosphoric triamide
Imd	imidazole
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilazane
LTMP	lithium 2,2,6,6-tetramethylpiperidine

Mes	mestyl
MVK	methyl vinyl ketone
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide
NMP	1-methyl-2-pyrrolidinone
Nu	nucleophile
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
SET	single electron transfer
S_NAr	nucleophilic substitution on an aromatic ring
S_N1	unimolecular nucleophilic substitution
S_N2	bimolecular nucleophilic substitution
TBAF	tetrabutylammonium fluoride
TBDMS	*tert*-butyldimethylsilyl
TBS	*tert*-butyldimethylsilyl
Tf	trifluoromethanesulfonyl (triflyl)
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
TFP	tri-*o*-furylphosphine
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMEDA	*N,N,N',N'*-tetramethylethylenediamine
TMP	tetramethylpiperidine
TMS	trimethylsilyl
Tol	toluene or tolyl
Tol-BINAP	2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl
Ts	tosylate

Abnormal Claisen rearrangement

Further rearrangement of the normal Claisen rearrangement product with the β-carbon becoming attached to the ring.





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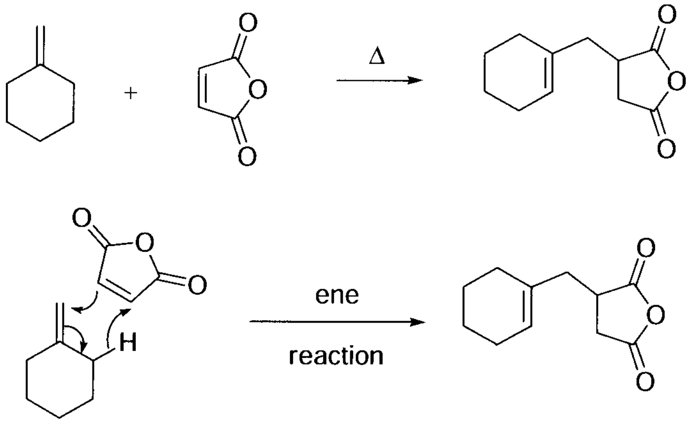
Alder ene reaction



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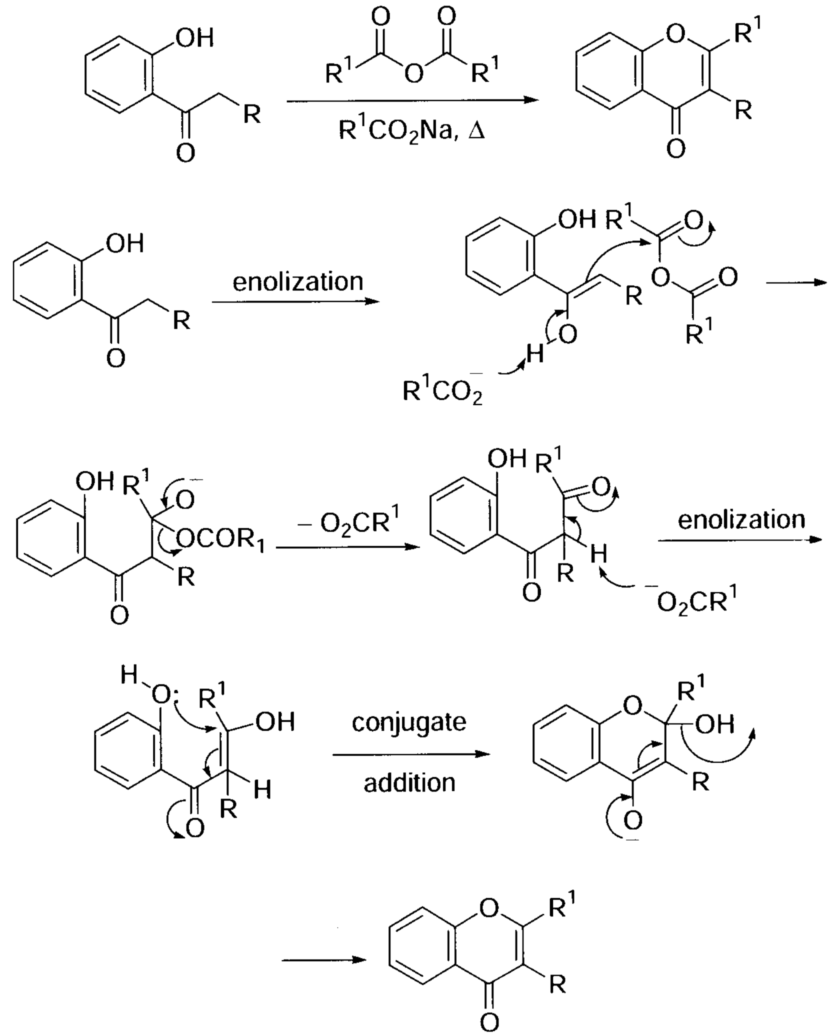
Allan–Robinson reaction

Synthesis of flavones or isoflavones.



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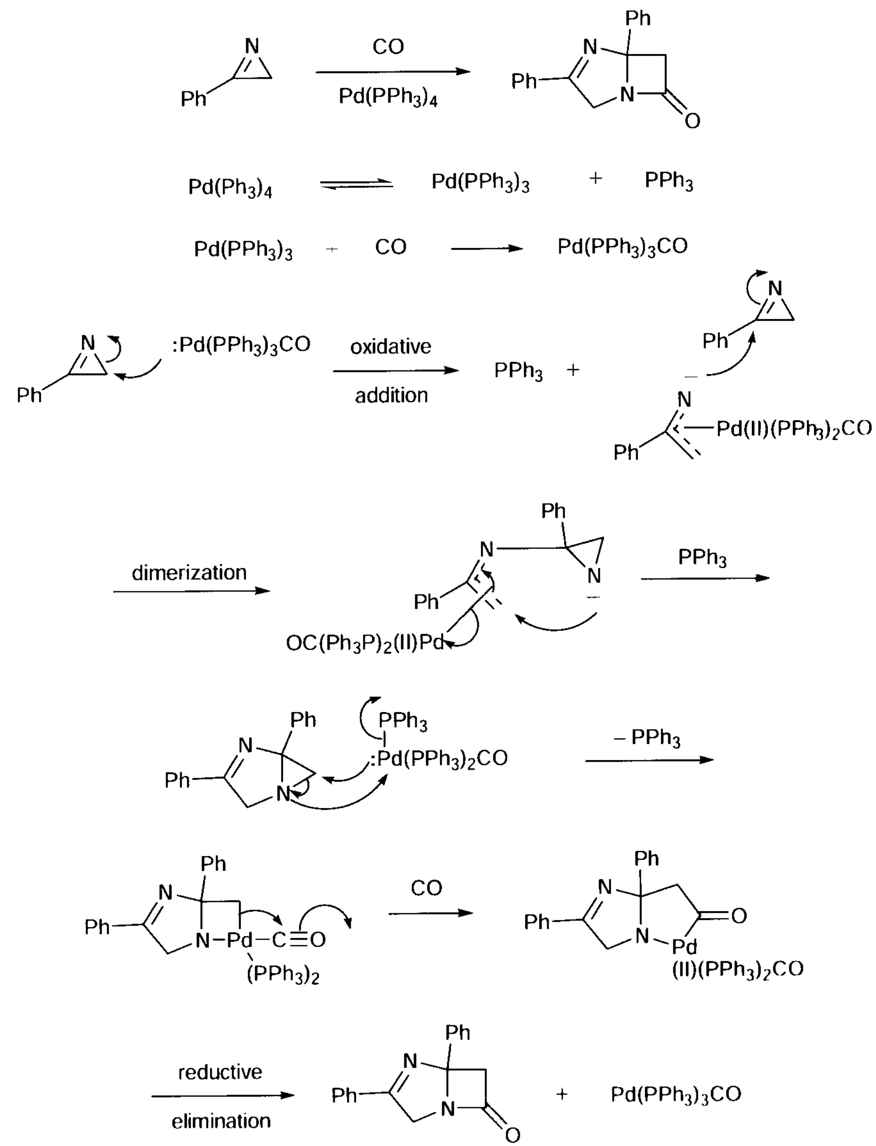
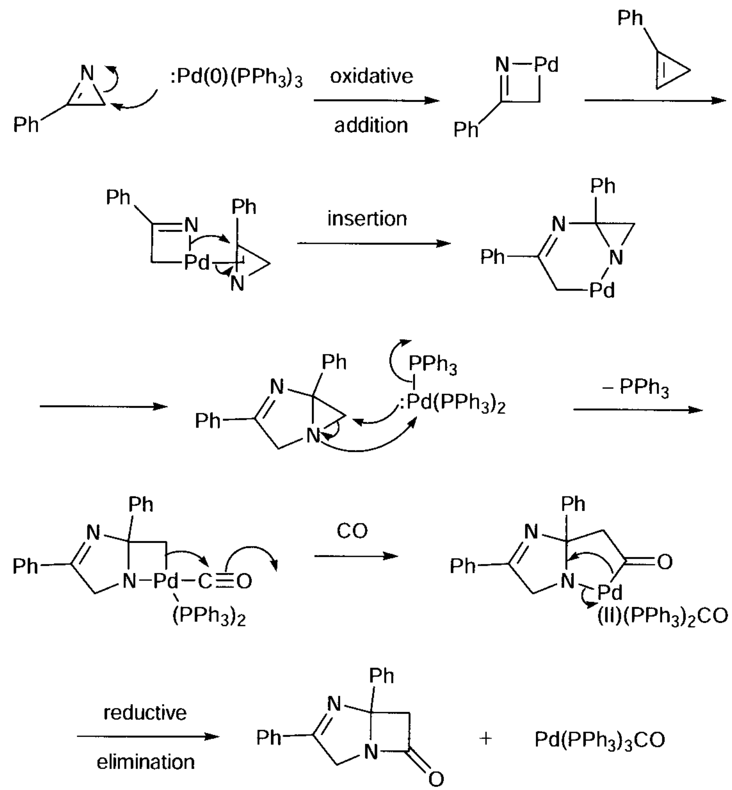
Alper carbonylation



An alternative mechanism:



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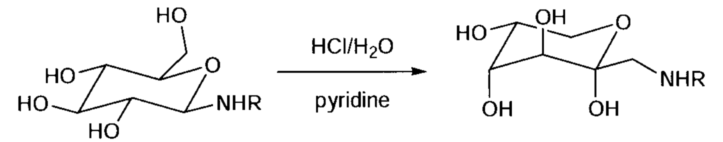
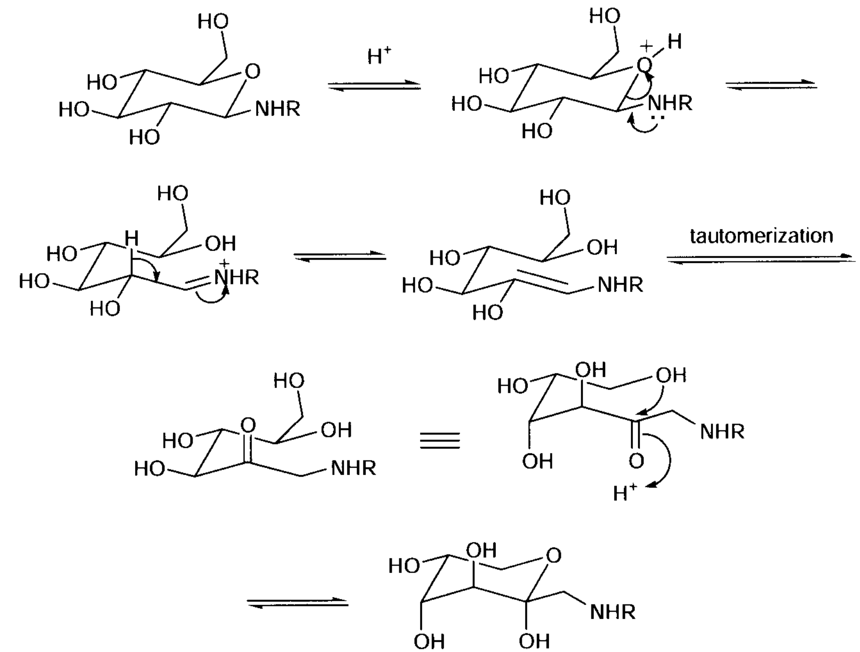
Amadori glucosamine rearrangement

Transformation of an aldose to a ketose using an amine.



glycosylamine 1-amino-1-deoxyketose



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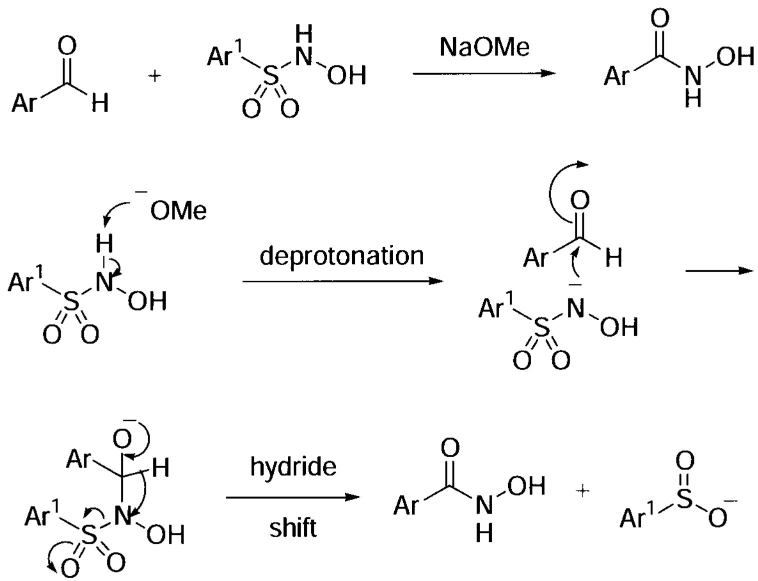
Angeli–Rimini hydroxamic acid synthesis



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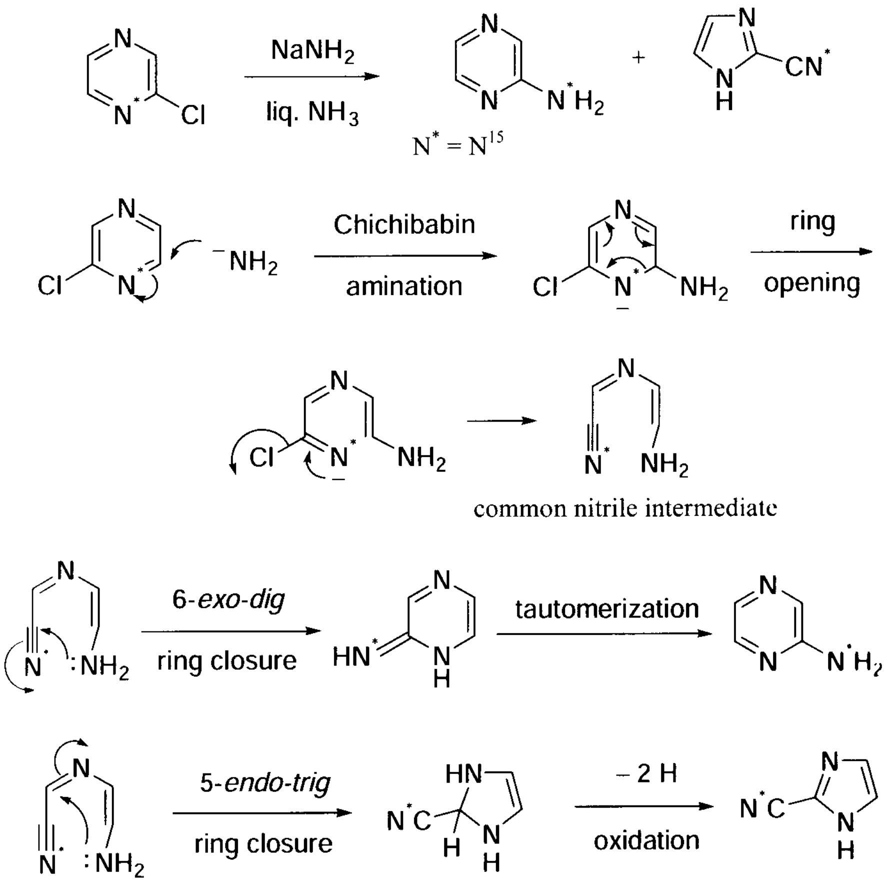
ANRORC mechanism

Addition of Nucleophiles, Ring Opening and Ring Closure.



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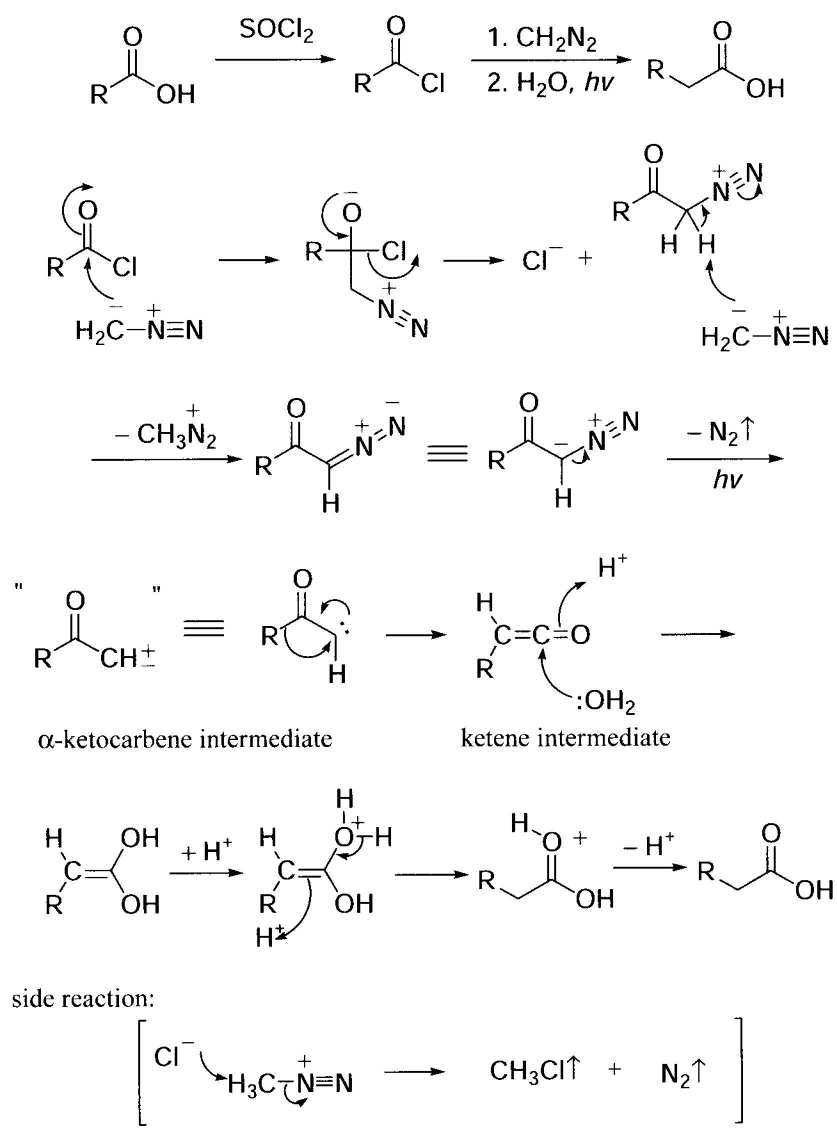
Arndt–Eistert homologation

One carbon homologation of carboxylic acids using diazomethane.



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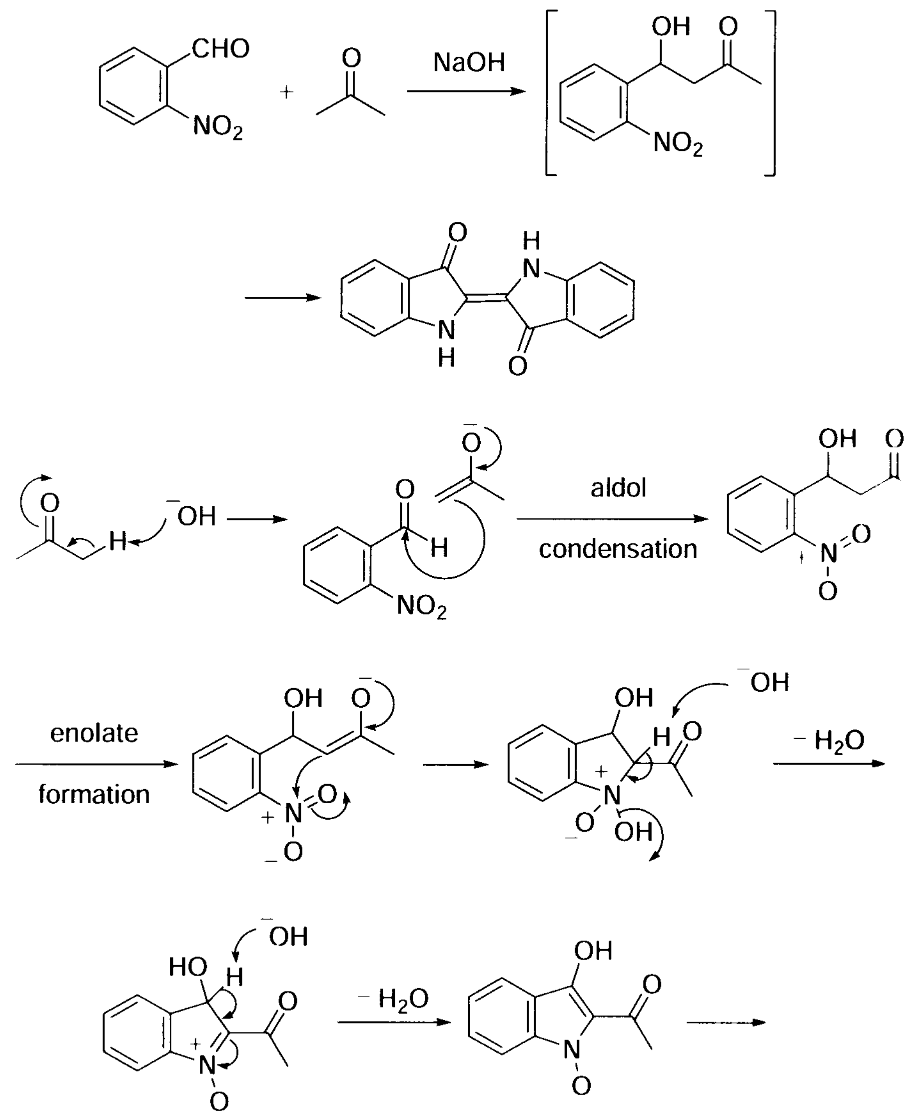
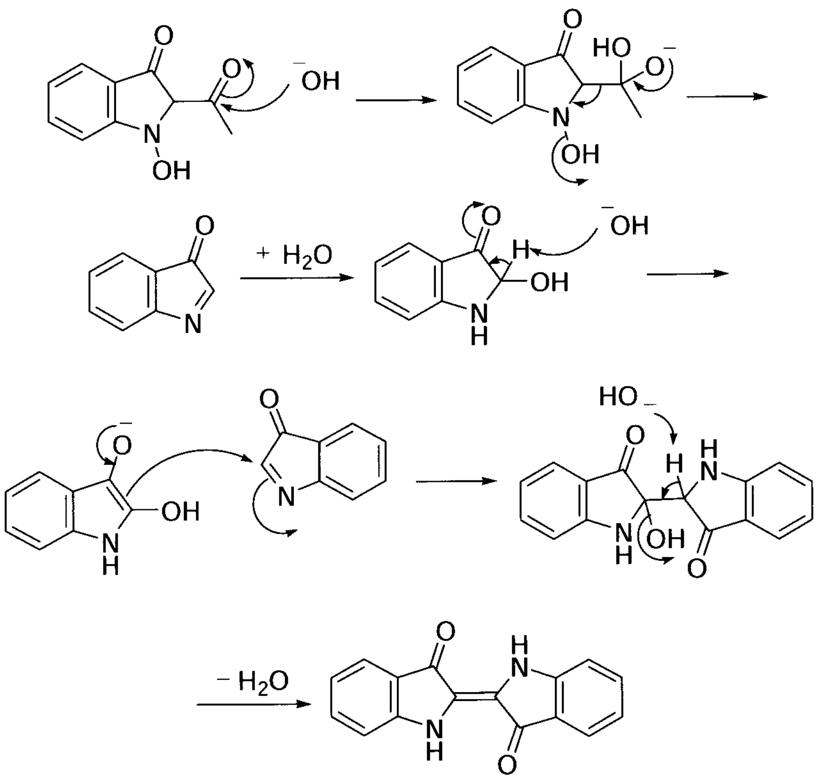
Baeyer–Drewson indigo synthesis

Applicable for the detection of *o*-nitrobenzaldehyde.





indigo

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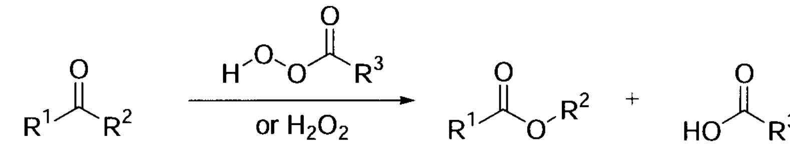
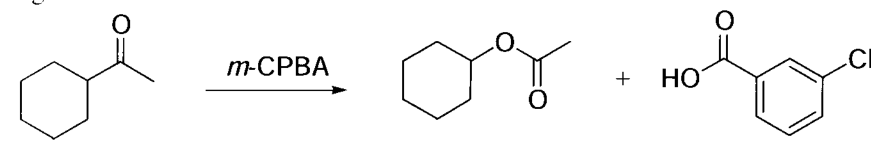
Baeyer–Villiger oxidation

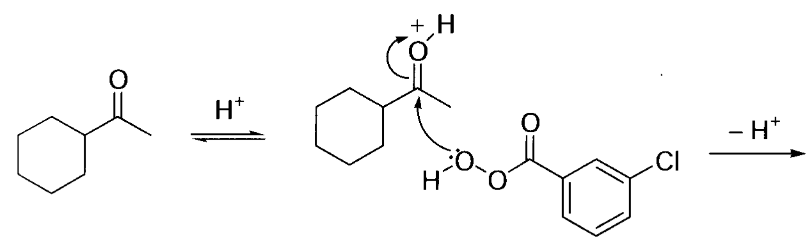
General scheme:

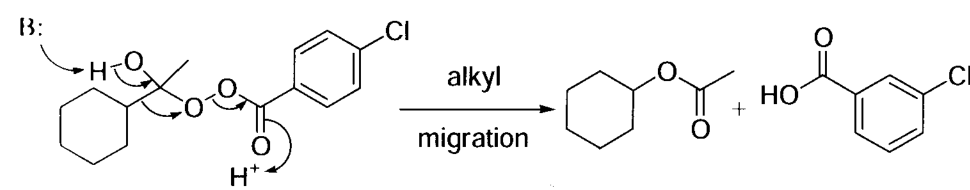


The most electron-rich alkyl group (more substituted carbon) migrates first. The general migration order: tertiary alkyl > secondary alkyl > cyclohexyl > benzyl > phenyl > primary alkyl > methyl >> H

e.g.:







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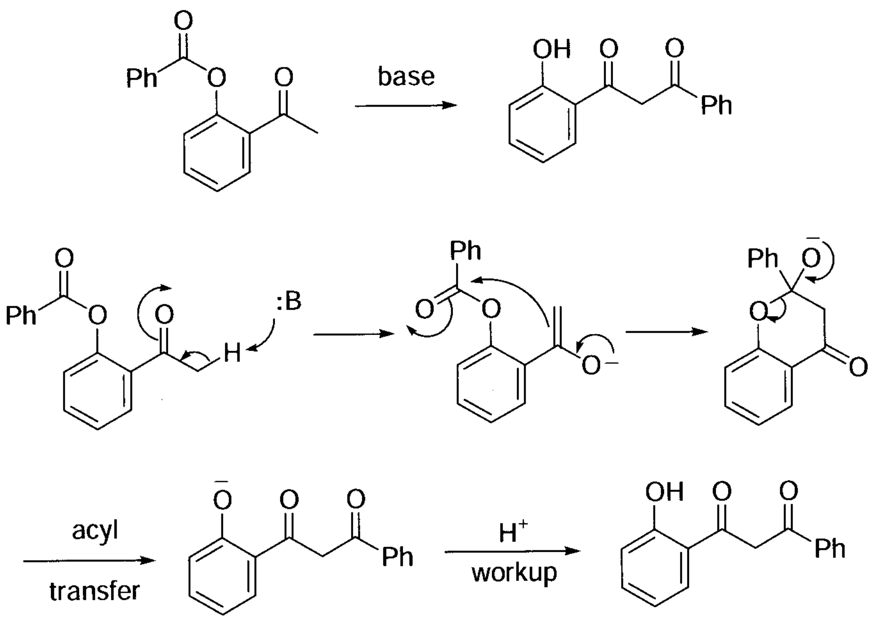
Baker–Venkataraman rearrangement



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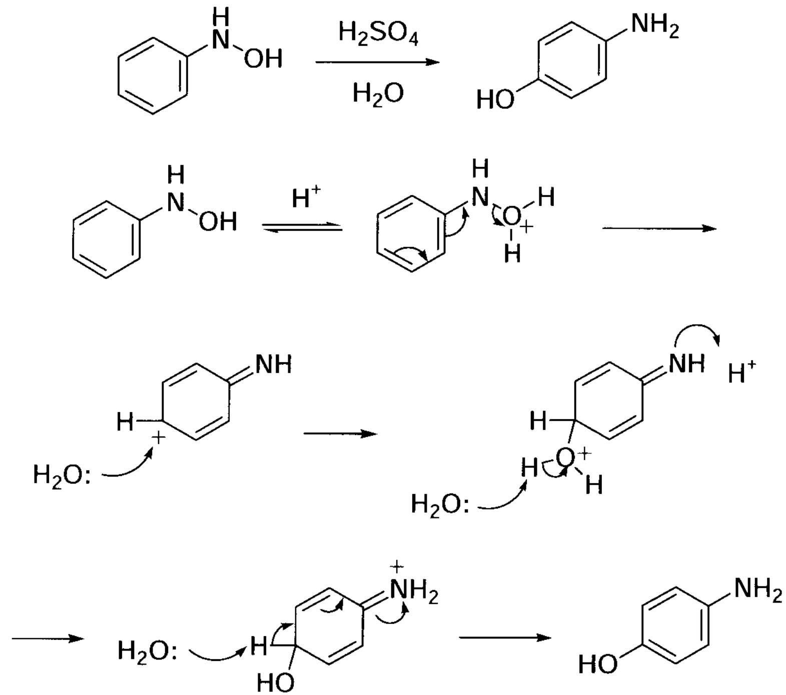
Bamberger rearrangement



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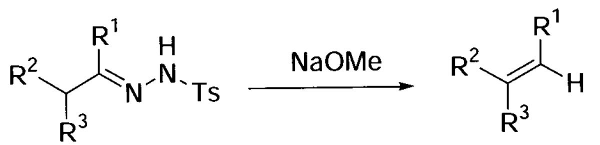
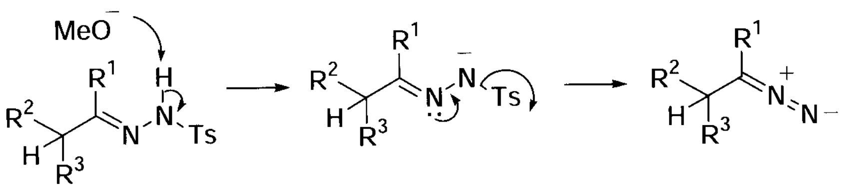
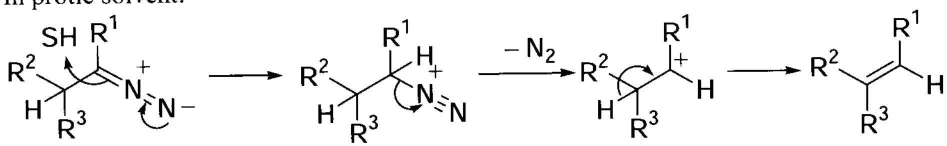
Bamford–Stevens reaction

The Bamford–Stevens reaction and the Shapiro reaction share a similar mechanistic pathway. The former uses a base such as Na, NaOMe, LiH, NaH, $NaNH_2$, *etc.*, whereas the latter employs a base such as alkyllithiums and Grignard reagents. As a result, the Bamford–Stevens reaction furnishes the more-substituted olefins as the thermodynamic products, while the Shapiro reaction generally affords the less-substituted olefins as the kinetic products.

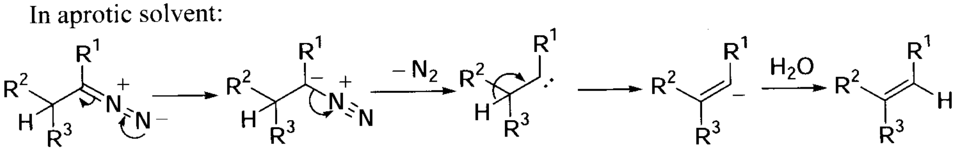




In protic solvent:



In aprotic solvent:



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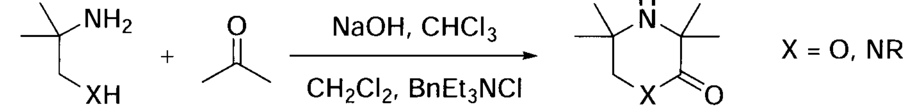
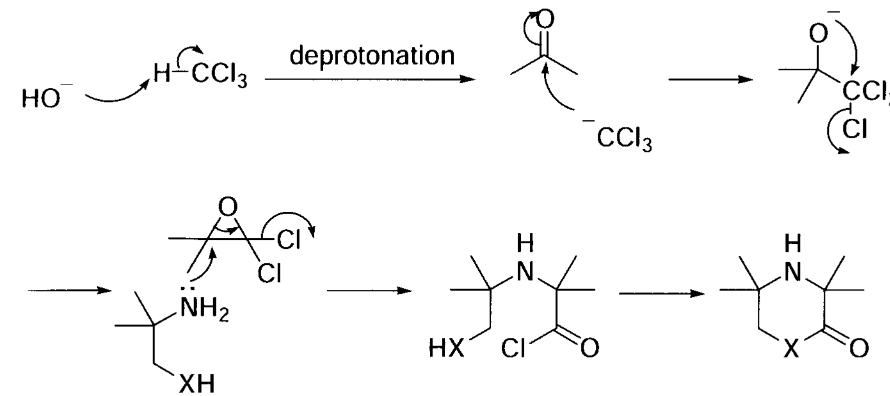
Bargellini reaction

Synthesis of hindered morpholinones and piperazinones from acetone and 2-amino-2-methyl-1-propanol or 1,2-diaminopropanes.





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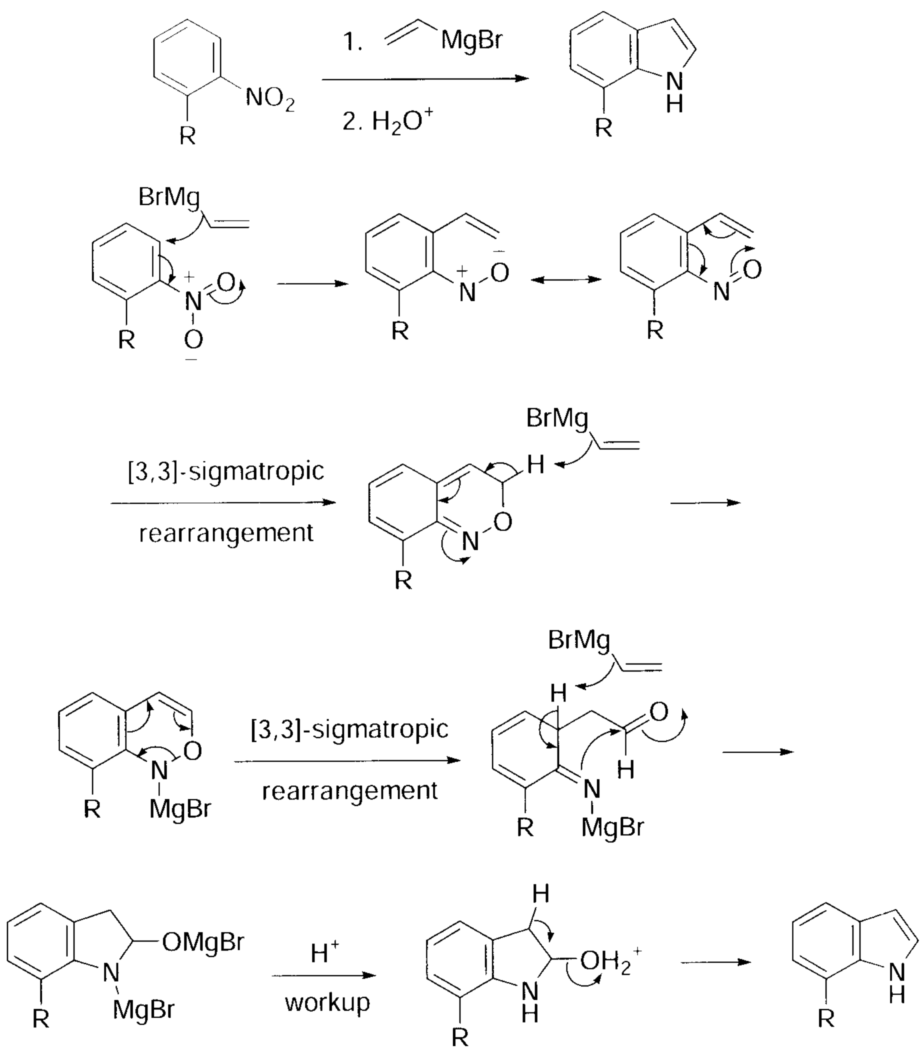
Bartoli indole synthesis



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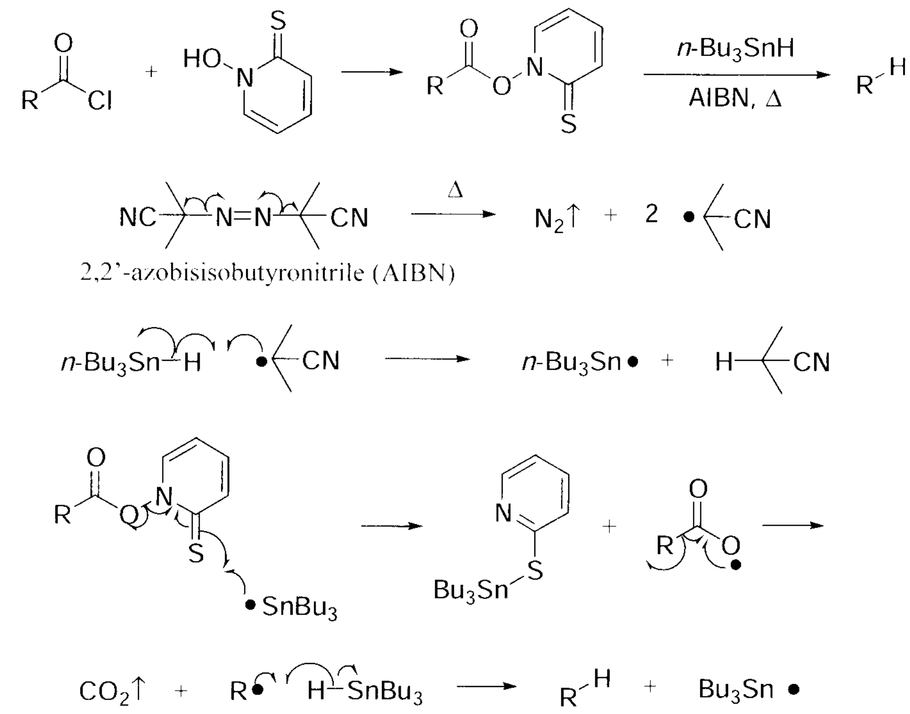
Barton decarboxylation reaction



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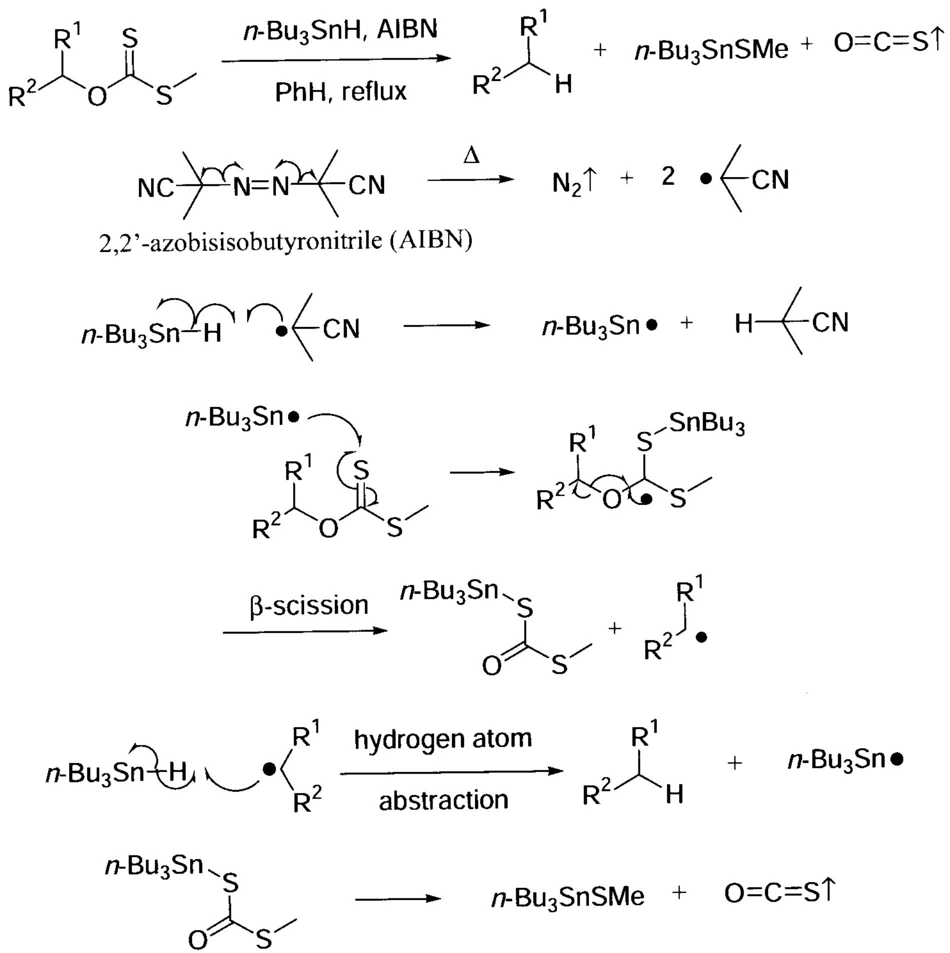
Barton–McCombie deoxygenation reaction

Deoxygenation of alcohols by means of radical scission of their corresponding thiocarbonyl intermediates.



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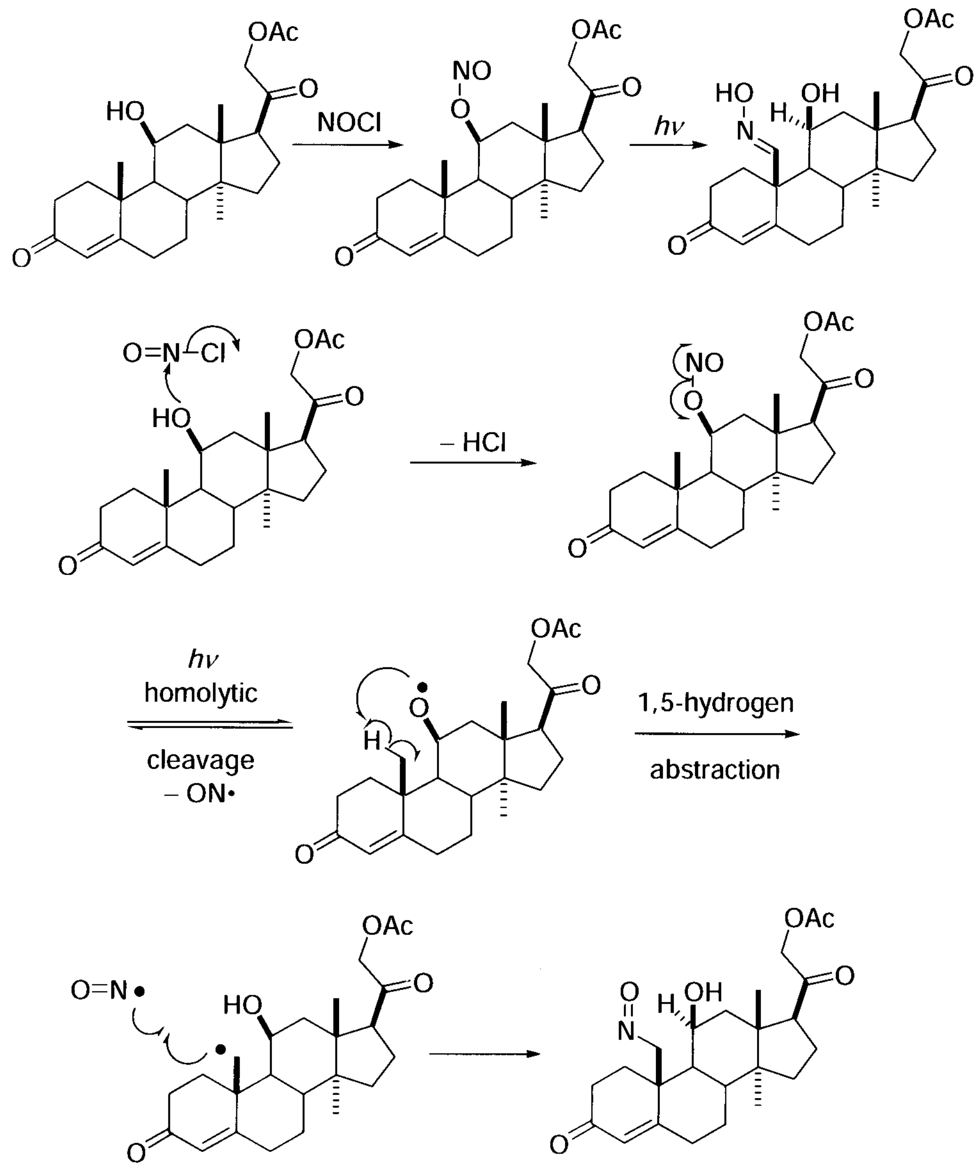
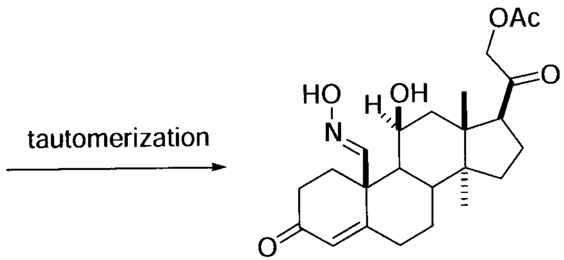
Barton nitrite photolysis



Nitric oxide radical is a stable, and therefore, long-lived radical

nitroso intermediate



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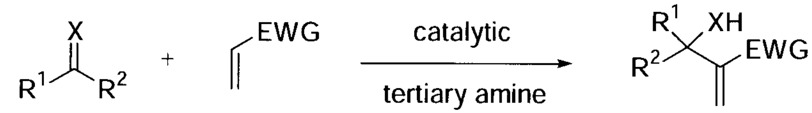
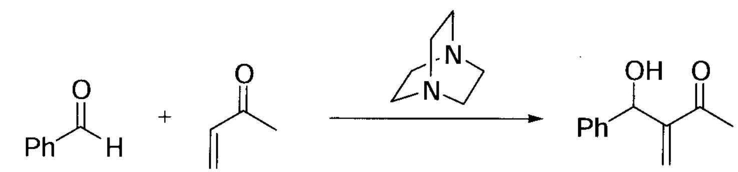
Baylis–Hillman reaction

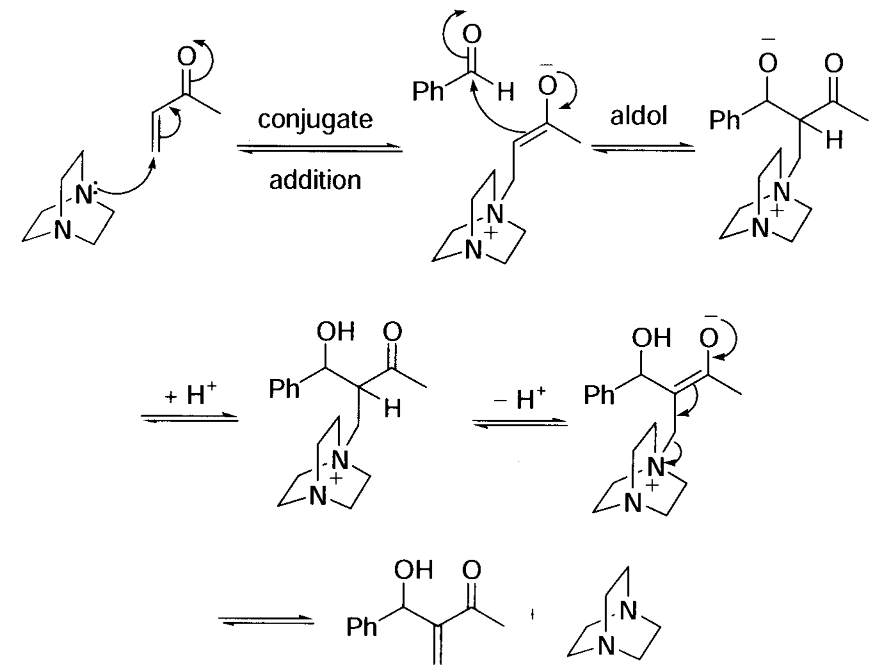
General scheme:



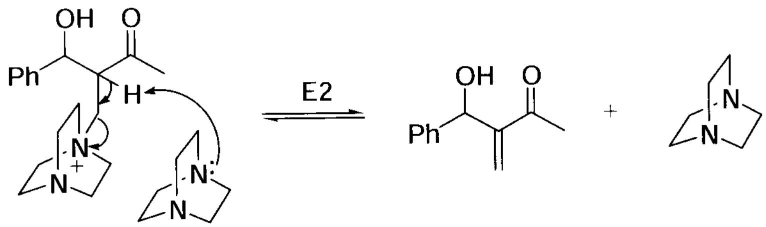
X = O, NR_2, EWR = CO_2R, COR, CHO, CN, SO_2R, SO_3R, $PO(OEt)_2$, $CONR_2$, $CH_2{=}CHCO_2Me$

e.g.:





E2 (bimolecular elimination) mechanism is also operative here:



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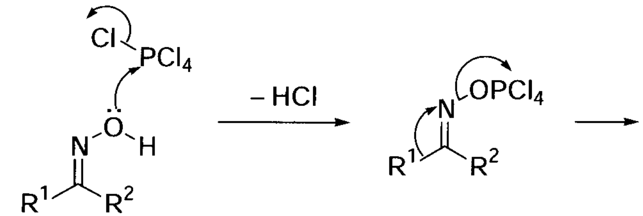
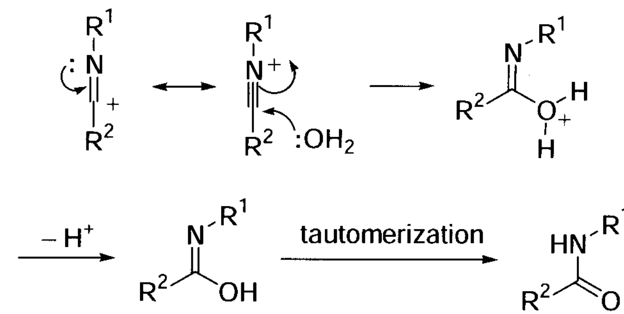
Beckmann rearrangement

The acid-mediated isomerization of oximes to amides.



the substituent *trans* to the leaving group migrates



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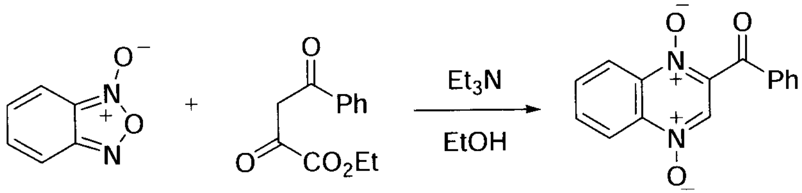
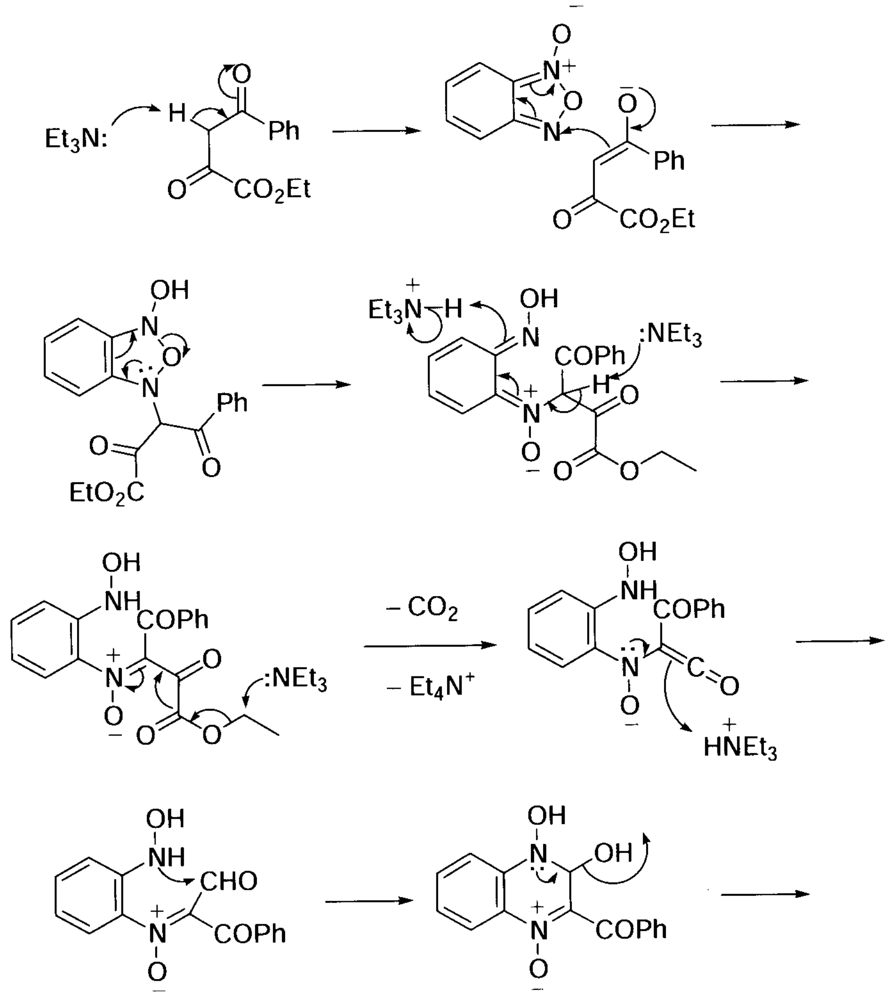
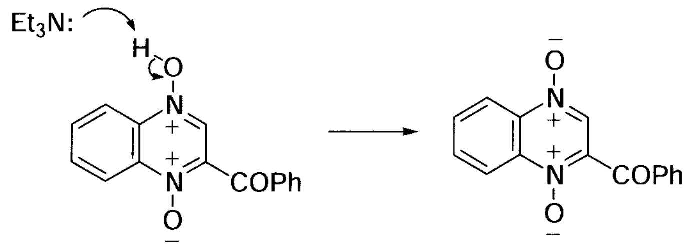
Beirut reaction

Synthesis of quinoxaline-1,4-dioxide from benzofurazan oxide.







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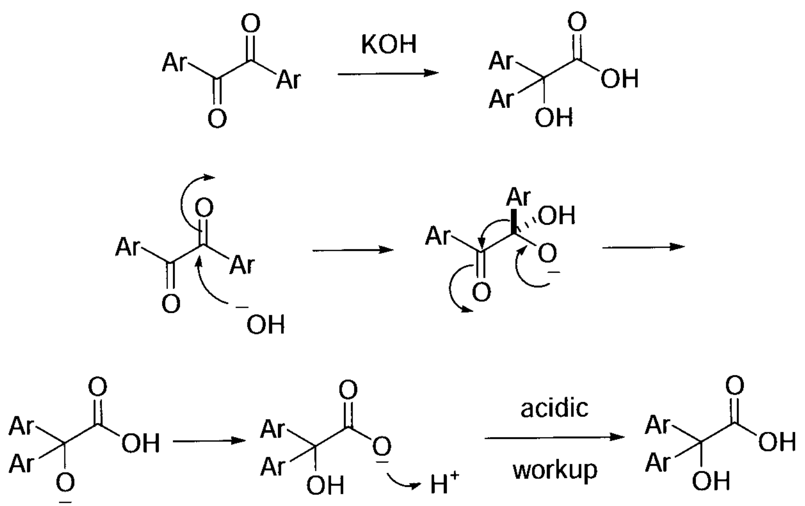
Benzilic acid rearrangement



Final deprotonation of the carboxylic acid drives the reaction forward.

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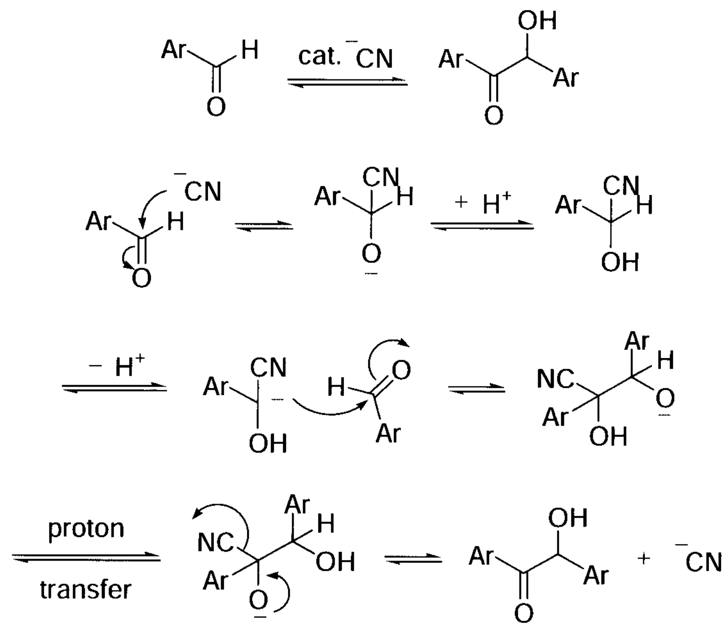
Benzoin condensation



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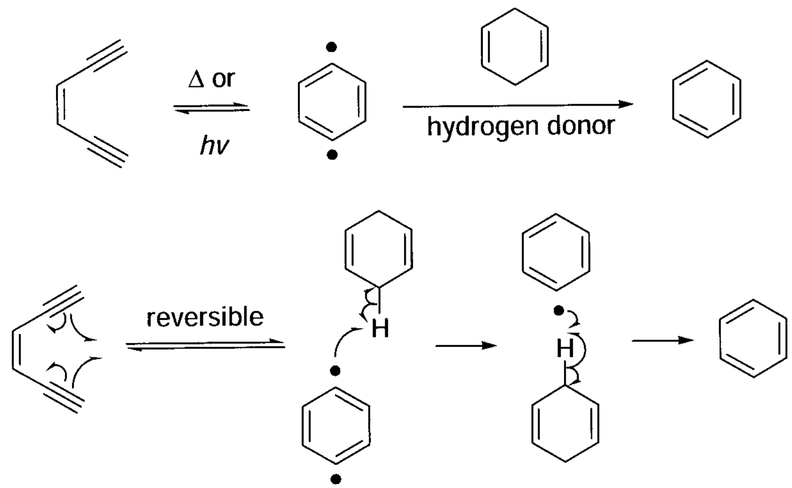
Bergman cyclization



enediyne 1,4-benzenediyl diradical

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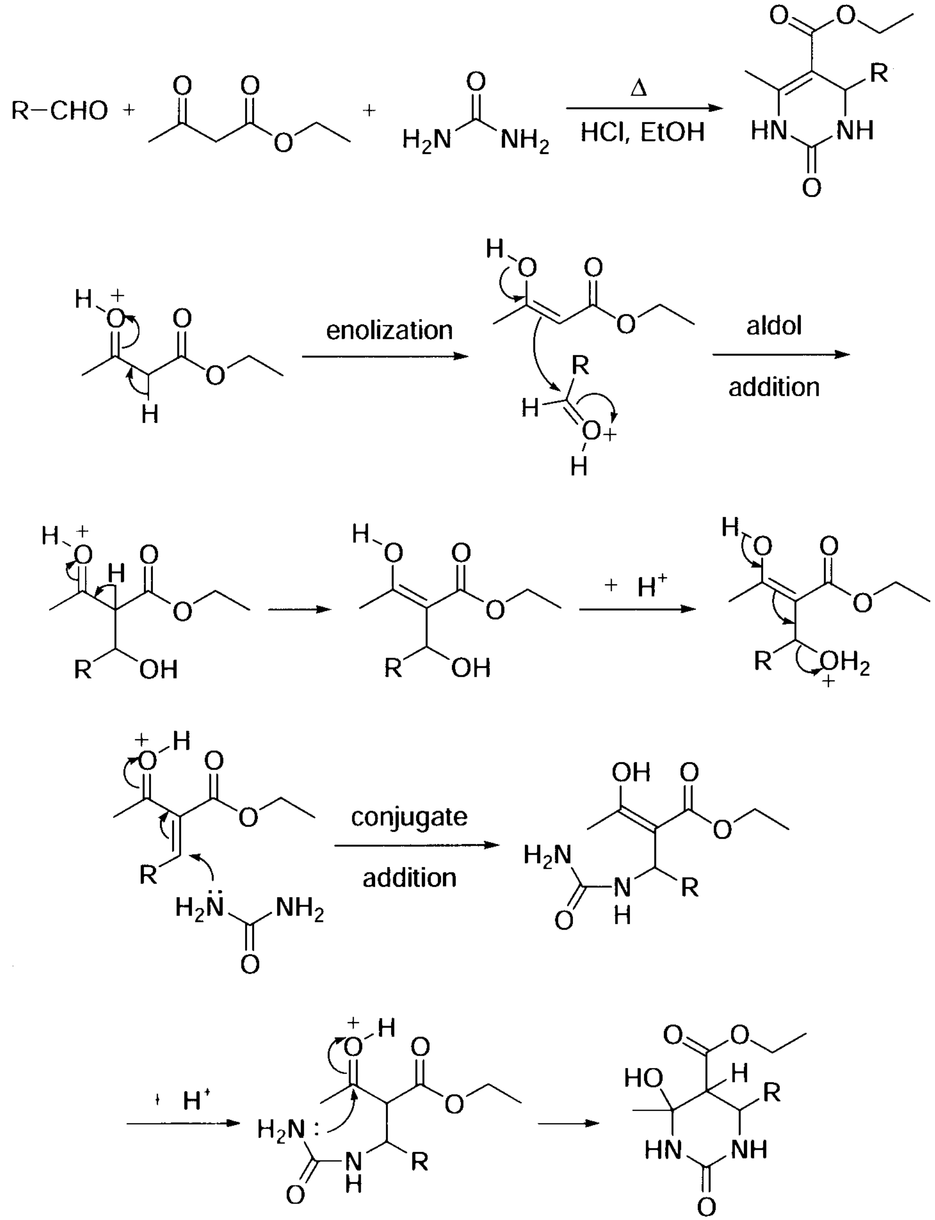
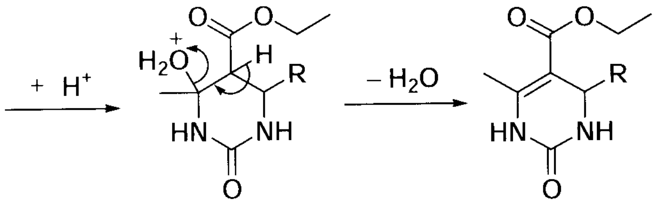
Biginelli pyrimidone synthesis

One-pot condensation reaction of an aromatic aldehyde, urea, and ethyl acetoacetate in acidic ethanolic solution and expansion of such a condensation thereof.





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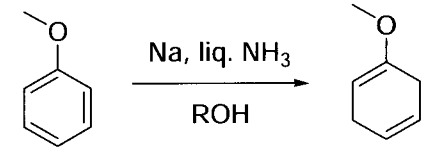
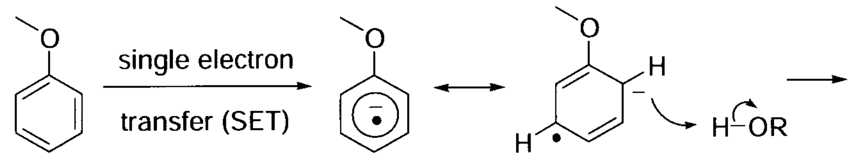
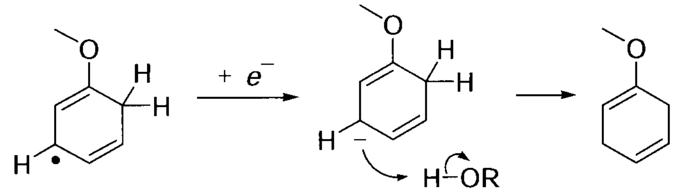
Birch reduction

Benzene ring bearing an electron-donating substituent:

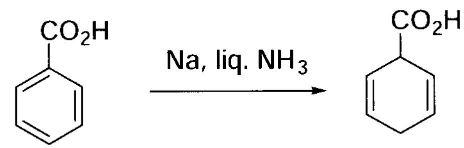


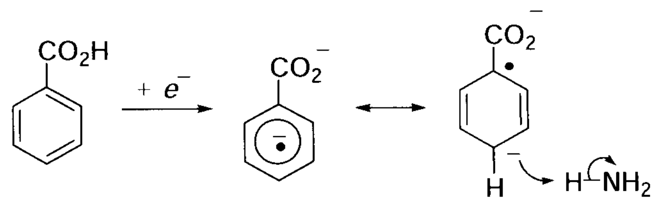


radical anion

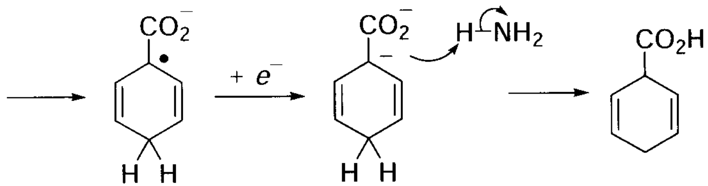


Benzene ring with an electron-withdrawing substituent:





radical anion



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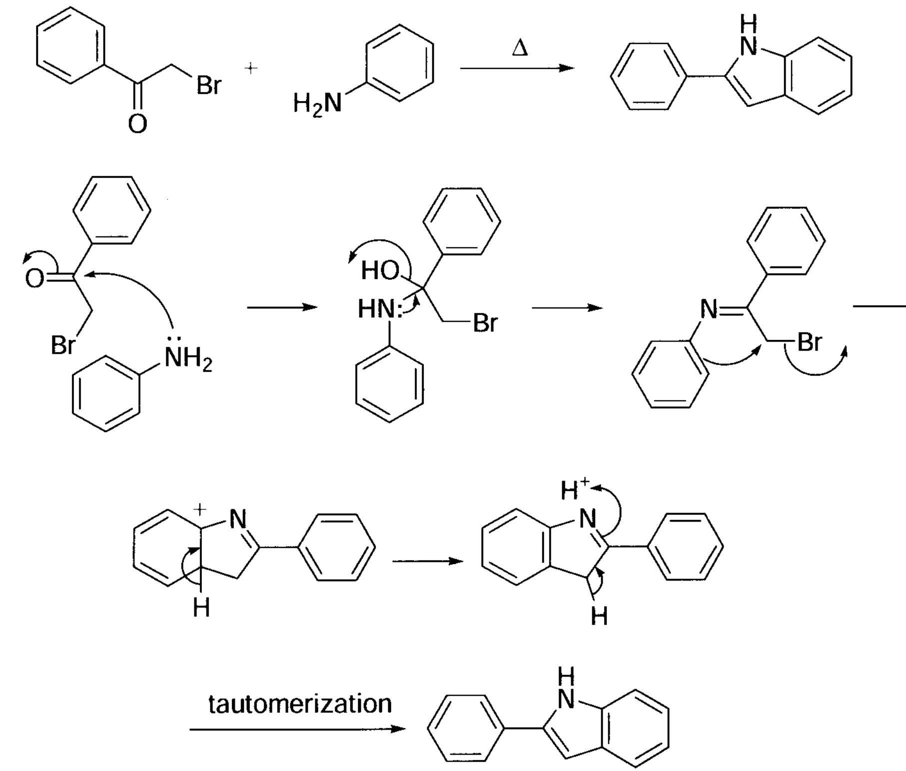
Bischler–Möhlau indole synthesis



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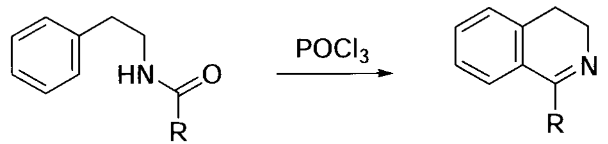
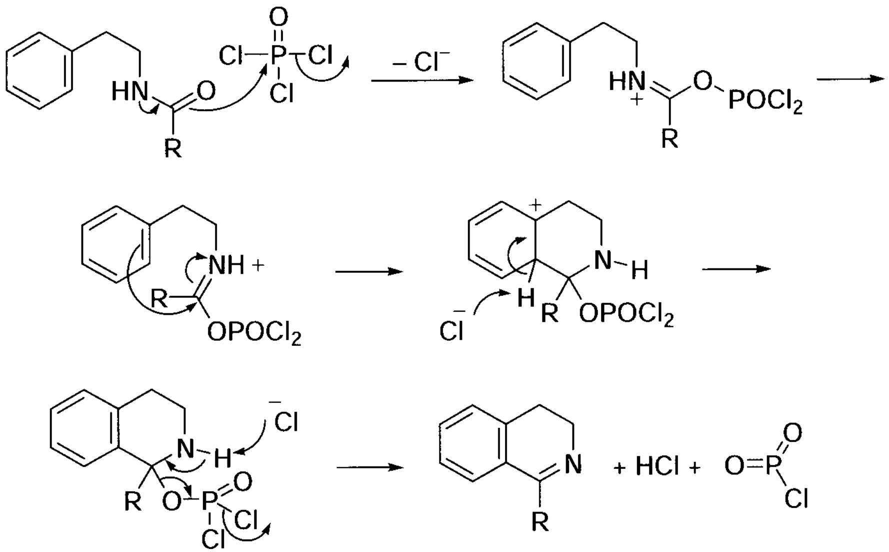
Bischler–Napieralski reaction

Dihydroisoquinoline synthesis from β-phenethylamides.





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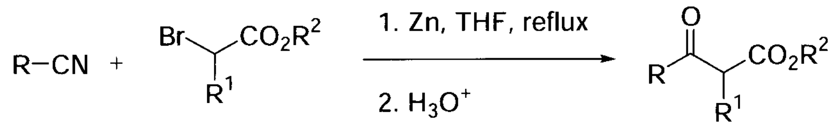
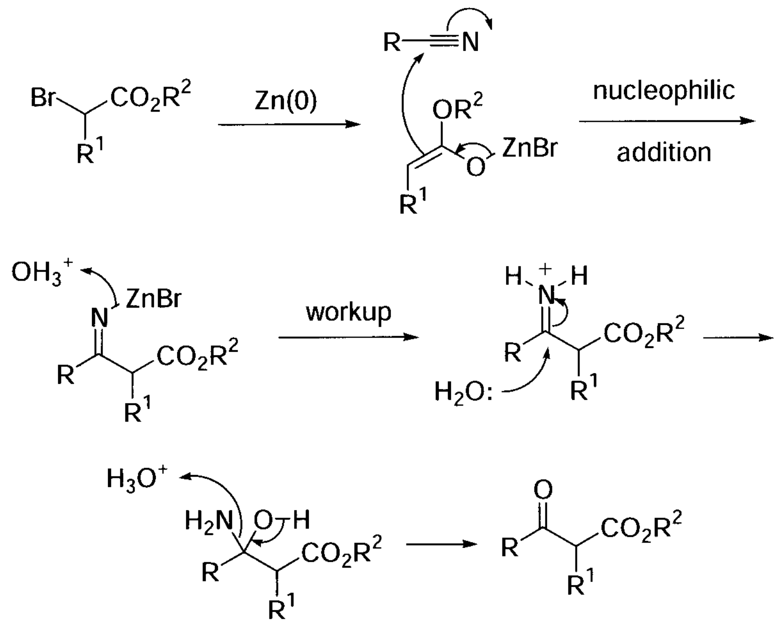
Blaise reaction

β-Ketoesters from nitriles and α-haloesters using Zn.





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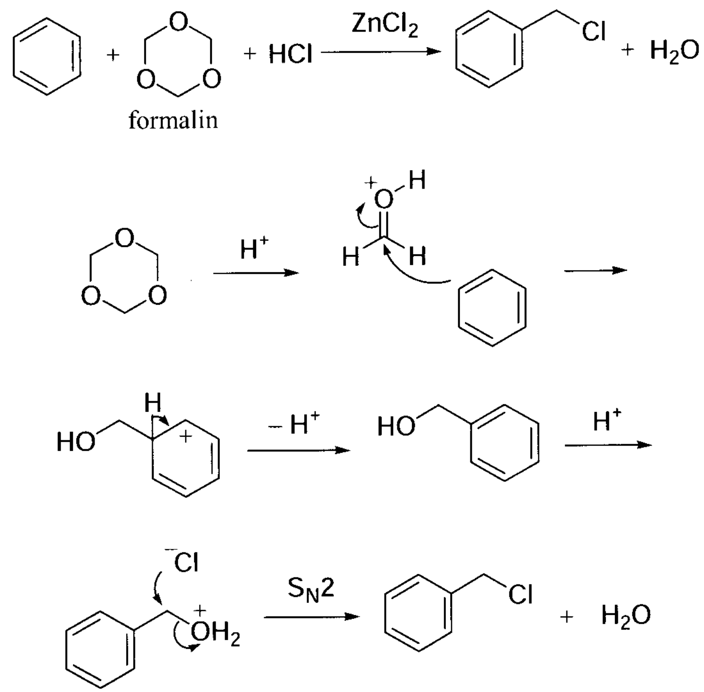
Blanc chloromethylation reaction



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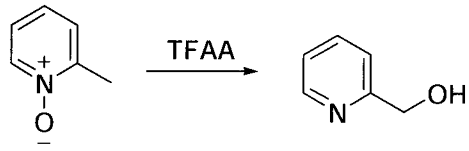
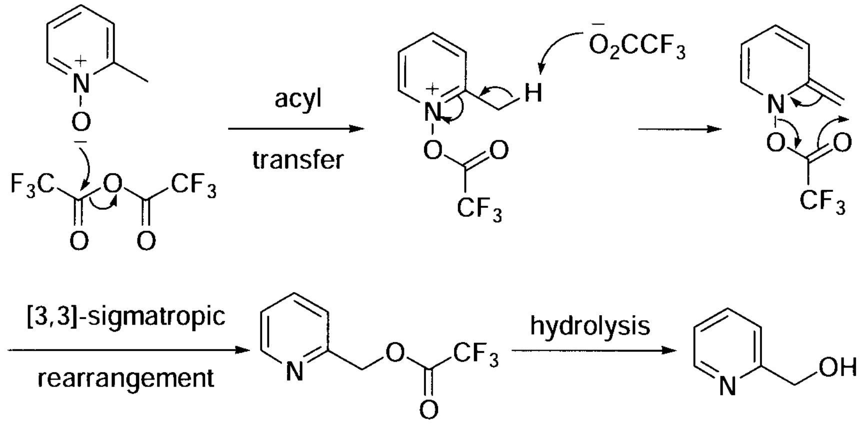
Boekelheide reaction



TFAA, trifluoroacetic anhydride



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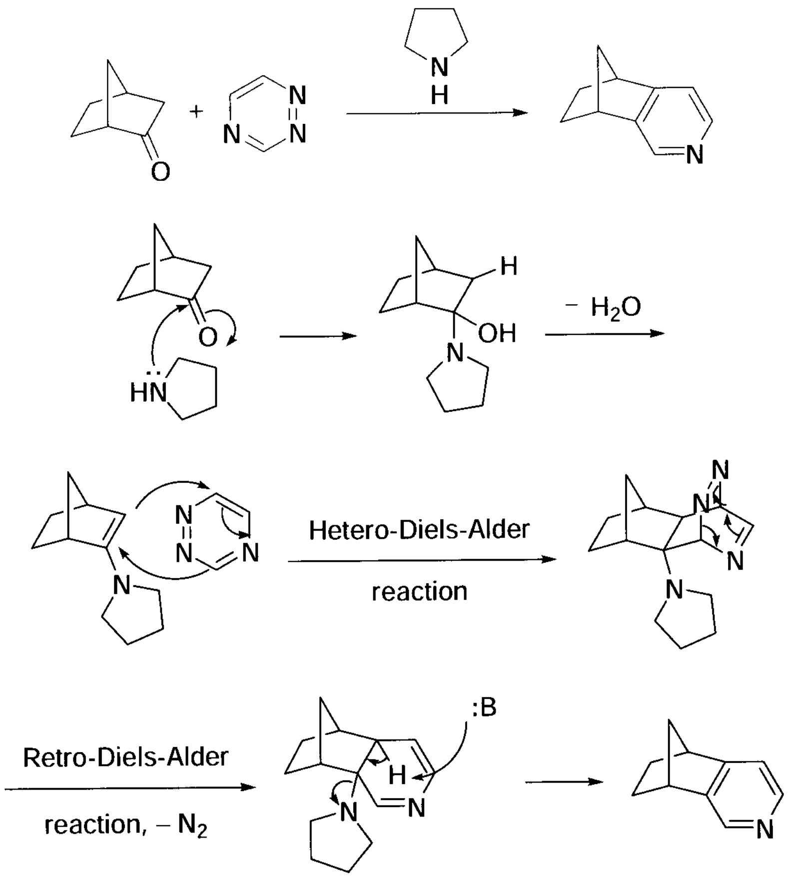
Boger pyridine synthesis



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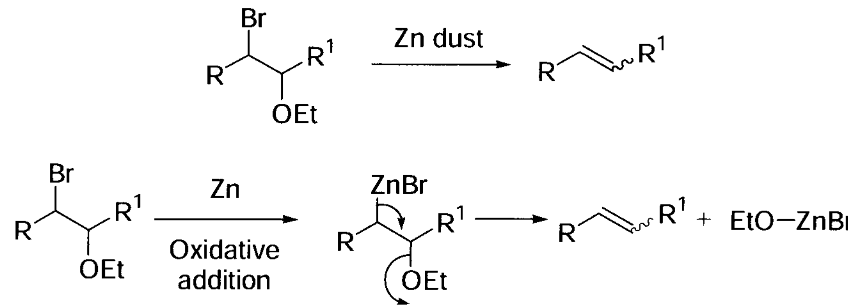
Boord reaction



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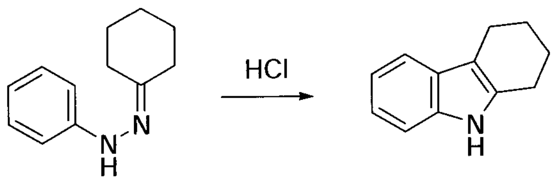
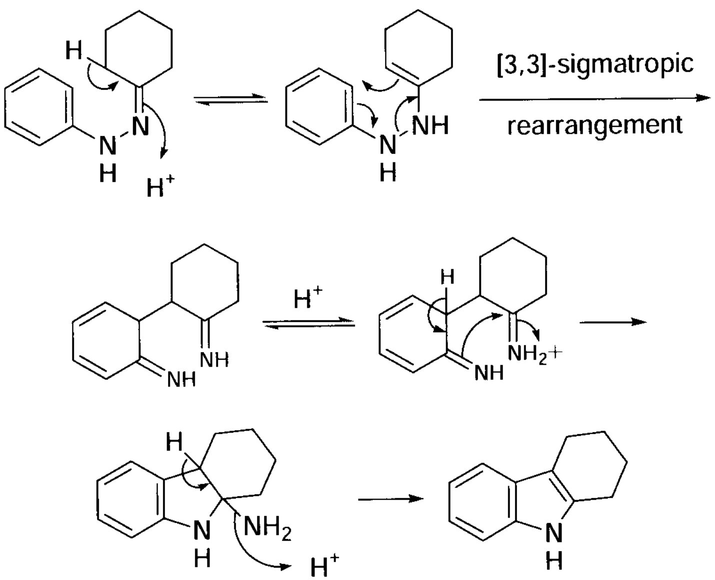
Borsche–Drechsel cyclization

Cf. Fisher indole synthesis.





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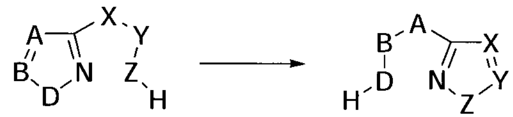
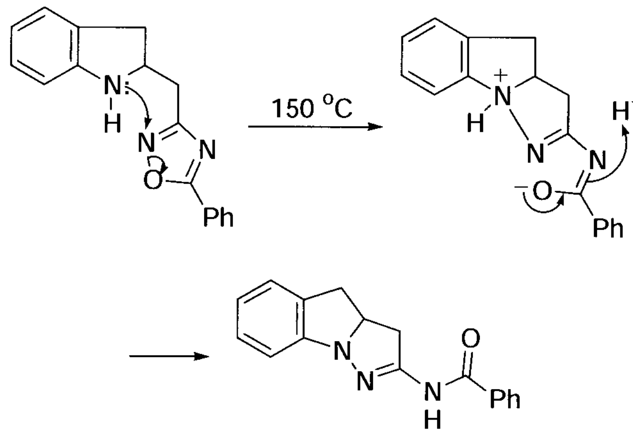
Boulton–Katritzky rearrangement

Rearrangement of one five-membered heterocycle into another under thermolysis.



e.g. [ref. 9]:



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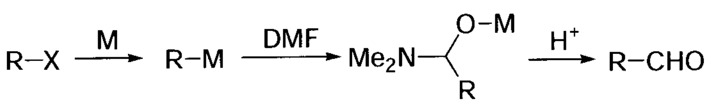
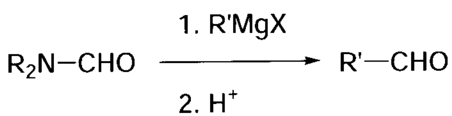
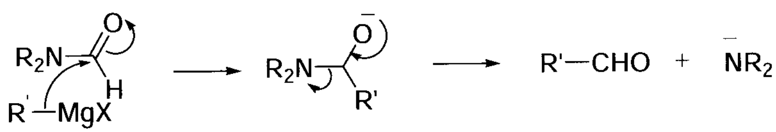
Bouveault aldehyde synthesis

Formylation of an alkyl or aryl halide to the homologous aldehyde by transformation to the corresponding organometallic reagent then addition of DMF.



A modification by Comins [3]:





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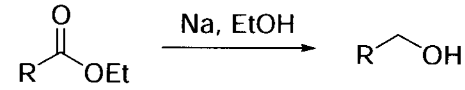
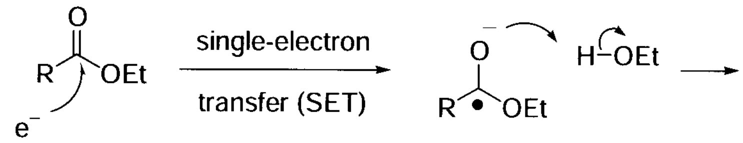
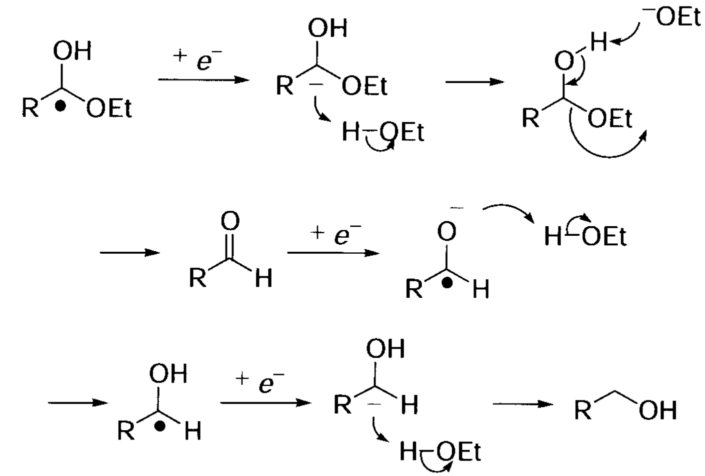
Bouveault–Blanc reduction





ketyl (radical anion)



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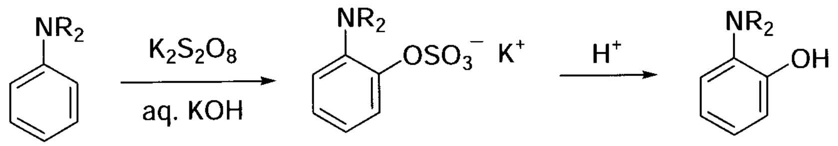
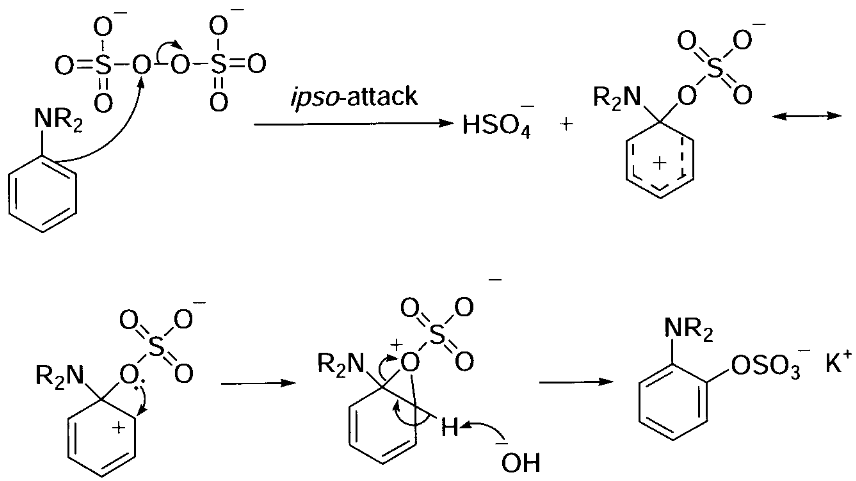
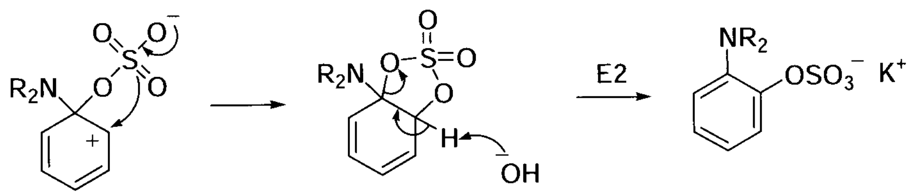
Boyland–Sims oxidation

Oxidation of aromatic amines to phenols using alkaline persulfate.





Another pathway is also operative:



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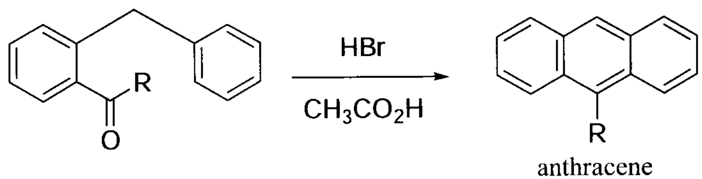
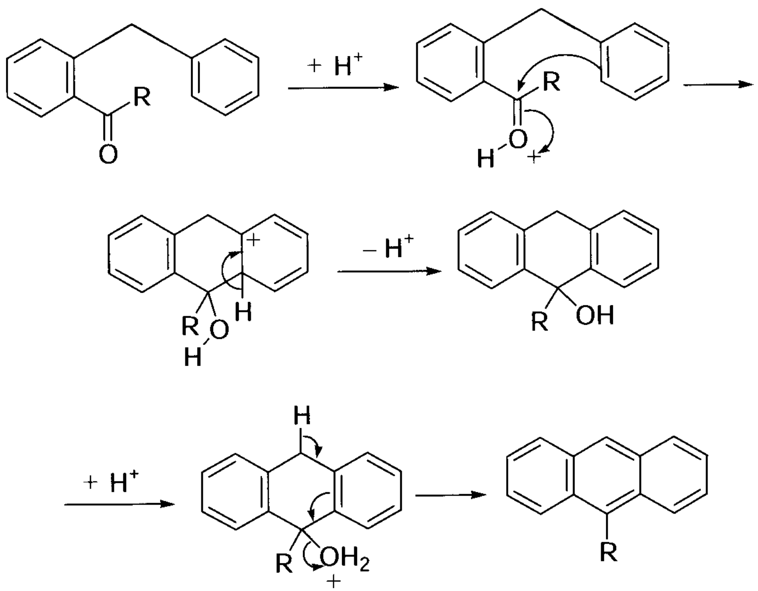
Bradsher reaction





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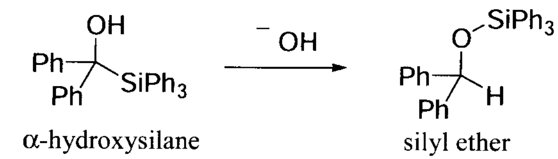
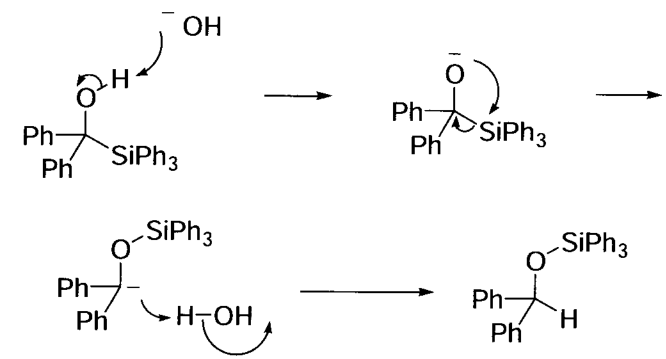
Brook rearrangement

Base-catalyzed silicon migration from carbon to oxygen.





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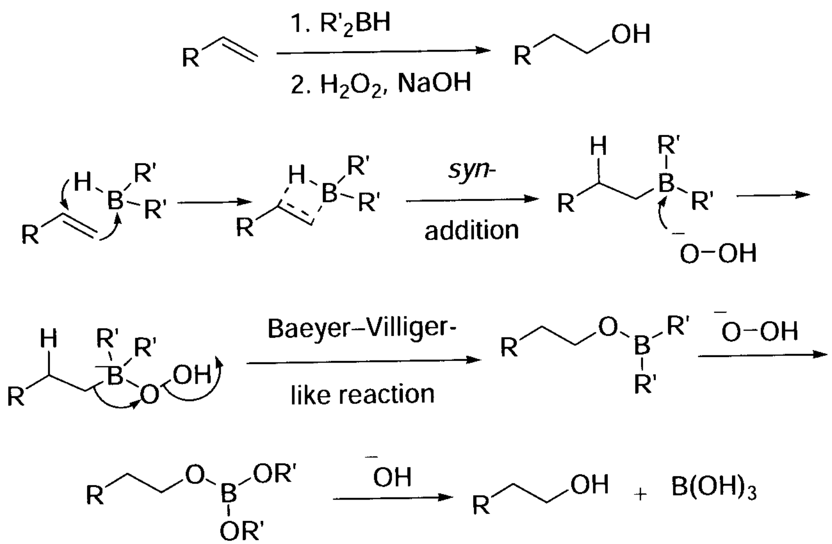
Brown hydroboration reaction

Addition of boranes to olefins, followed by basic oxidation of the organoboranes, resulting in alcohols.



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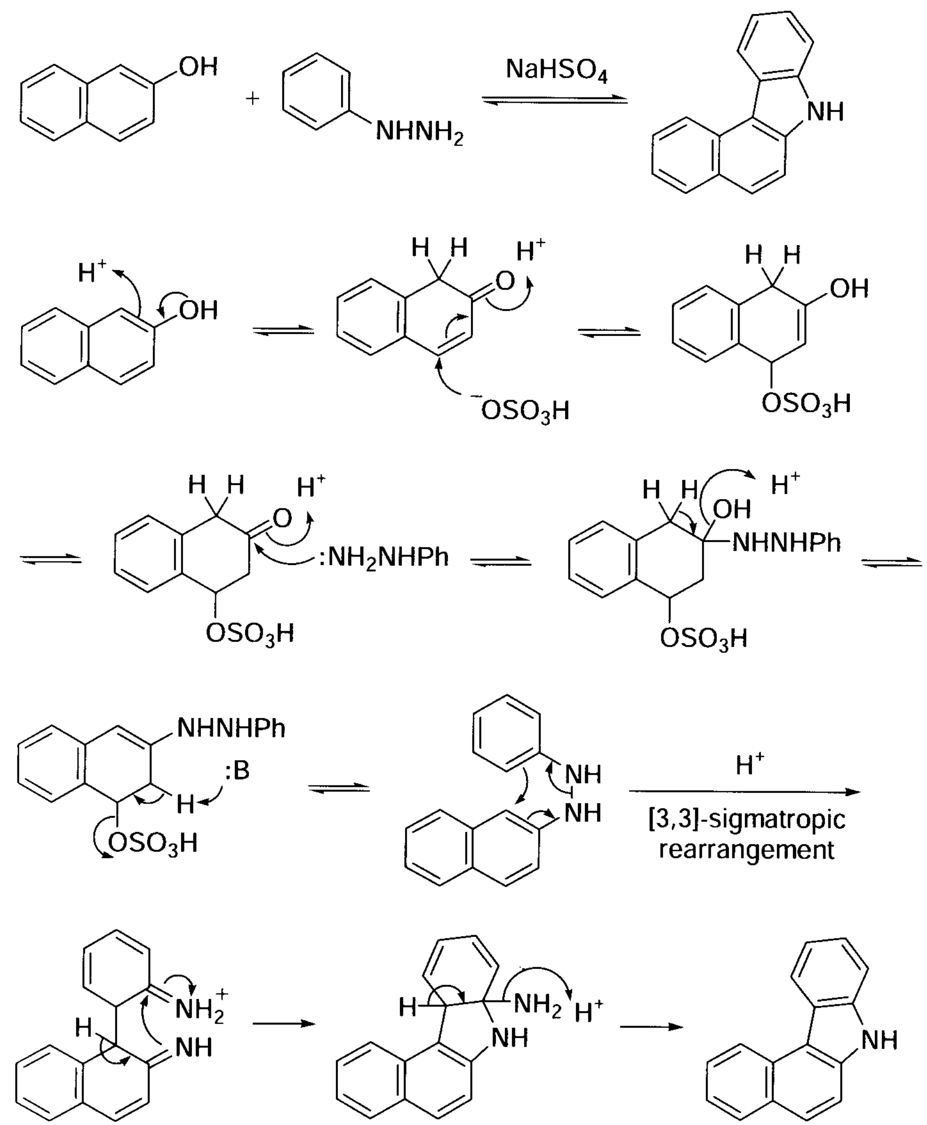
Bucherer carbazole synthesis



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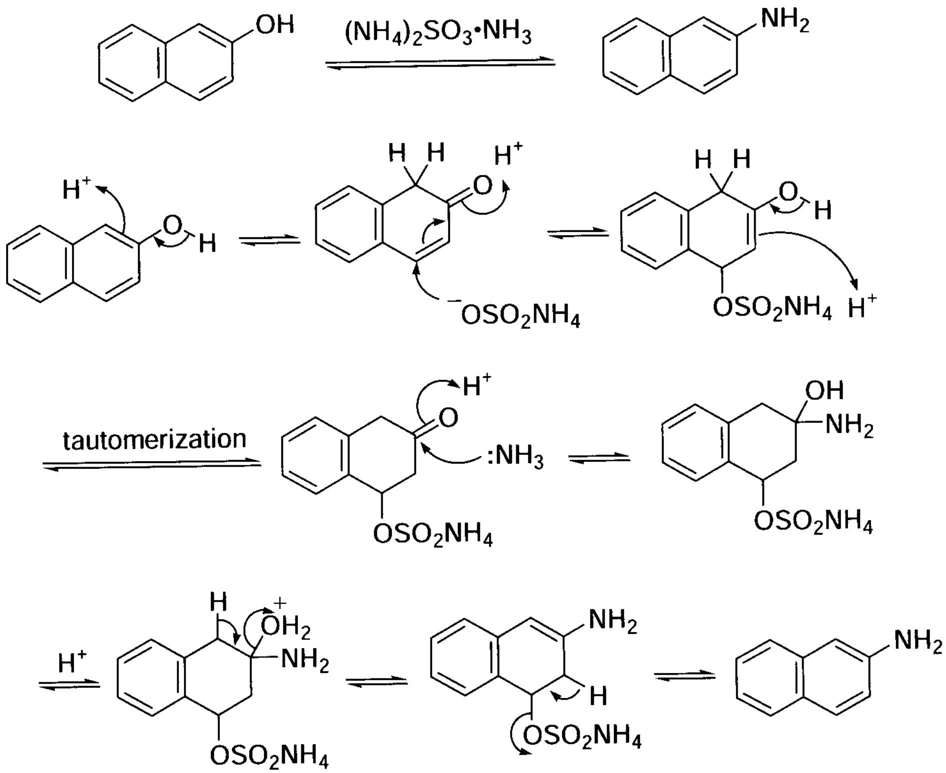
Bucherer reaction



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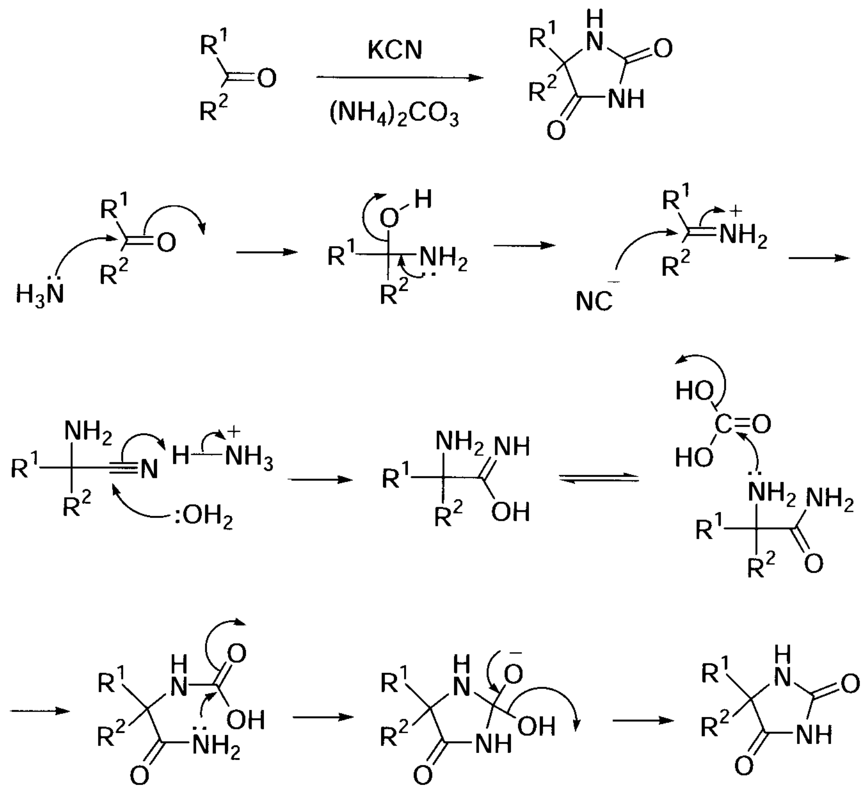
Bucherer–Bergs reaction



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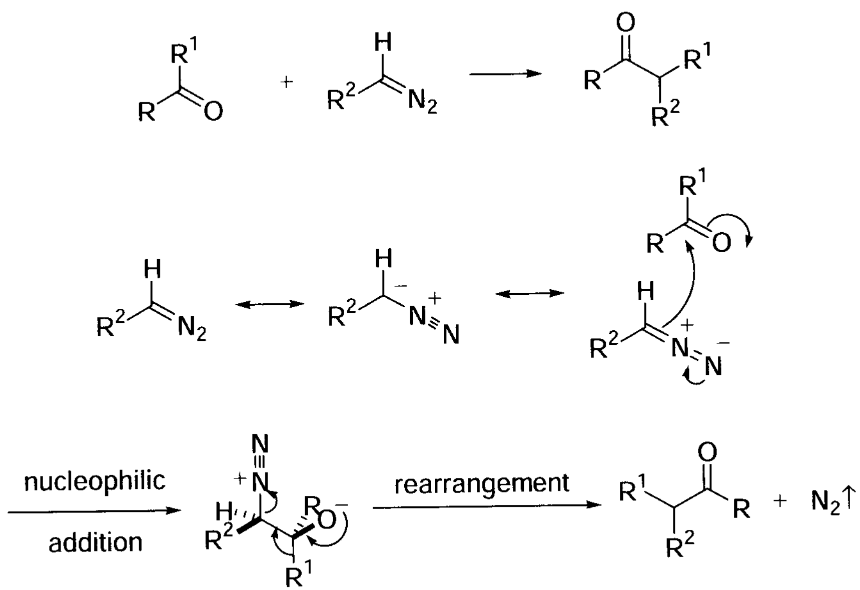
Buchner–Curtius–Schlotterbeck reaction



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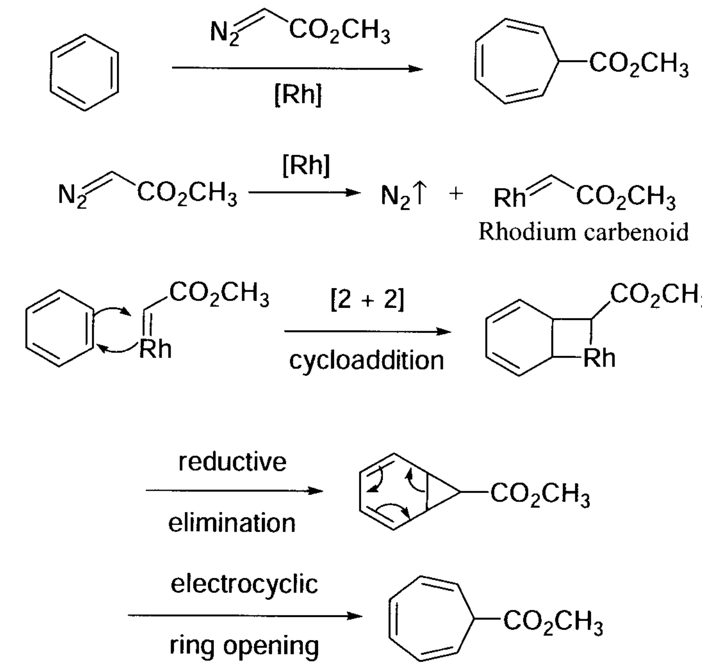
Buchner method of ring expansion



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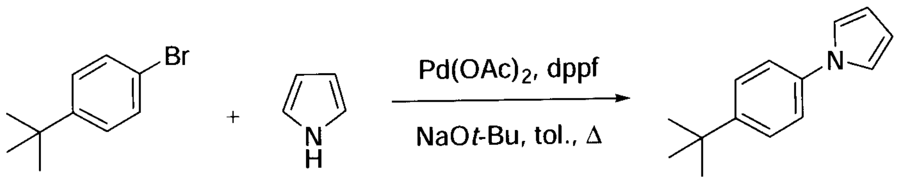
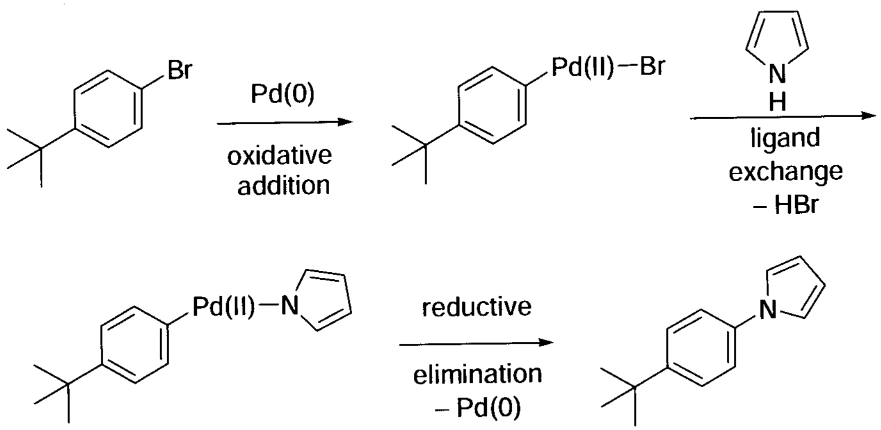
Buchwald–Hartwig C–N bond and C–O bond formation reactions

Direct Pd-catalyzed C–N and C–O bond formation of aryl halides with amines in the presence of stoichiometric amount of base.





The C–O bond formation reaction follows a similar mechanistic pathway [7–9].

References

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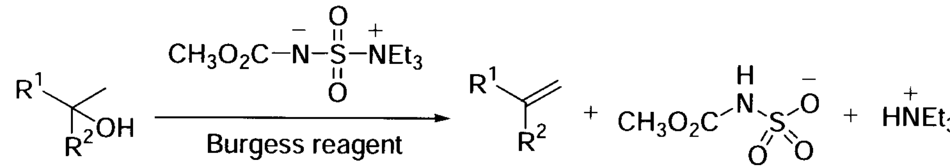
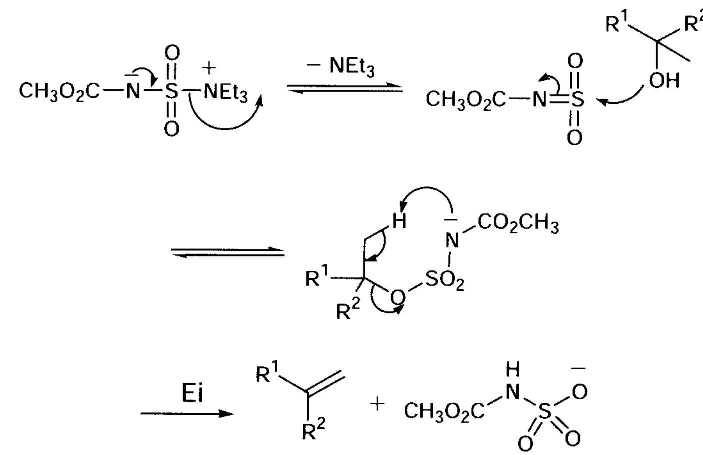
Burgess dehydrating reagent



Burgess dehydrating reagent is efficient at generating olefins from secondary and tertiary alcohols where Ei (during the elimination, the two groups leave at about the same time and bond to each other concurrently) mechanism prevails:



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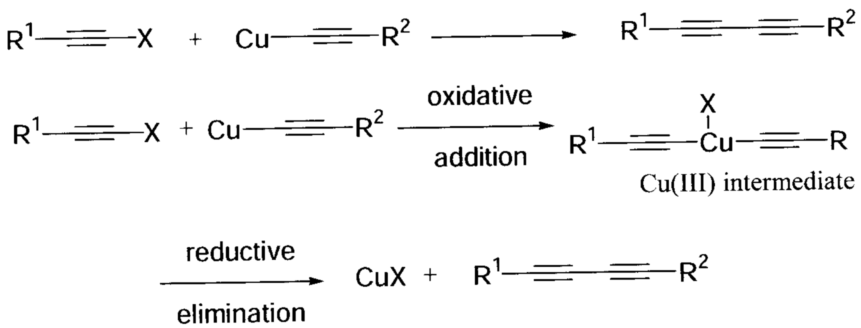
Cadiot–Chodkiewicz coupling

Bis-acetylene synthesis from alkynyl halides and alkynyl copper reagents.
Cf. Castro–Stephens reaction.



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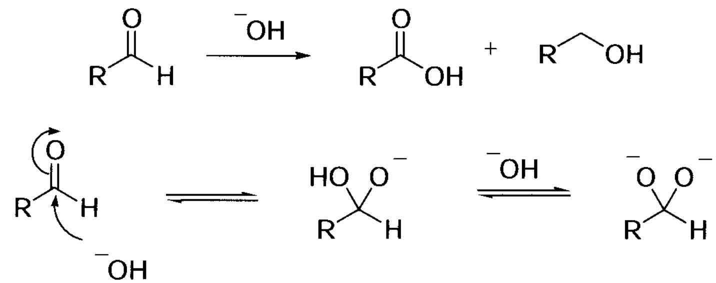
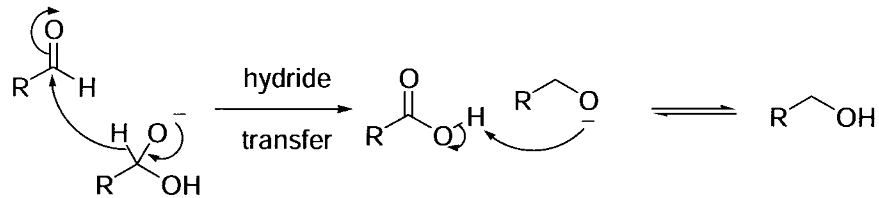
Cannizzaro disproportionation reaction

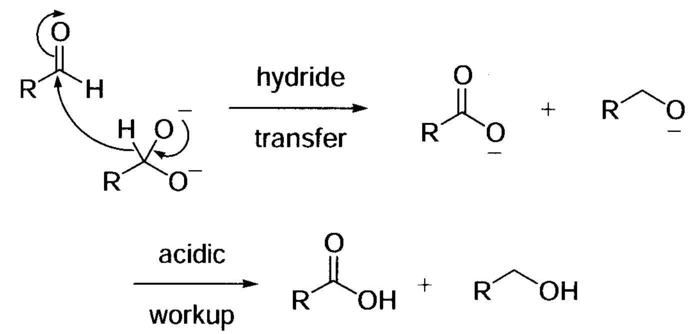


Pathway a:



Final deprotonation of the carboxylic acid drives the reaction forward.

Pathway b:



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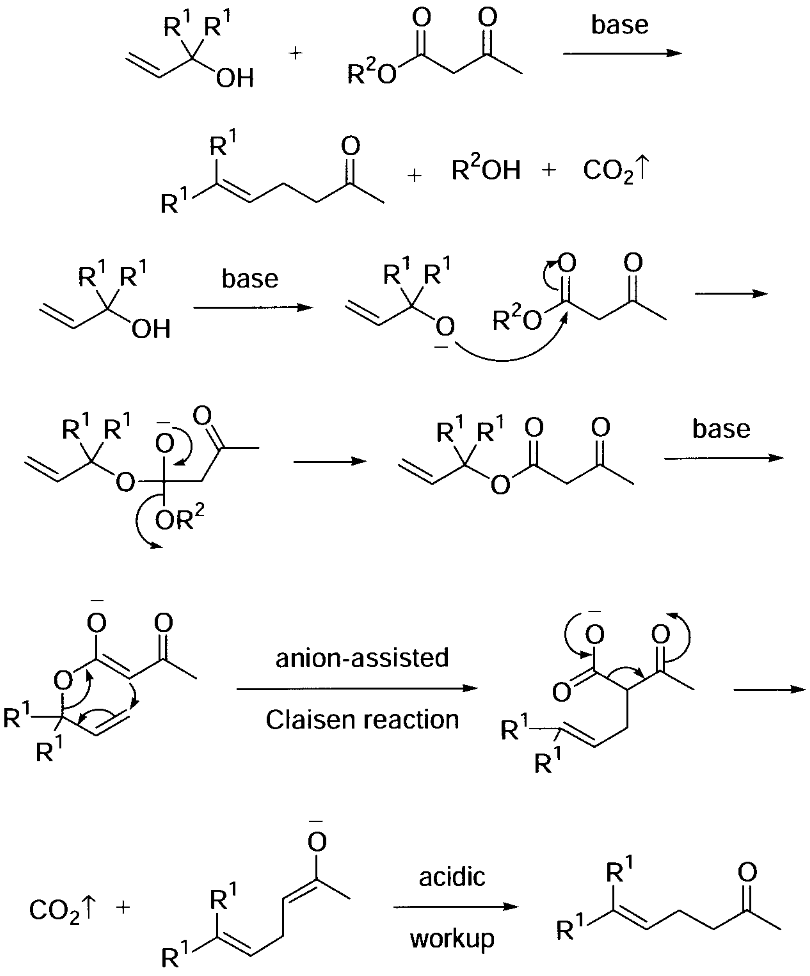
Carroll rearrangement



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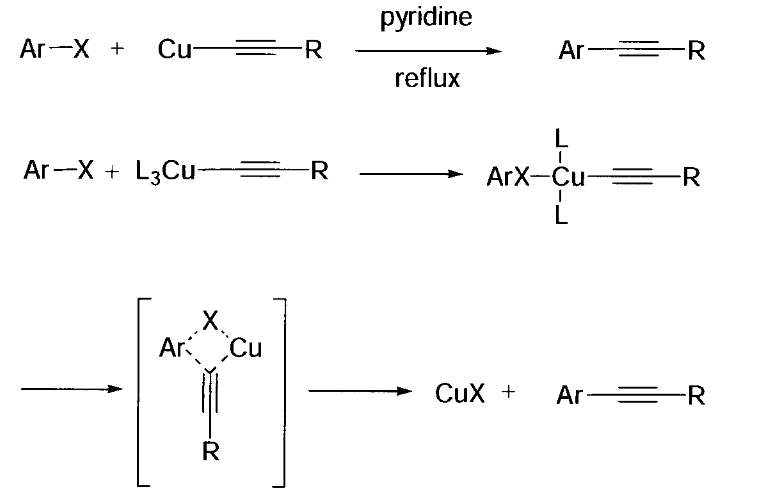
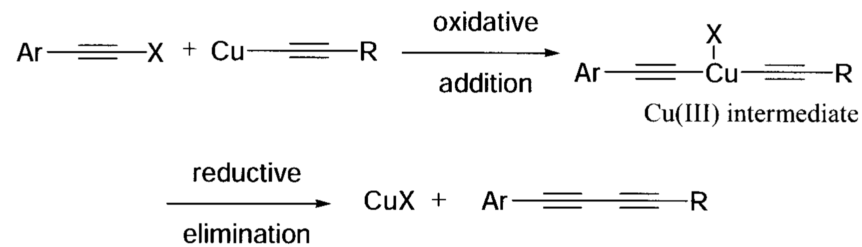
Castro–Stephens coupling

Aryl-acetylene synthesis, *Cf.* Cadiot–Chodkiewicz coupling.



An alternative mechanism similar to that of the Cadiot–Chodkiewicz coupling:



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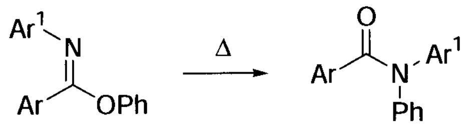
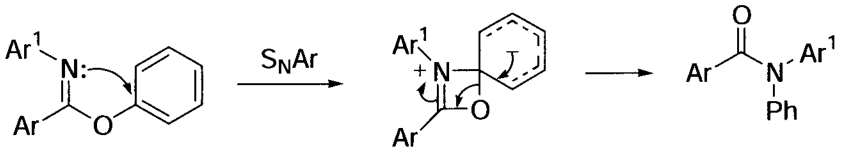
Chapman rearrangement

Thermal aryl rearrangement of *O*-aryliminoethers to amides.





oxazete intermediate

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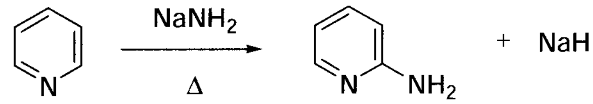
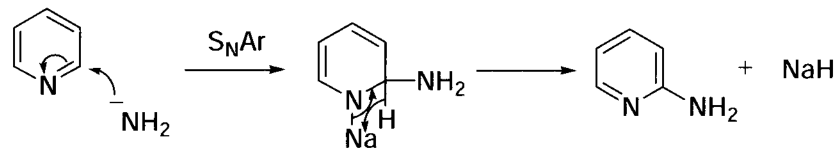
Chichibabin amination reaction





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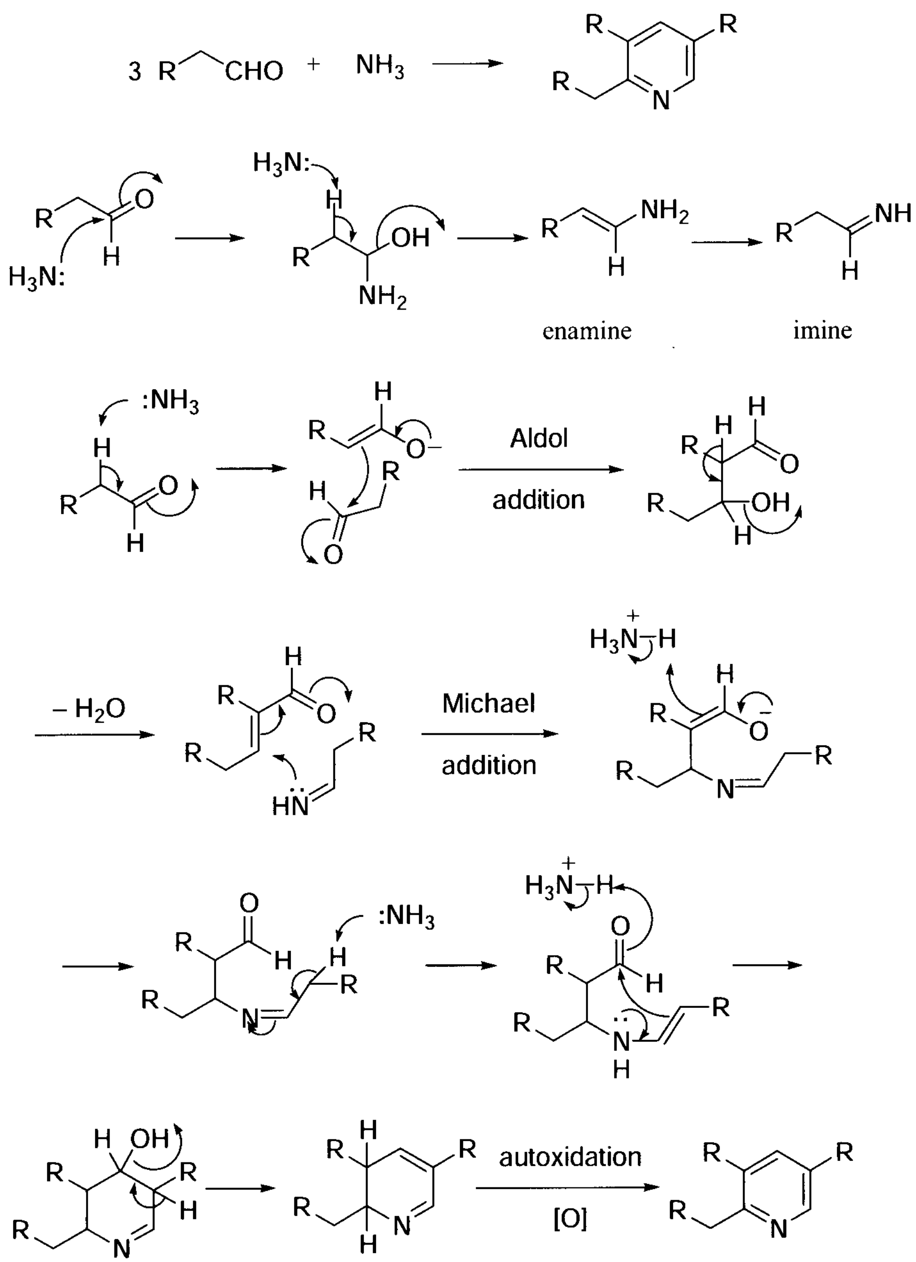
Chichibabin pyridine synthesis



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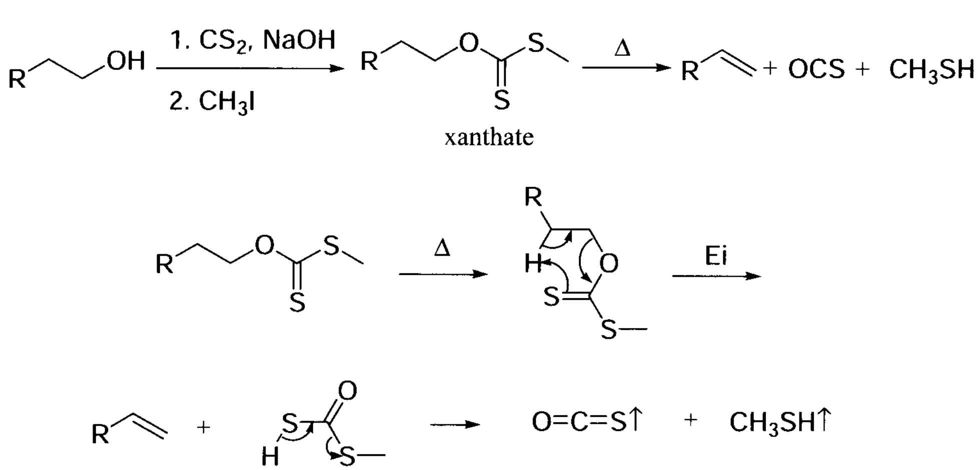
Chugaev elimination

Thermal elimination of xanthates to olefins.



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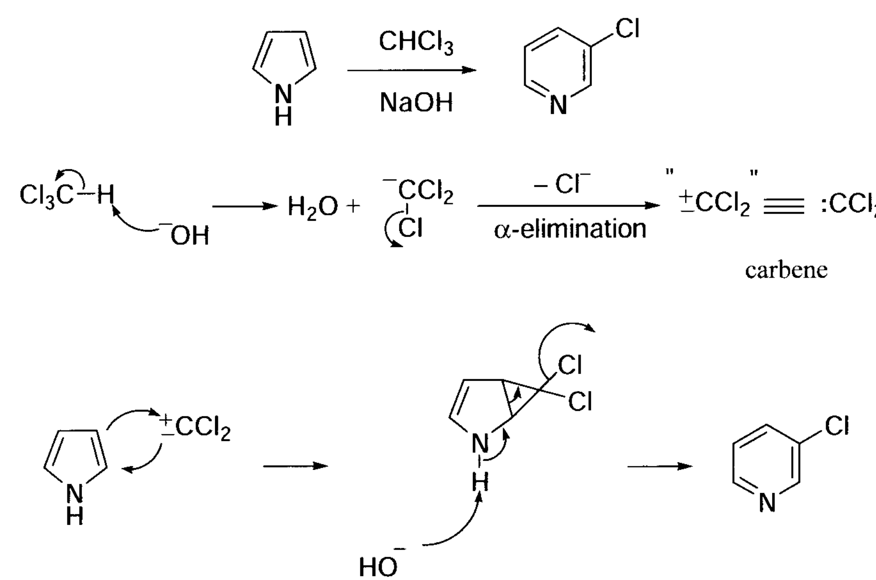
Ciamician–Dennsted rearrangement



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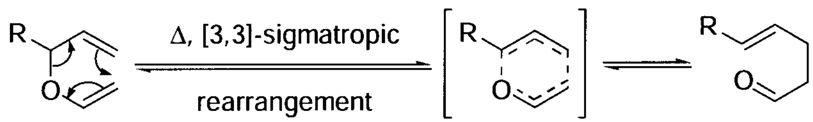
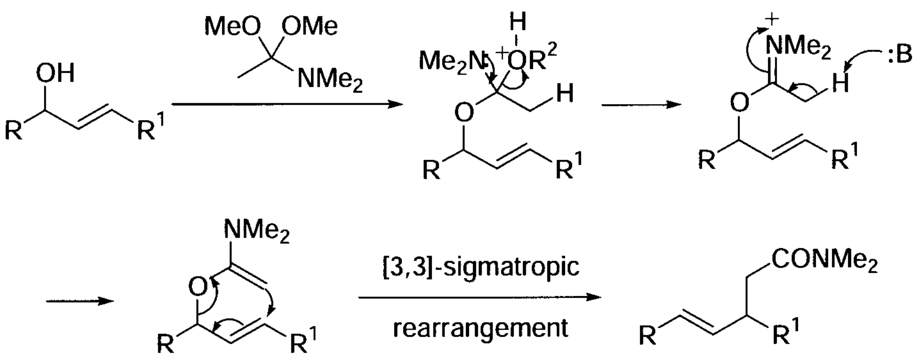
Claisen, Eschenmoser–Claisen, Johnson–Claisen, and Ireland–Claisen rearrangements

The Claisen, Johnson–Claisen, Ireland–Claisen, para-Claisen rearrangements, along with the Carroll rearrangement belong to the category of *[3,3]-sigmatropic rearrangements*, which is a concerted process. The arrow-pushing here is merely illustrative. For the abnormal Claisen rearrangement, see page 1.

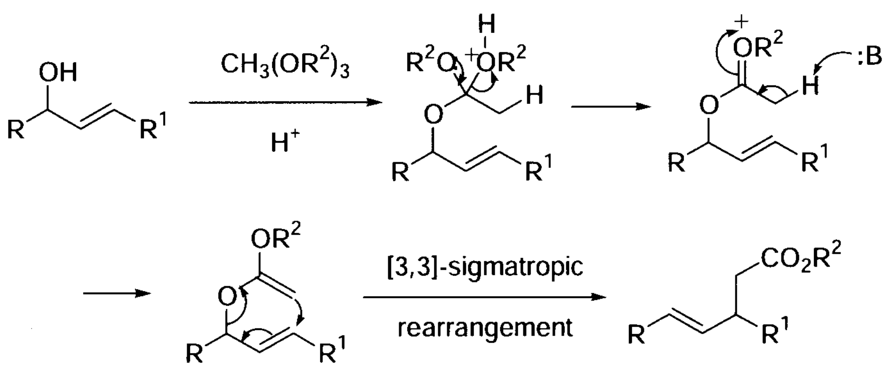
Claisen rearrangement



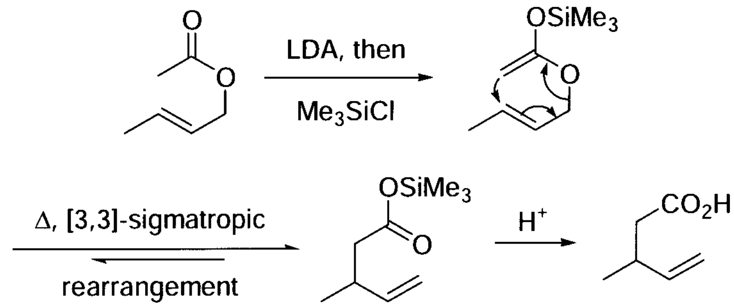
Eschenmoser–Claisen (amide acetal) rearrangements



Johnson–Claisen (orthoester) rearrangement



Ireland–Claisen (silyl ester) rearrangement



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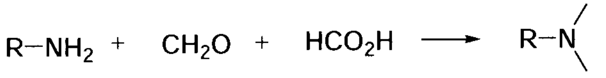
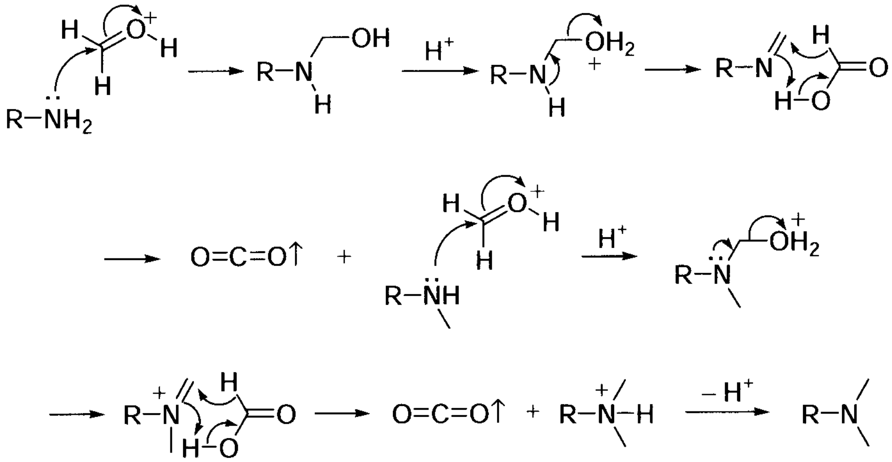
Clark–Eschweiler reductive alkylation of amines



formic acid is the hydrogen source as a reducing agent



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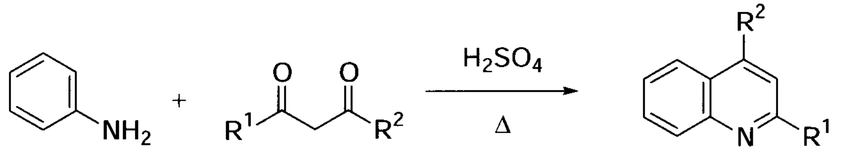
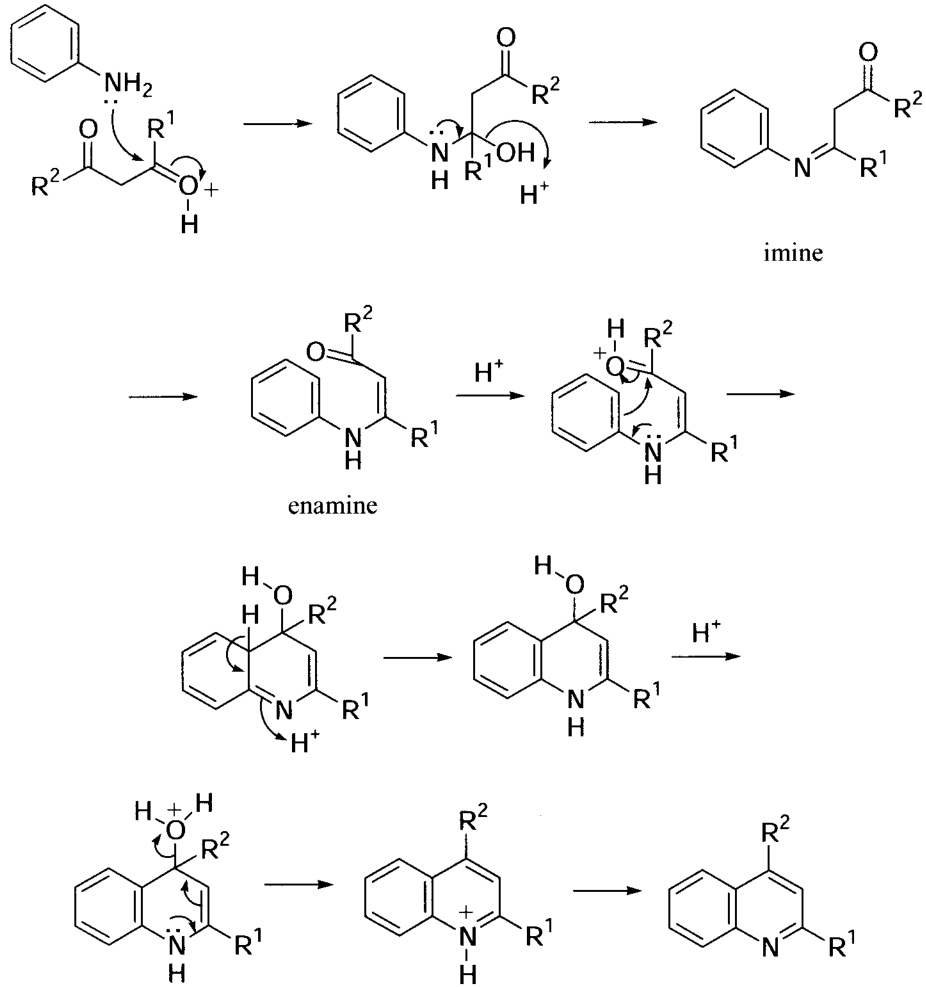
Combes quinoline synthesis





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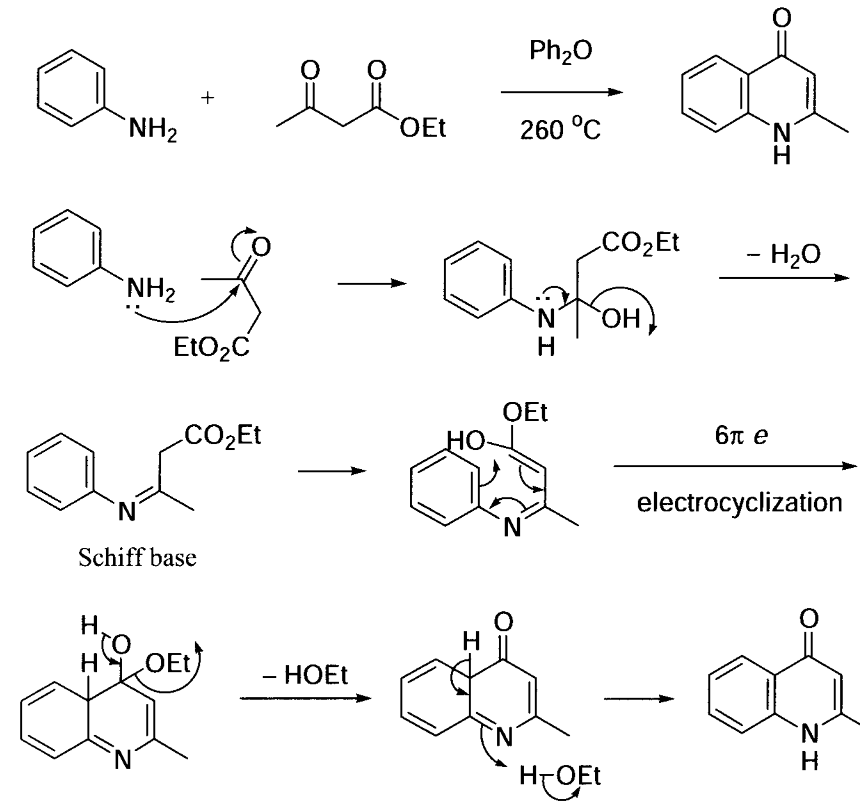
Conrad–Lipach reaction



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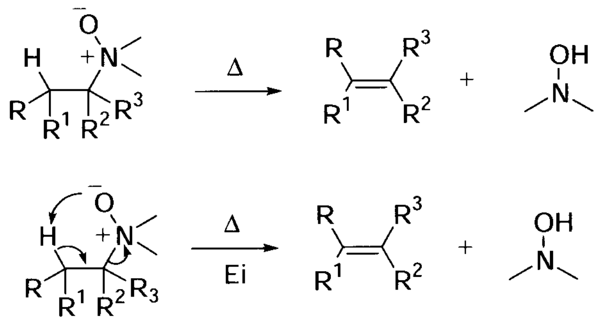
Cope elimination reaction

Thermal elimination of *N*-oxides to olefins.



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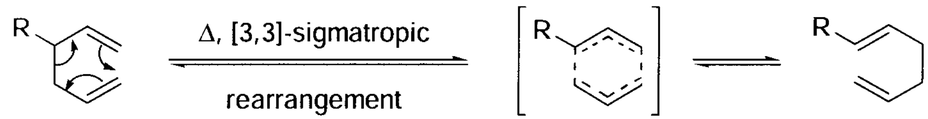
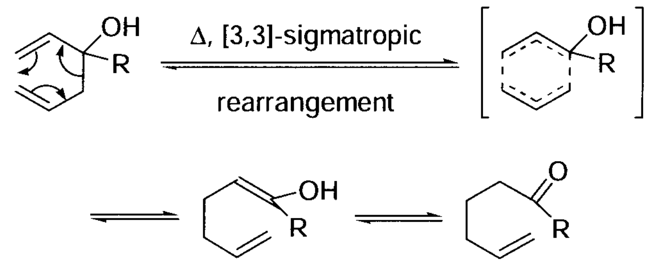
Cope, oxy-Cope, and anionic oxy-Cope rearrangements

The Cope, oxy-Cope, and anionic oxy-Cope rearrangements belong to the category of *[3,3]-sigmatropic rearrangements*, which is a concerted process. The arrow-pushing here is only illustrative.

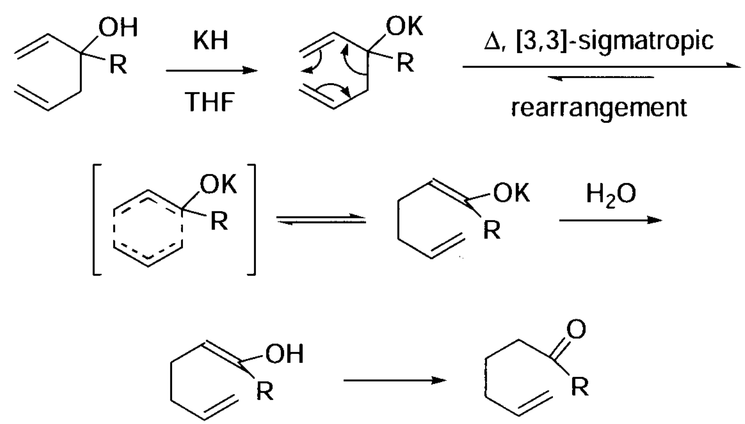
Cope rearrangement



oxy-Cope rearrangement



anionic oxy-Cope rearrangement



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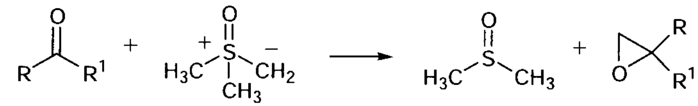
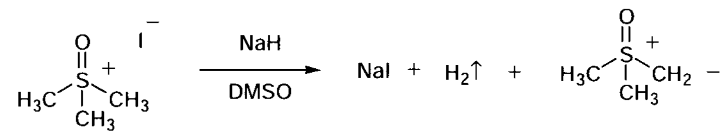
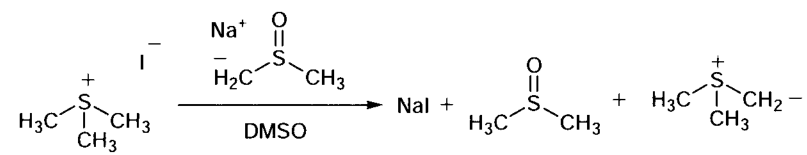
Corey–Chaykovsky epoxidation

Epoxidation of carbonyls using dimethylsulfoxonium methylide or dimethylsulfonium methylide.

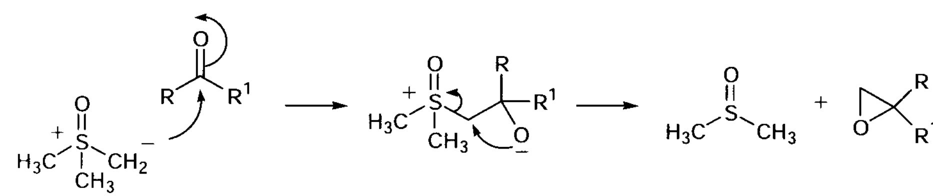




dimethylsulfoxonium methylide (DMSY)



dimethylsulfonium methylide



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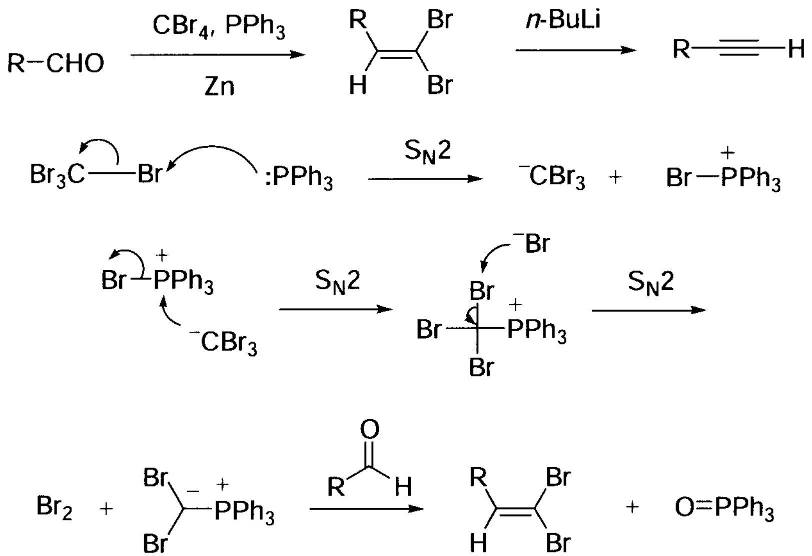
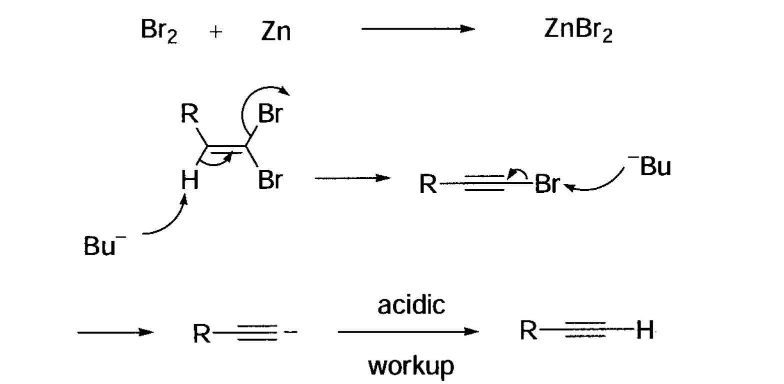
Corey–Fuchs reaction



Wittig reaction (see page 396 for the mechanism)



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2 For the synthesis of 1-bromalkynes, see, Grandjean, D.; Pale, P.; Chuche, J. *ibid.* **1994**, *35*, 3529.
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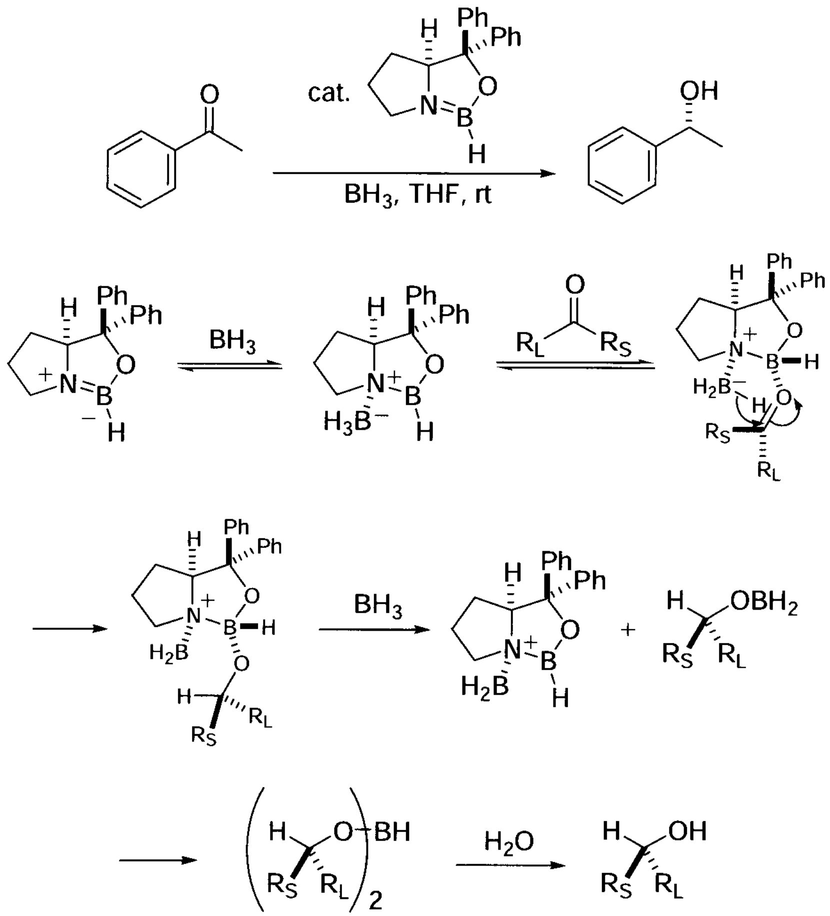
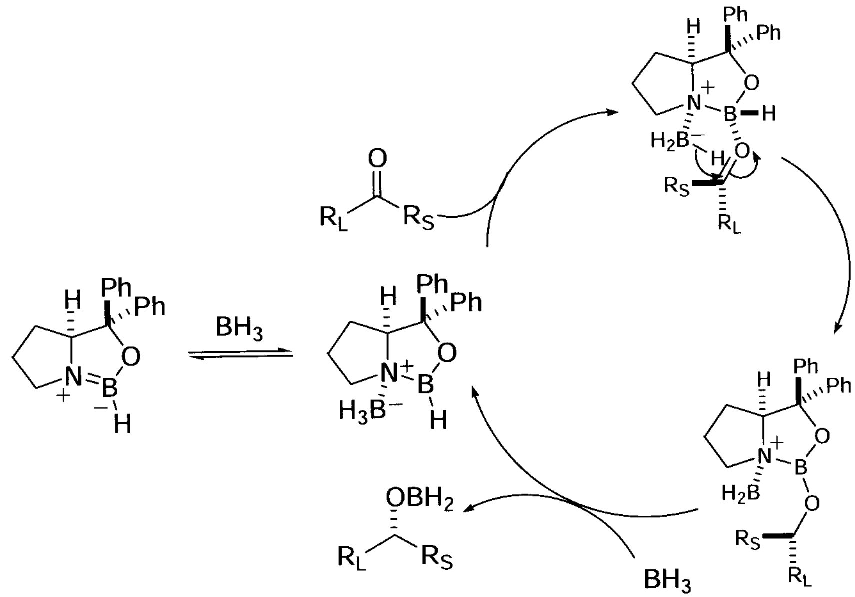
Corey–Bakshi–Shibata (CBS) reduction

Enantioselective borane reduction of ketones catalyzed by chiral oxaborolidines.



The catalytic cycle:



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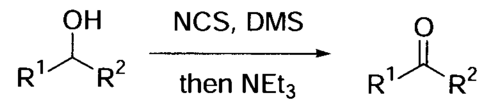
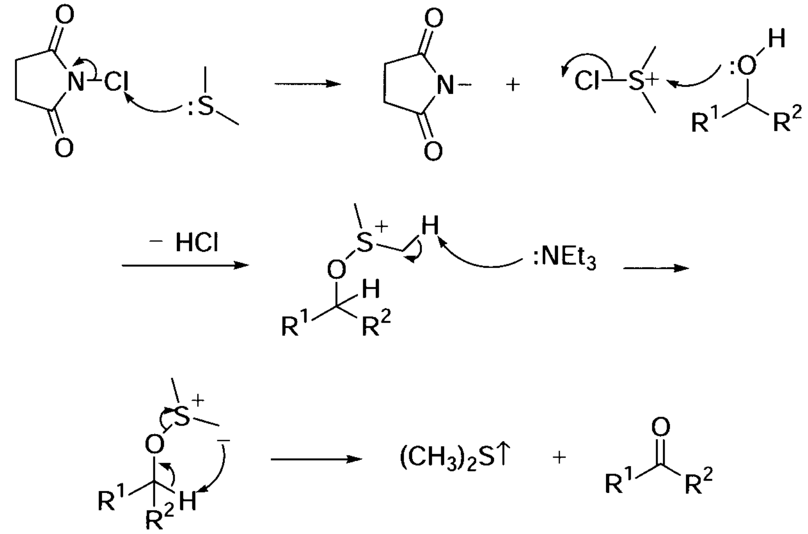
Corey–Kim oxidation

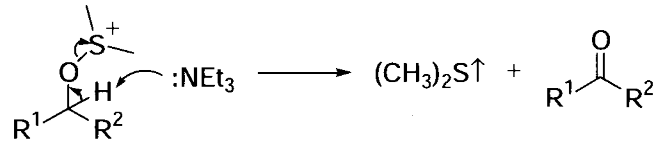
Oxidation of alcohols to the corresponding aldehyde or ketone using NCS/DMF, followed by treatment with a base.



NCS = *N*-Chlorosuccinamide; DMS = **Dimethylsulfide**.



Alternatively:



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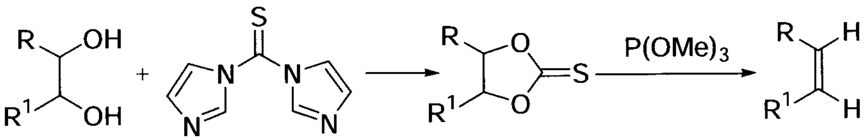
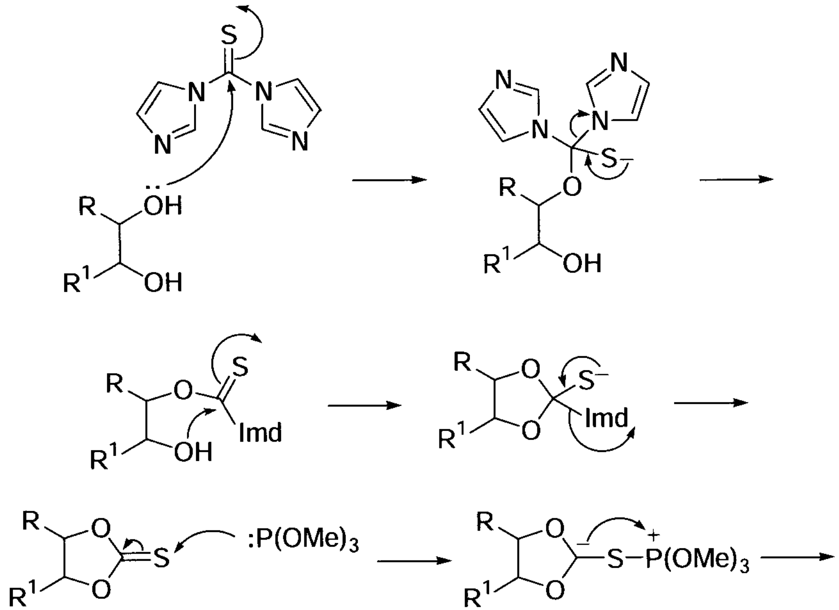
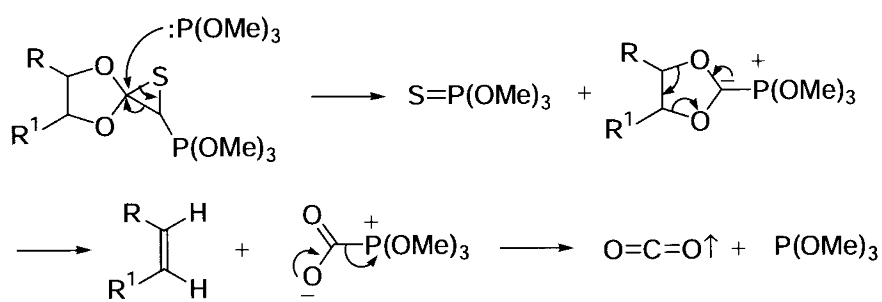
Corey–Winter olefin synthesis

Transformation of diols to the corresponding olefins by sequential treatment with 1,1'-thiocarbonyldiimidazole and trimethylphosphite.

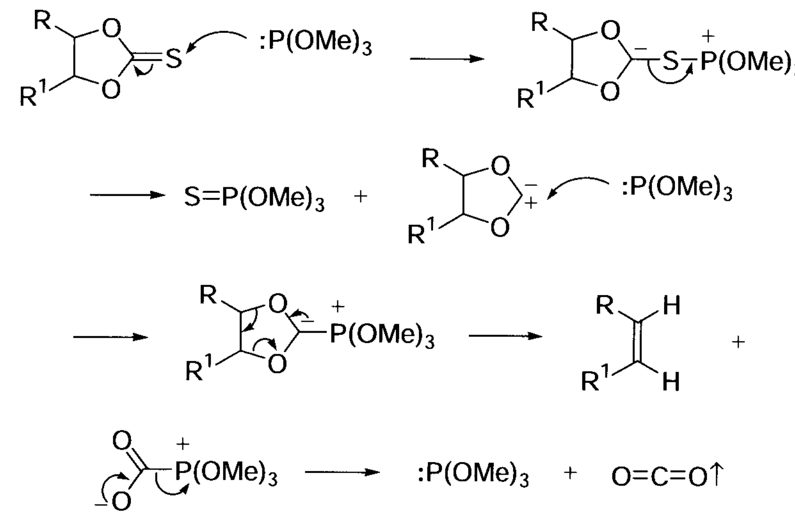




1,3-dioxolane-2-thione (cyclic thionocarbonate)



A mechanism involving a carbene intermediate is also viable as it is supported by pyrolysis studies:



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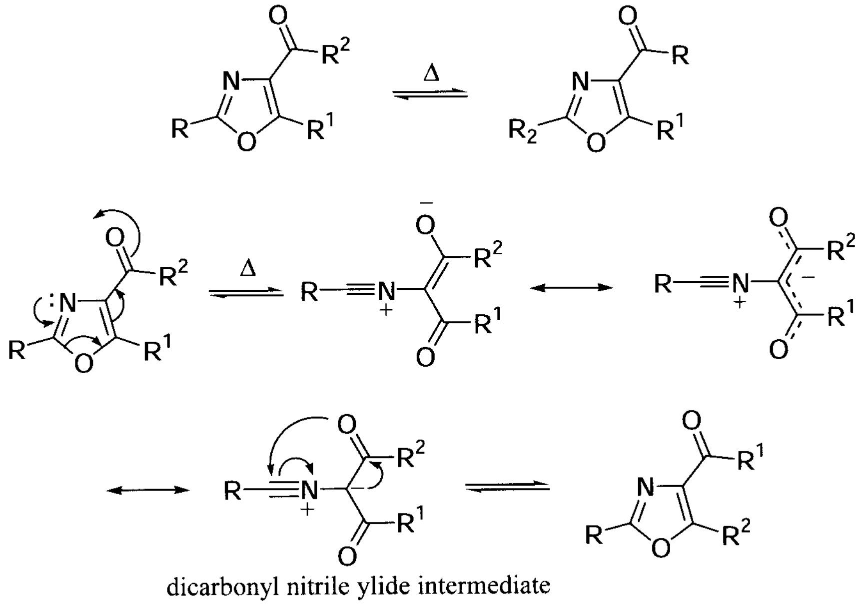
Cornforth rearrangement

Thermal rearrangement of keto-oxazoles.



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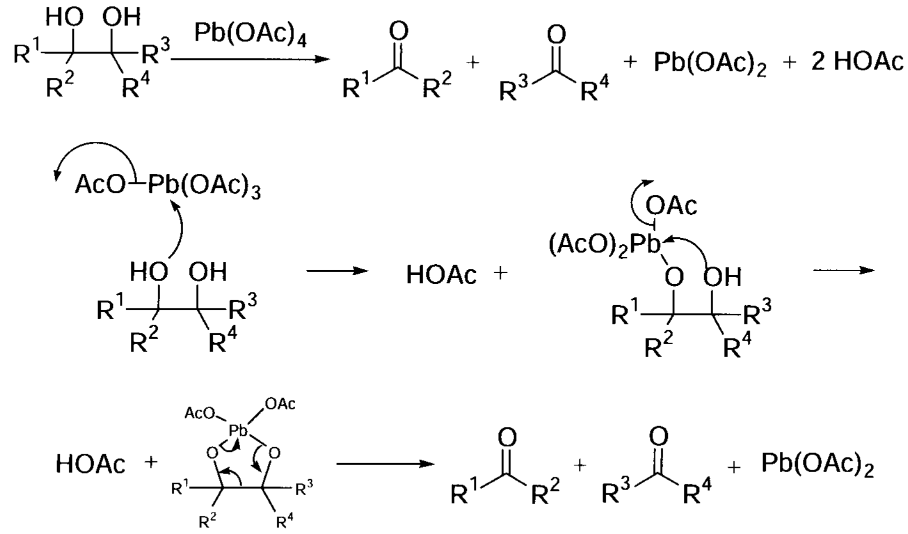
Criegee glycol cleavage

Vicinal diol is oxidized to the two corresponding carbonyl compounds using $Pb(OAc)_4$.



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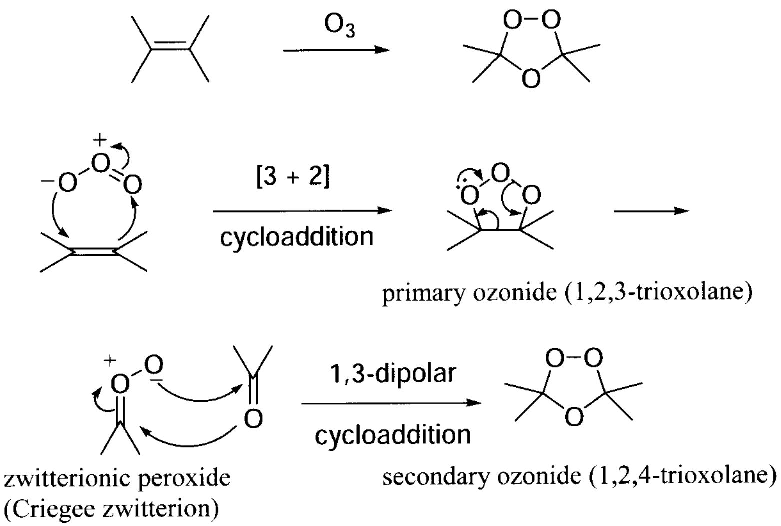
Criegee mechanism of ozonolysis



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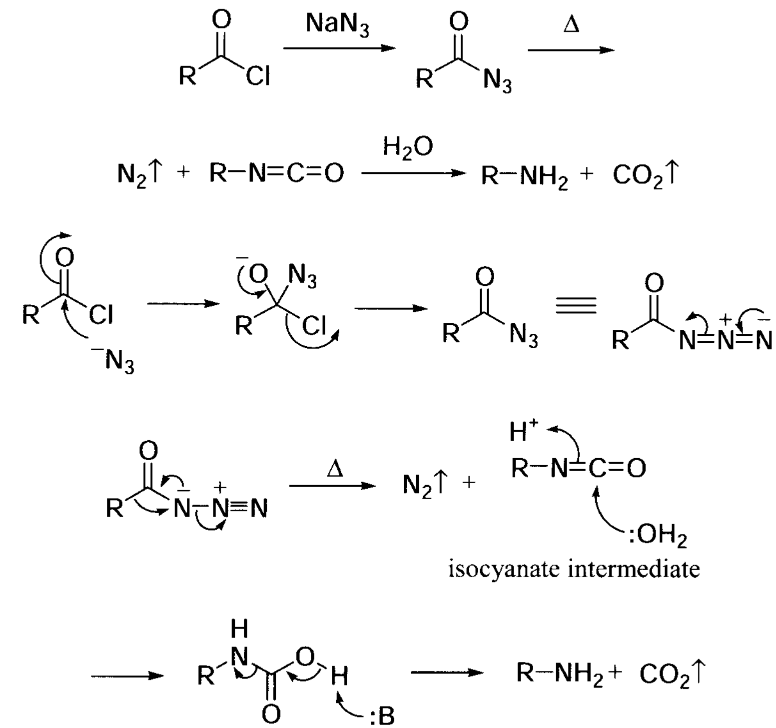
Curtius rearrangement



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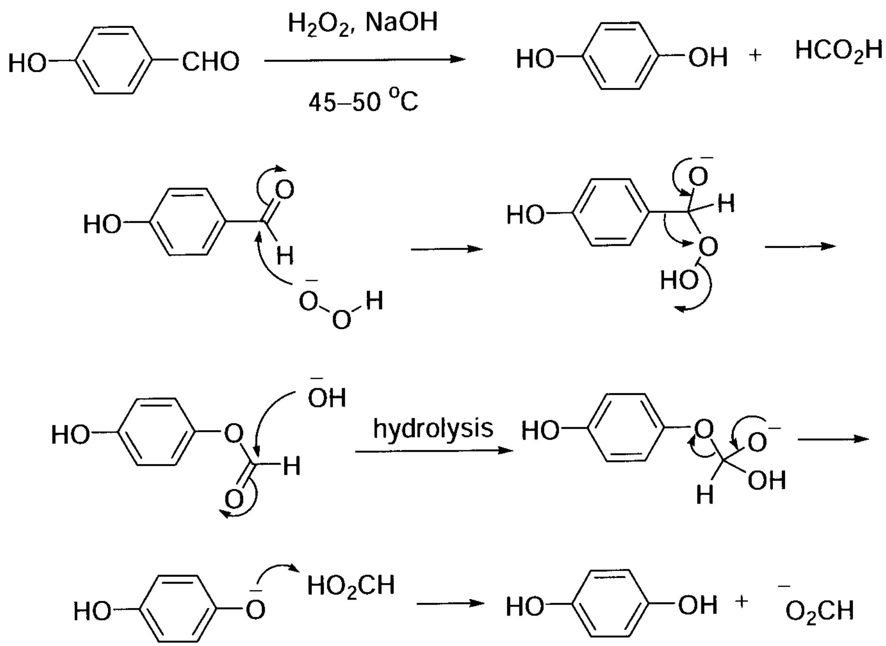
Dakin reaction

Cf. Baeyer–Villiger oxidation



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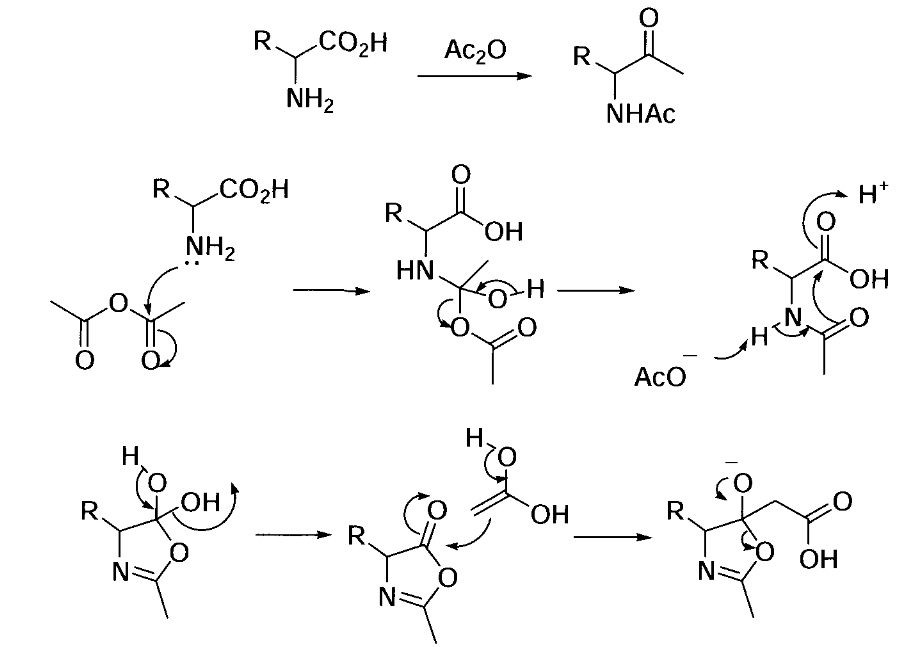
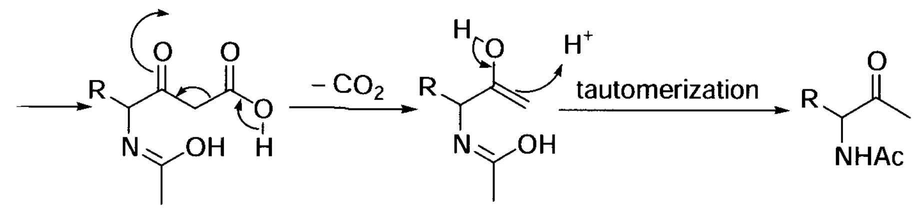
Dakin–West reaction



oxazolone intermediate



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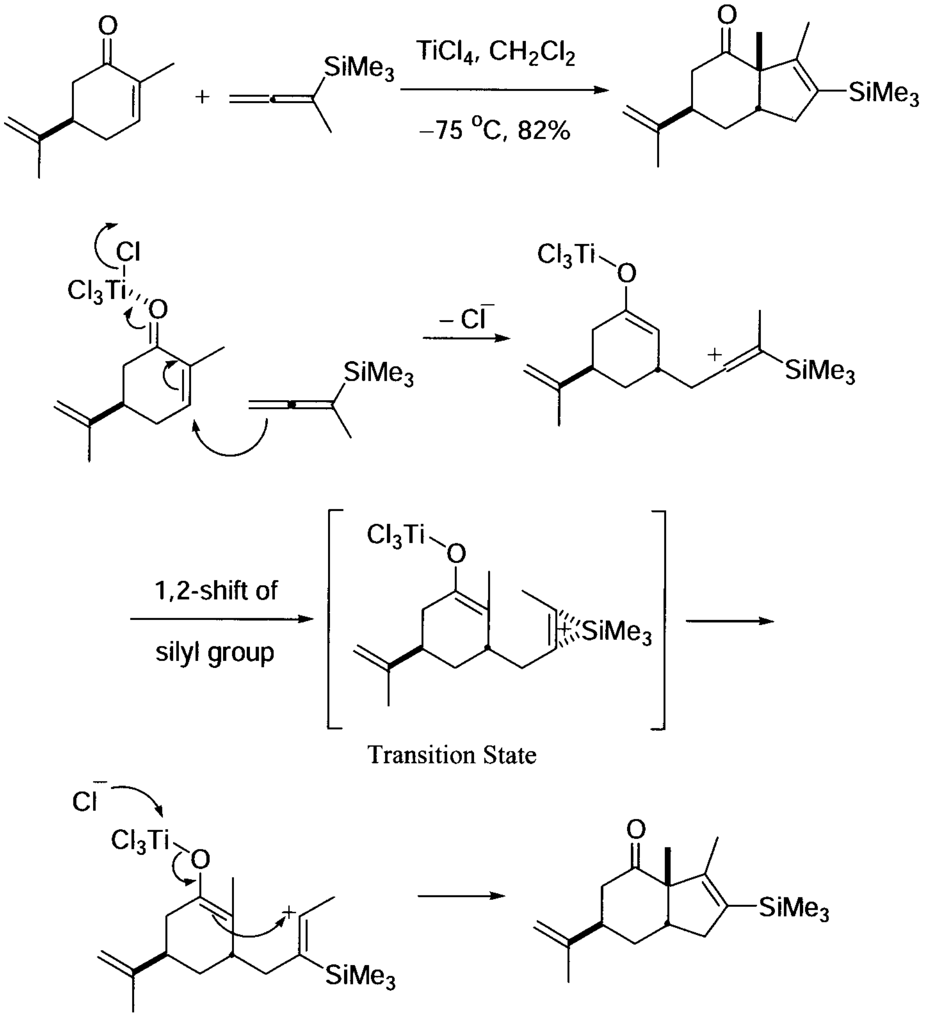
Danheiser annulation

Trimethylsilylcyclopentene annulation from an α,β-unsaturated ketone and trimethylsilylallene in the presence of a Lewis acid.



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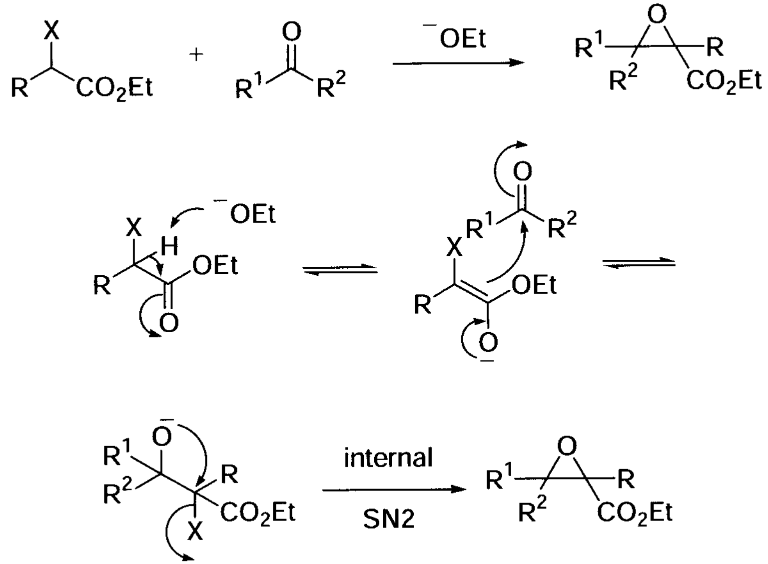
Darzens glycidic ester condensation



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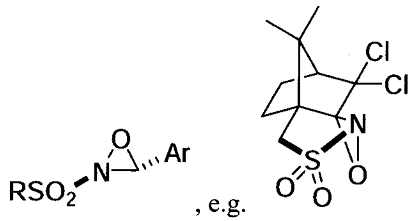
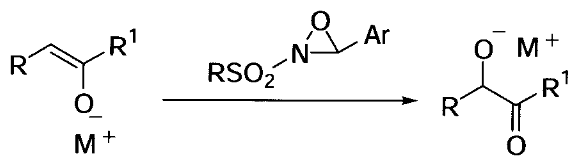
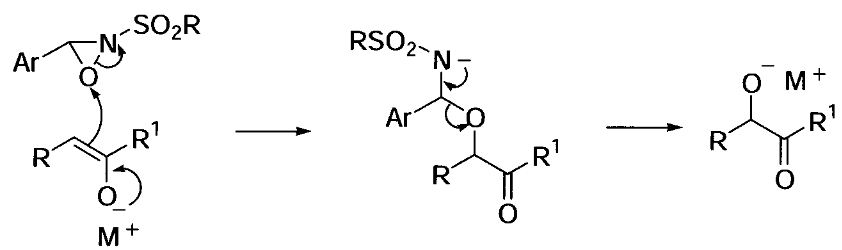
Davis chiral oxaziridine reagents

Chiral *N*-sulfonyloxaziridines employed for asymmetric hydroxylation *etc.*







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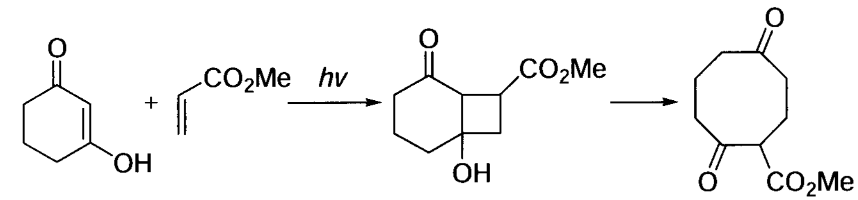
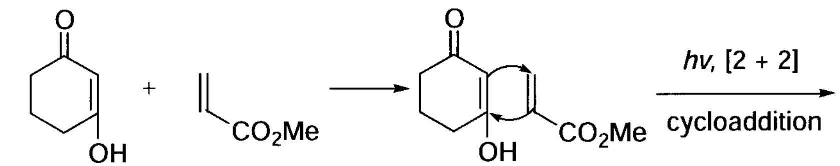
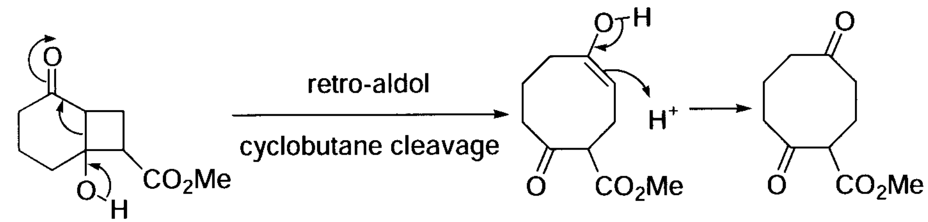
de Mayo reaction

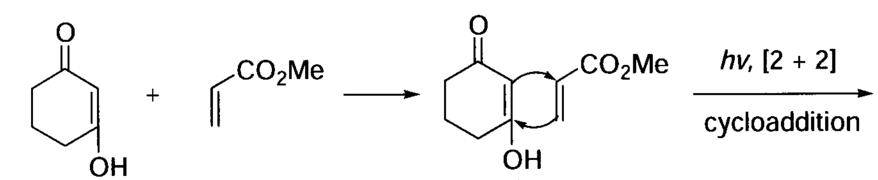




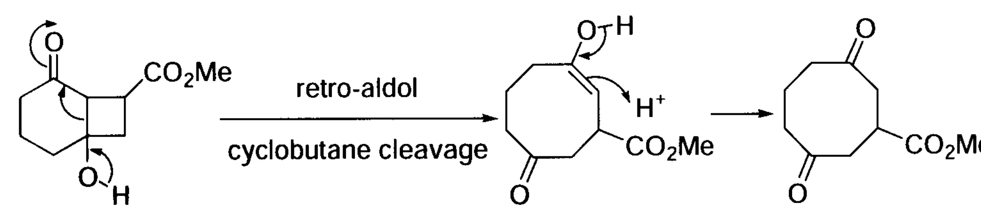
head-to-tail alignment



A minor regioisomer:



head-to-head alignment



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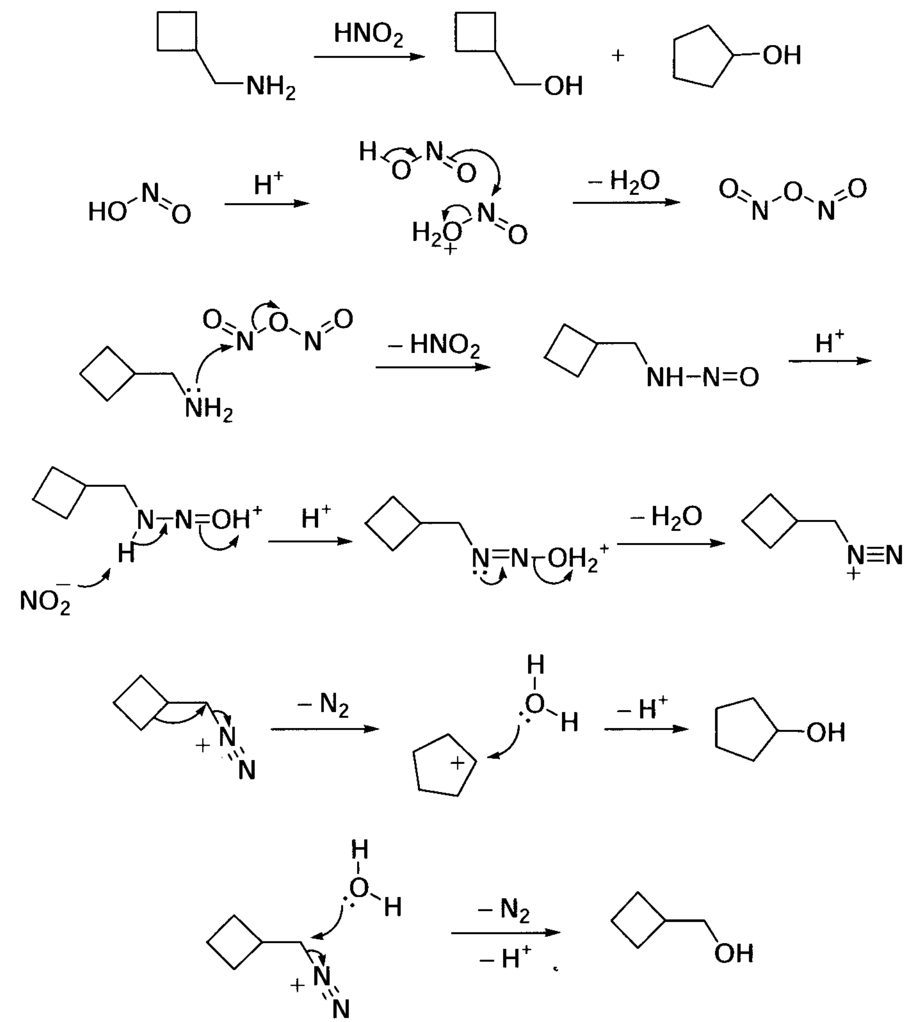
Demjanov rearrangement



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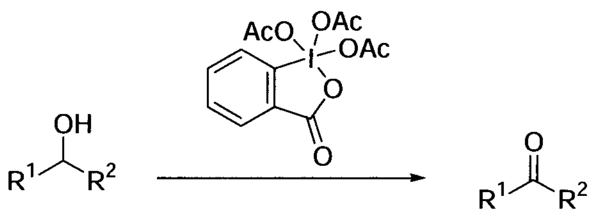
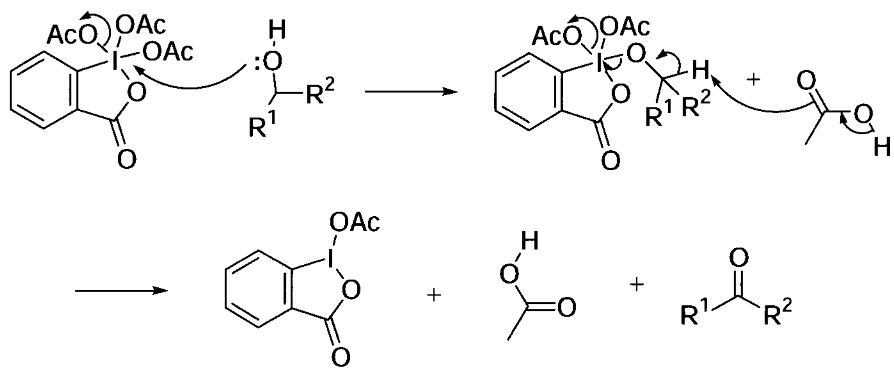
Dess–Martin periodinane oxidation





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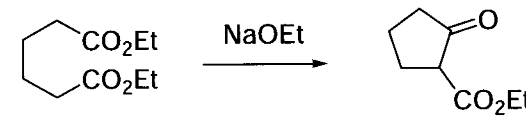
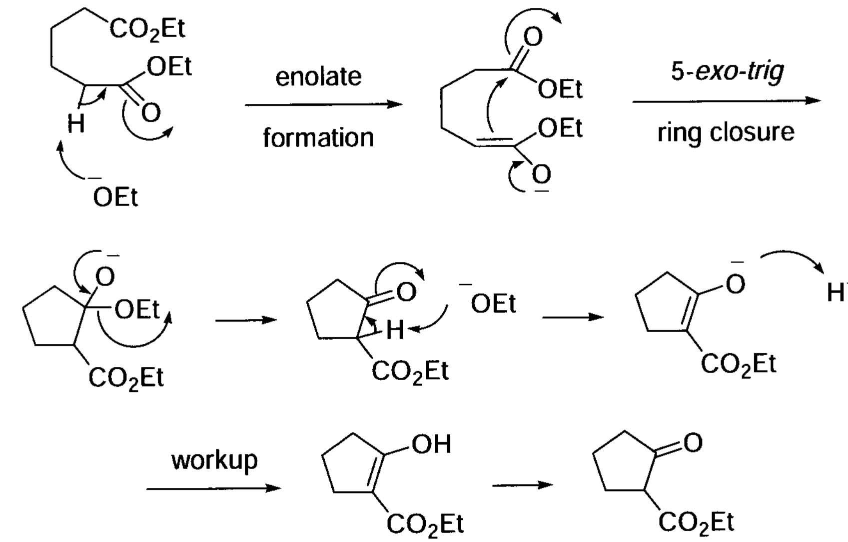
Dieckmann condensation

The Dieckmann condensation is the intramolecular version of the Claisen condensation.





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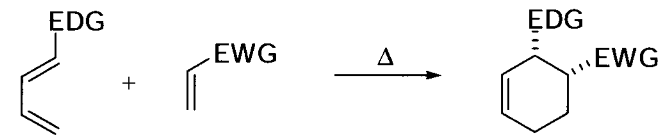
Diels–Alder reaction, inverse electronic demand Diels–Alder reaction, hetero-Diels–Alder reaction

The Diels–Alder reaction, reverse electronic demand Diels–Alder reaction, as well as the hetero-Diels–Alder reaction, belong to the category of *[4+2]-cycloaddition reactions*, which is a concerted process. The arrow-pushing here is merely illustrative.

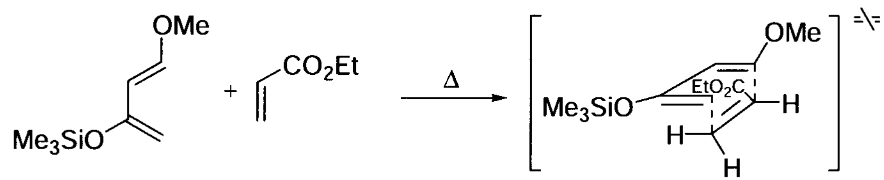
Normal Diels–Alder reaction



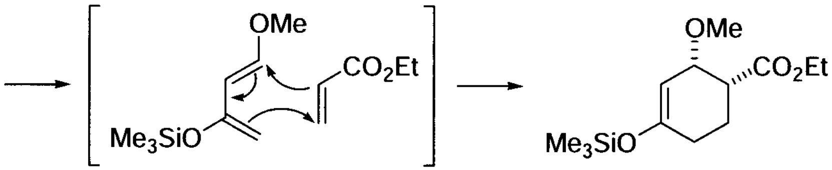
diene dienophile adduct

EDG = electron-donating group; EWG = electron-withdrawing group

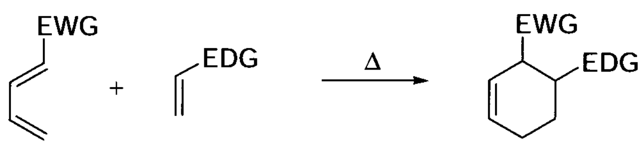
e.g.



Danishefsky diene Alder's *endo* rule

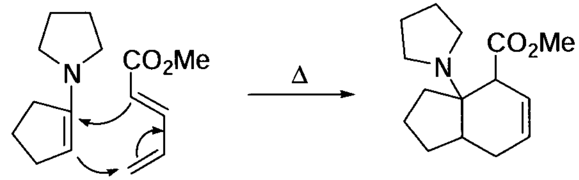


Inverse electronic demand Diels–Alder reaction



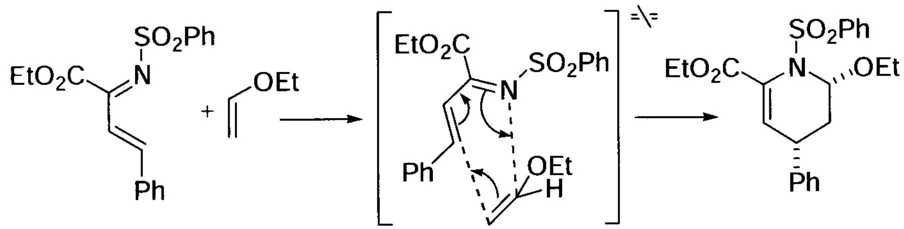
diene dienophile adduct

e.g.

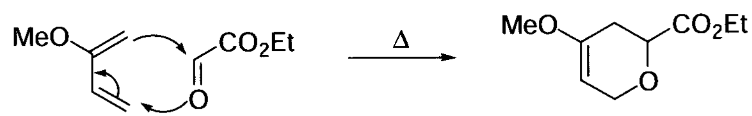


Hetero-Diels–Alder reaction

a. Heterodiene addition to dienophile



b. Heterodienophile addition to diene



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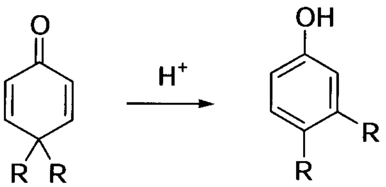
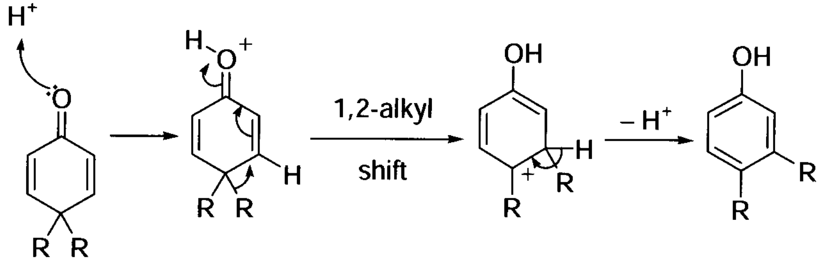
Dienone–phenol rearrangement





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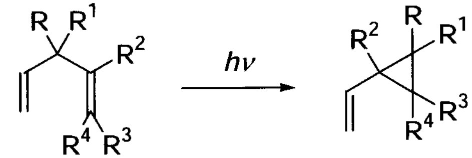
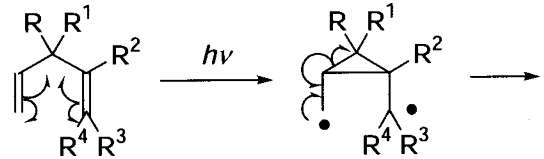
Di-π-methane rearrangement

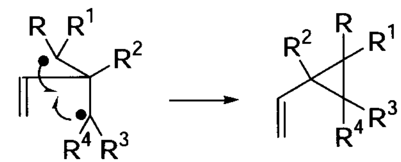
1,4-Dienes to vinylcyclopropanes under photolysis.



1,4-diene vinylcyclopropane



diradical



diradical

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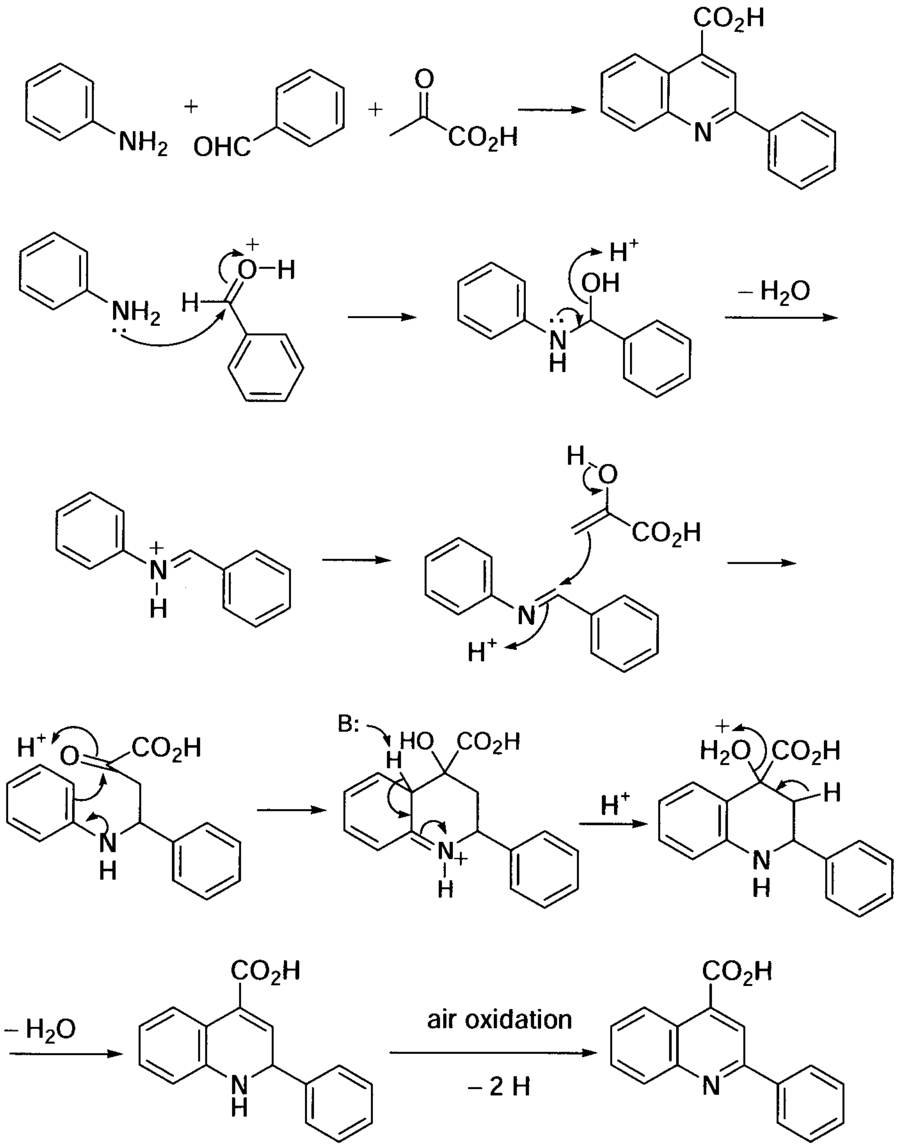
Doebner reaction

Three-component reaction yielding isoquinolines.



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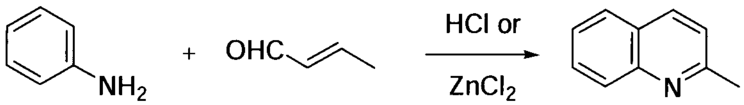
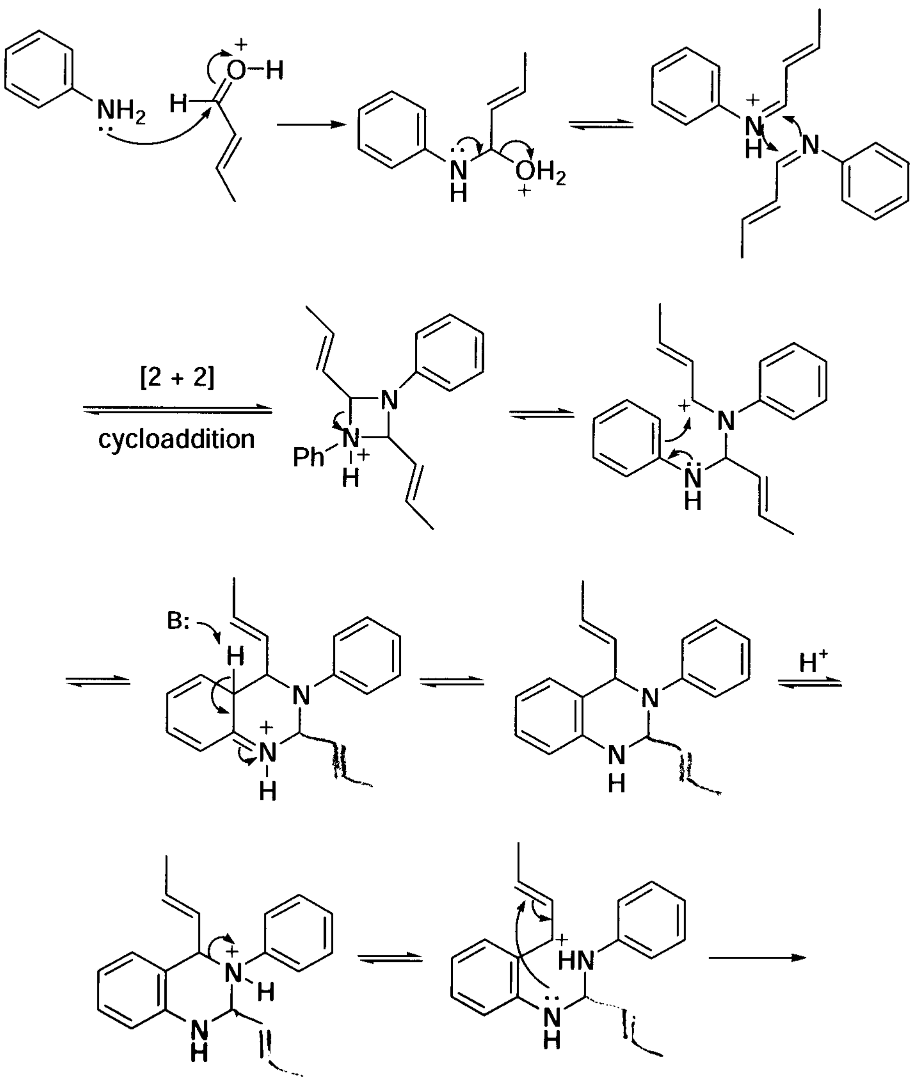
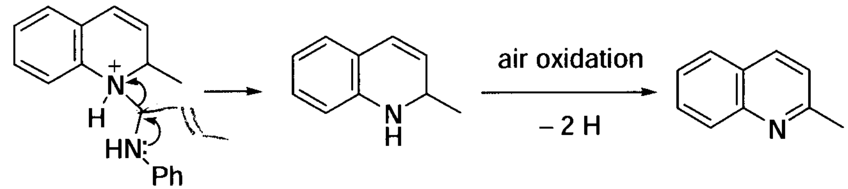
Doebner–von Miller reaction

Doebner–von Miller reaction is a variant of the Skraup reaction. Therefore, the mechanism for the Skraup reaction is also operative for the Doebner–von Miller reaction. An alternative mechanism shown below is based on the fact that the preformed imine (Schiff base) also gave 2-methylquinoline:







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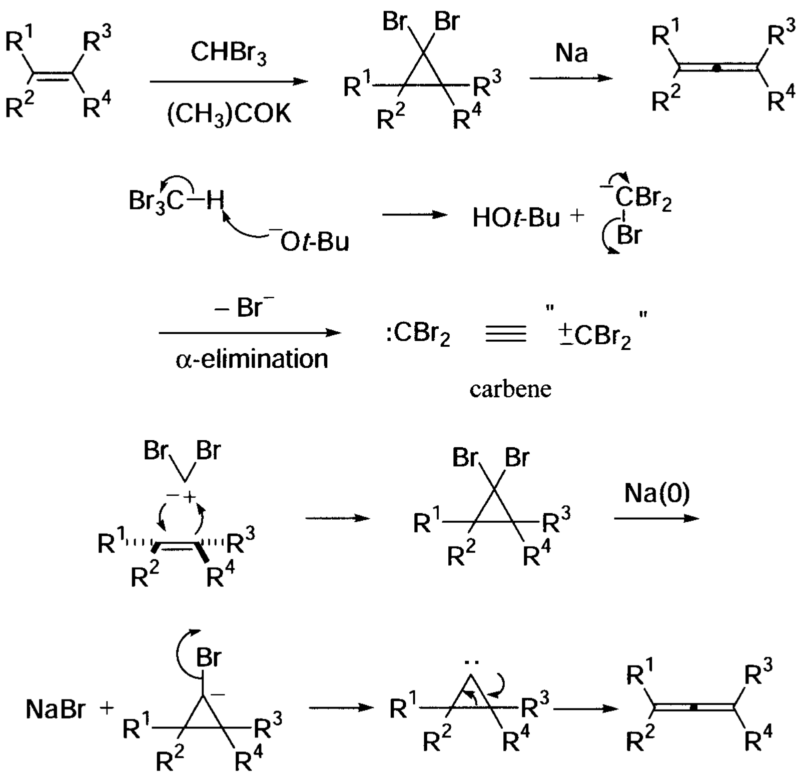
Doering–LaFlamme allene synthesis



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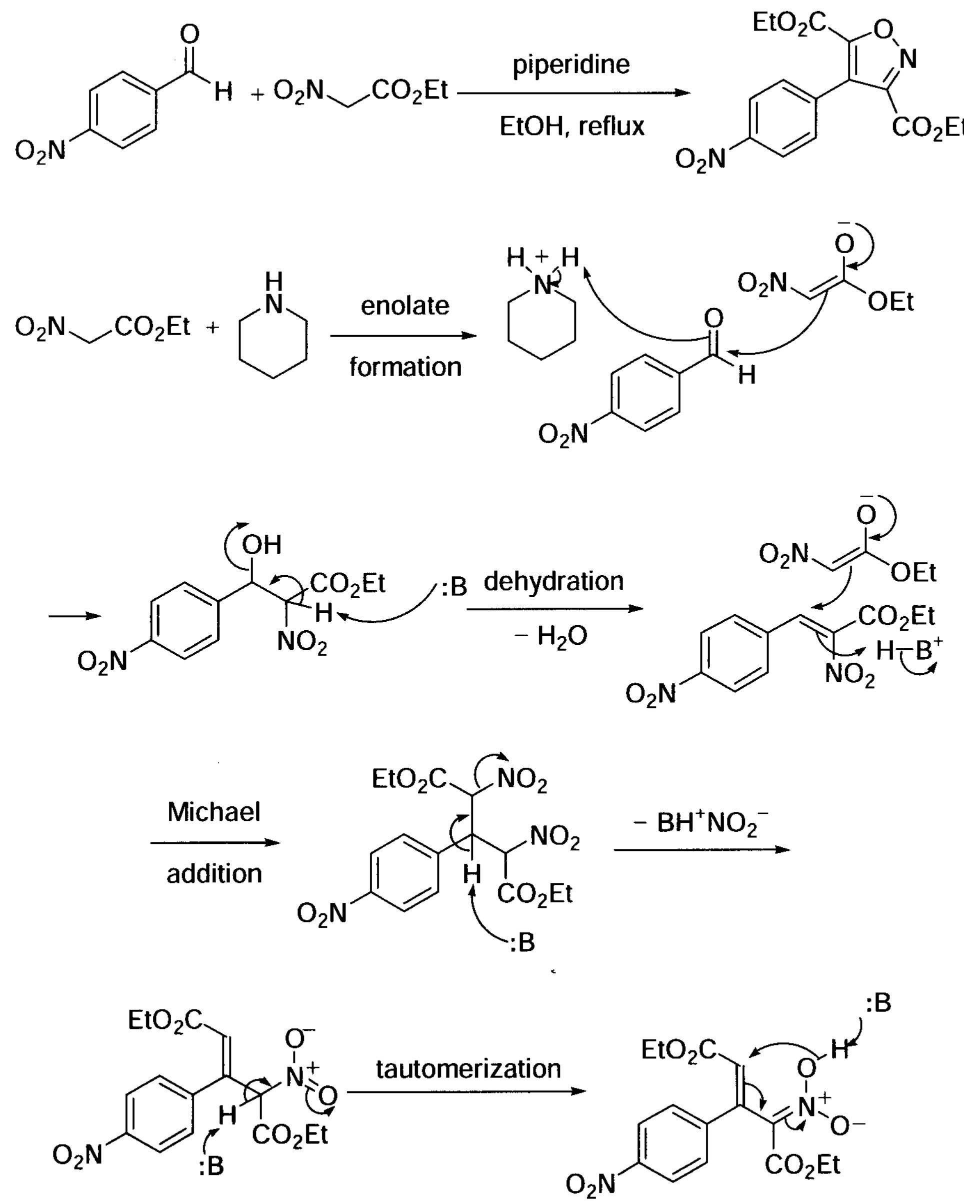
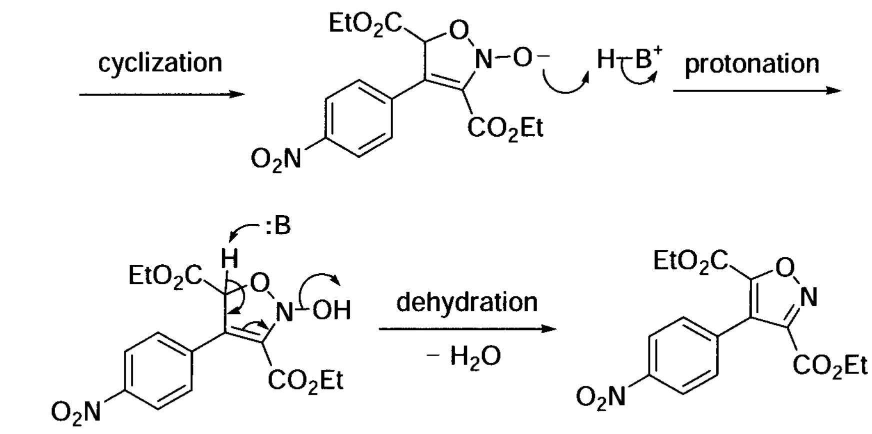
Dornow–Wiehler isoxazole synthesis





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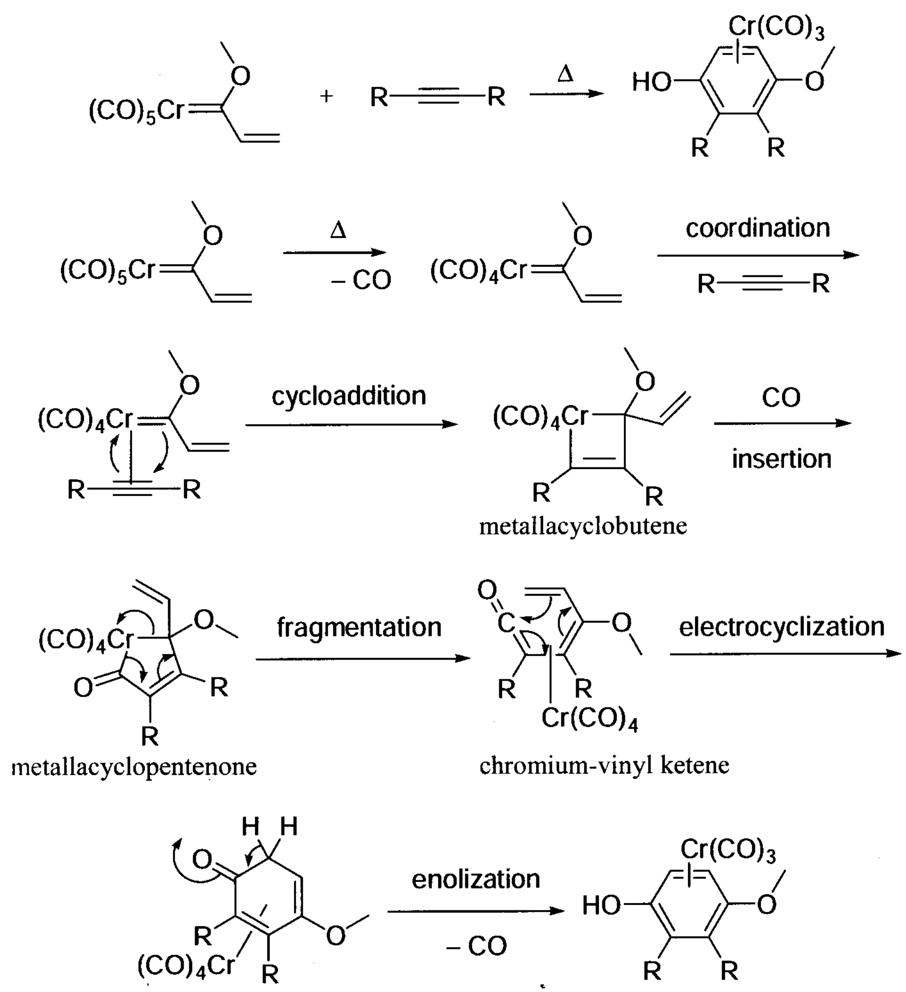
Dötz reaction



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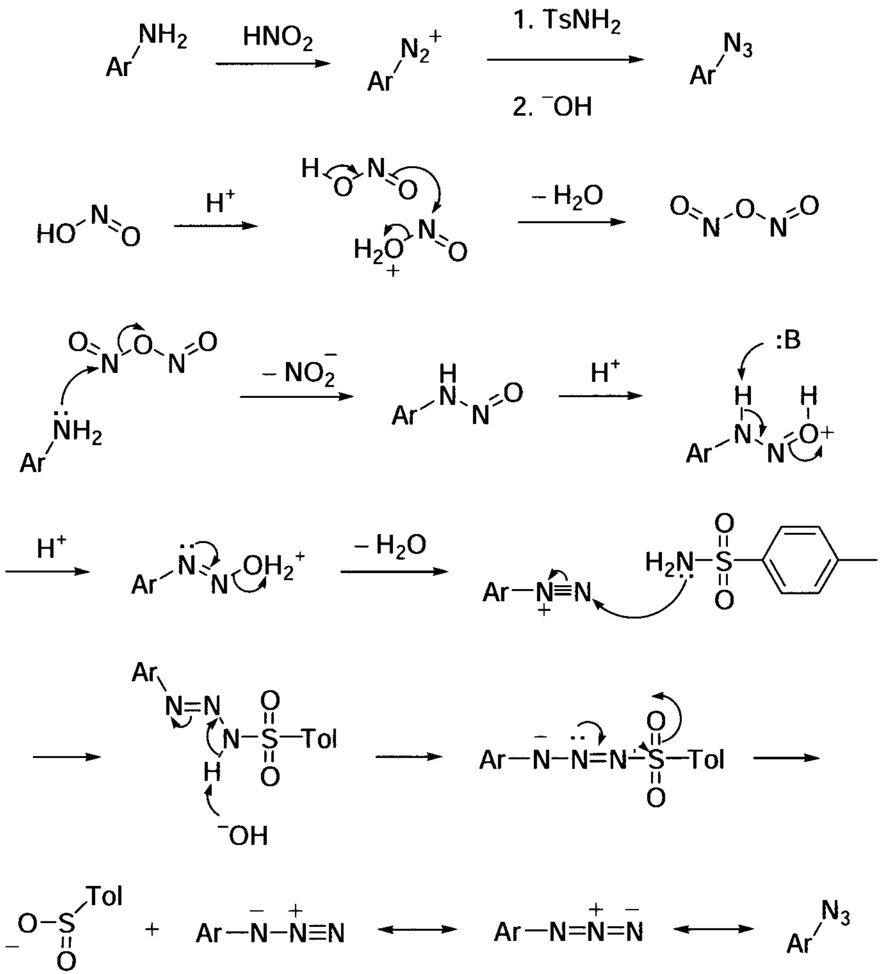
Dutt–Wormall reaction



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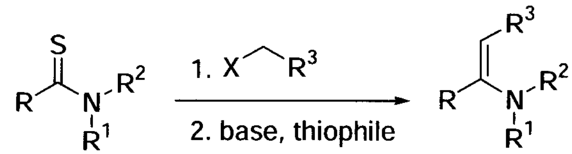
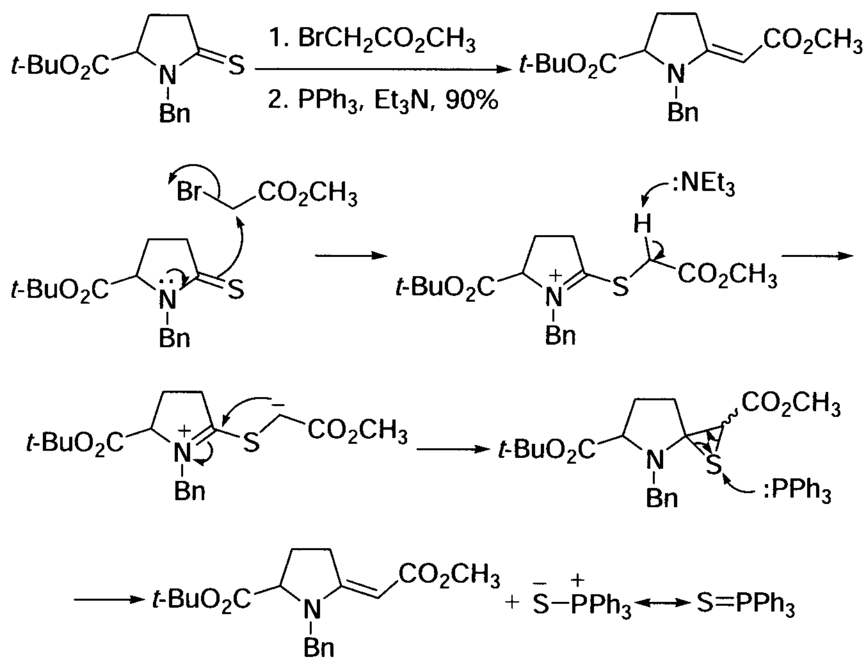
Eschenmoser coupling reaction

Enamine from thiamide and alkyl halide.



thiamide

e.g.



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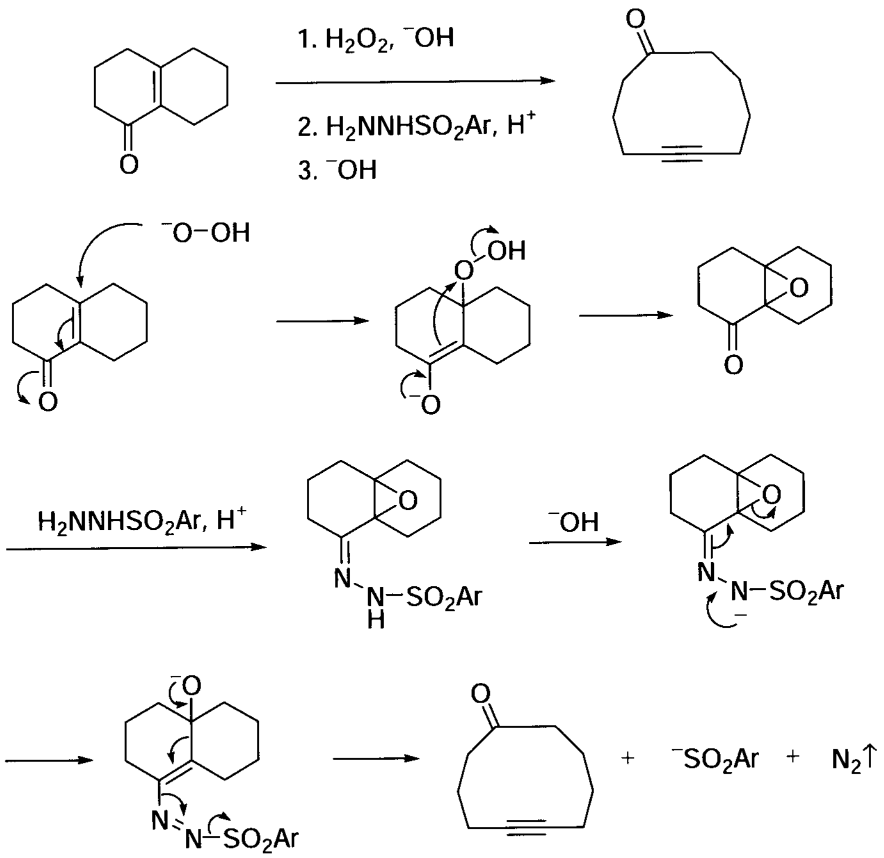
Eschenmoser–Tanabe fragmentation



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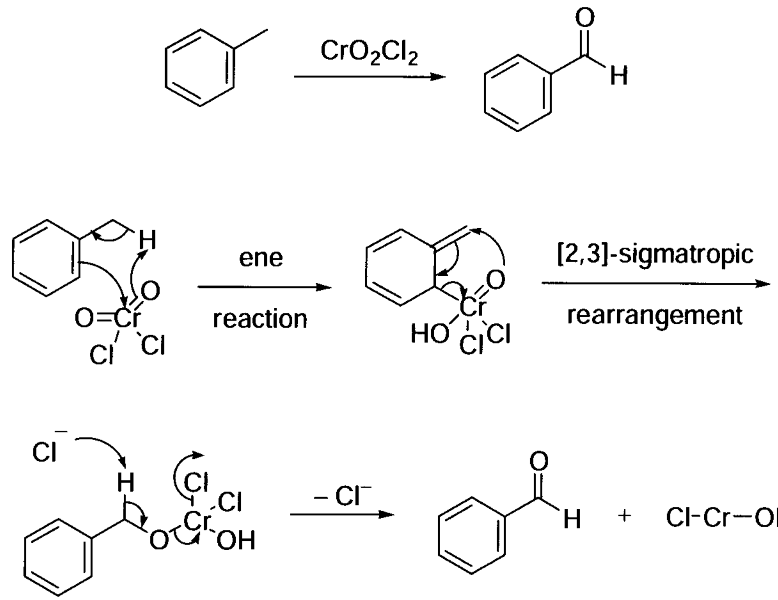
Étard reaction

Oxidation of an arylmethyl group to the corresponding aryl aldehyde using chromyl chloride.



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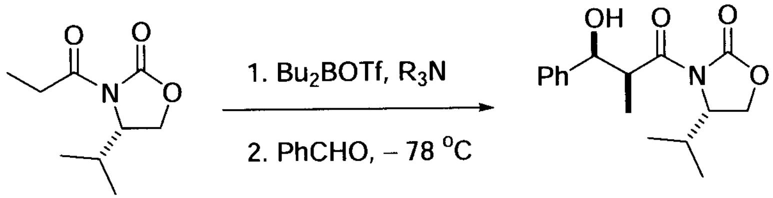
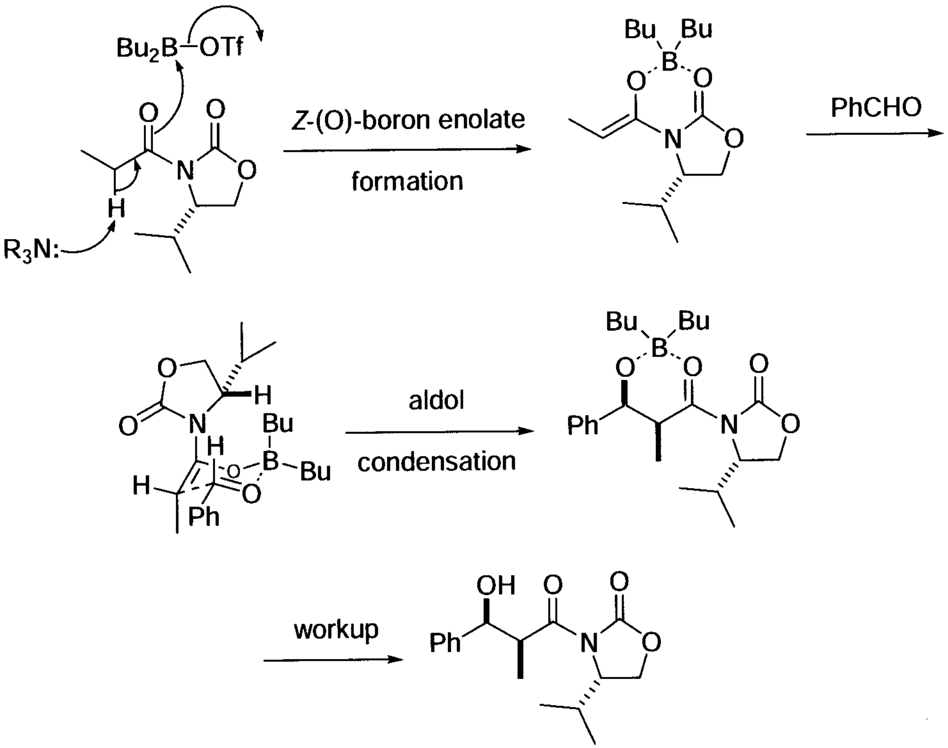
Evans aldol reaction

Asymmetric aldol condensation using an acyl oxazolidinone, the Evans chiral auxiliary.





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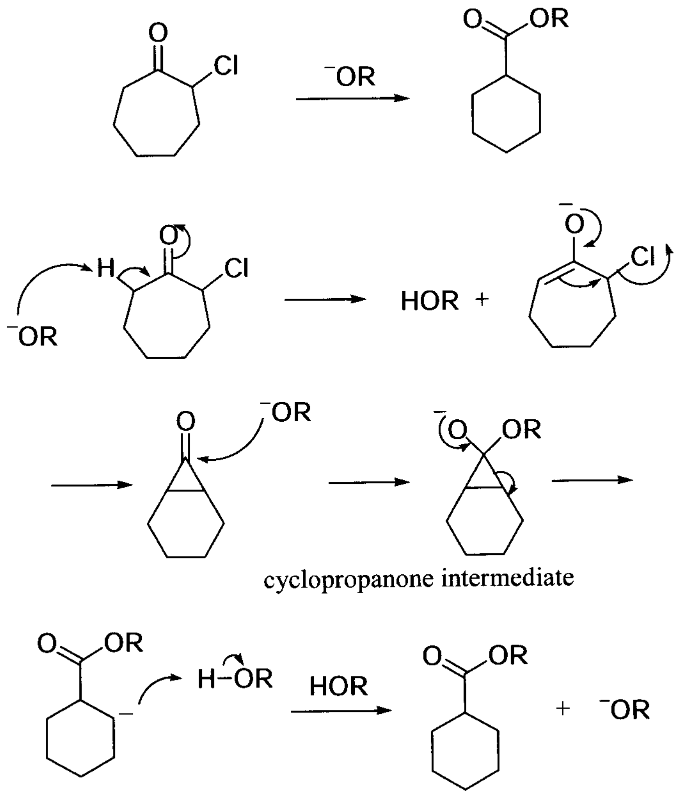
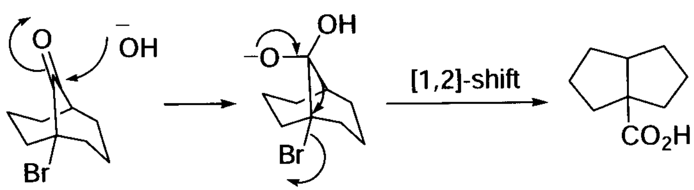
Favorskii rearrangement and Quasi-Favorskii rearrangement

Favorskii rearrangement



Quasi-Favorskii rearrangement



non-enolizable ketone

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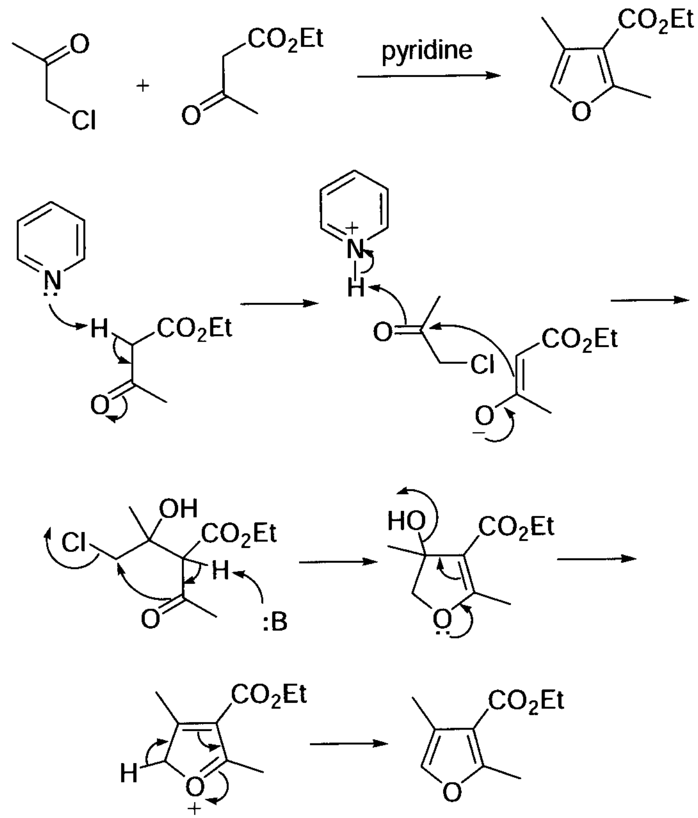
Feist–Bénary furan synthesis



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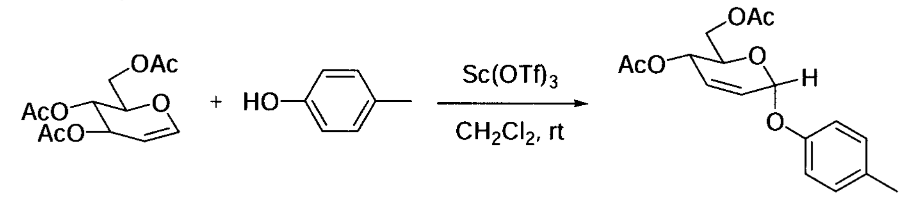
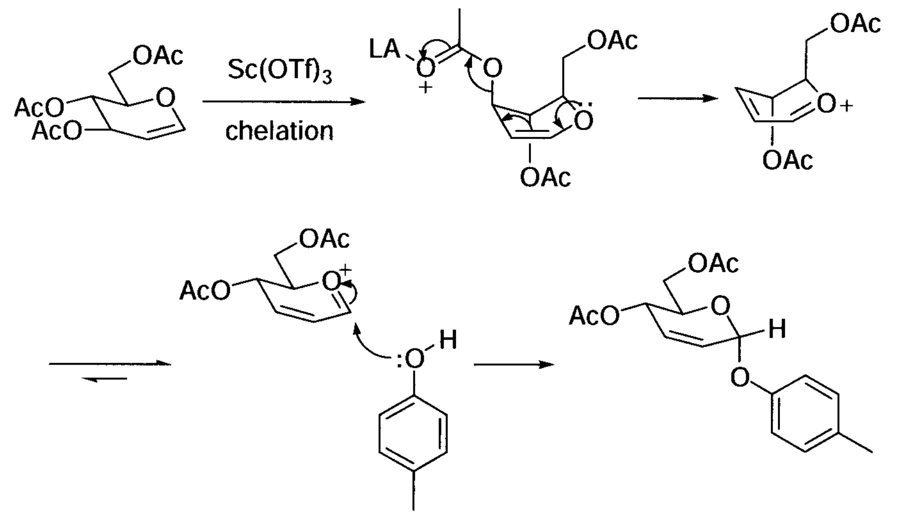
Ferrier rearrangement

Lewis-acid (such as $BF_3 \bullet OEt_2$, $SnCl_4$, *etc.*) promoted rearrangement of unsaturated carbohydrates.





The axial addition is favored due to the anomeric effect.

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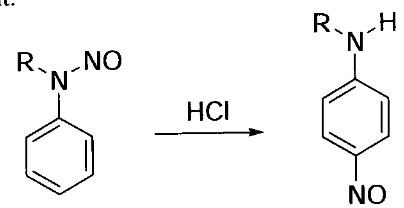
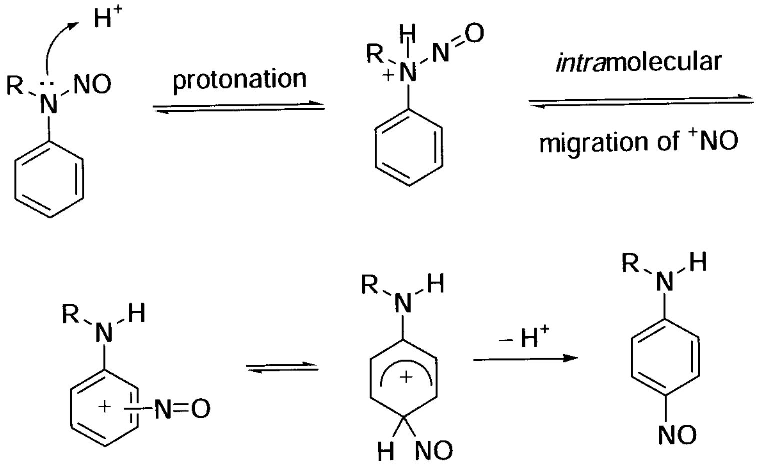
Fischer–Hepp rearrangement

Transformation of *N*-nitroso-anilines to the corresponding *para*-nitroso anilines. *Cf.* Orton rearrangement.





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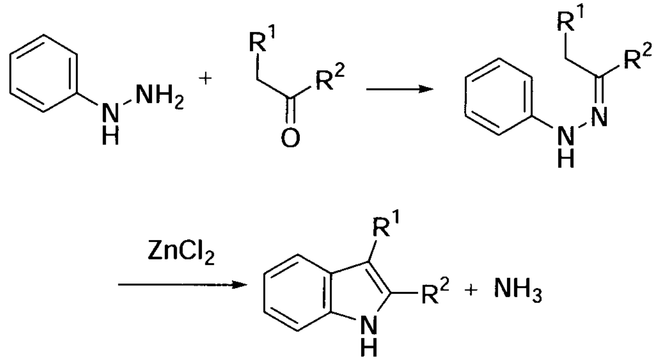
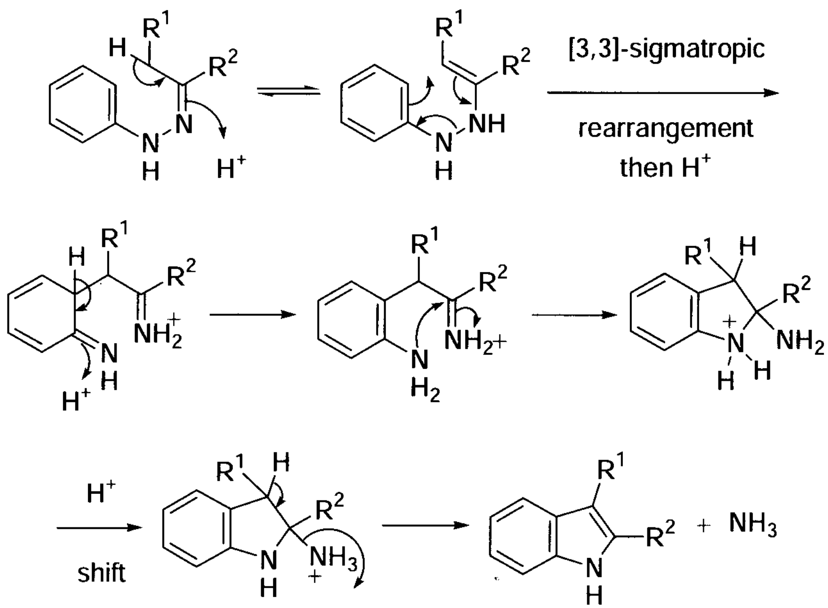
Fischer indole synthesis





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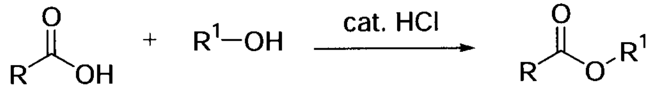
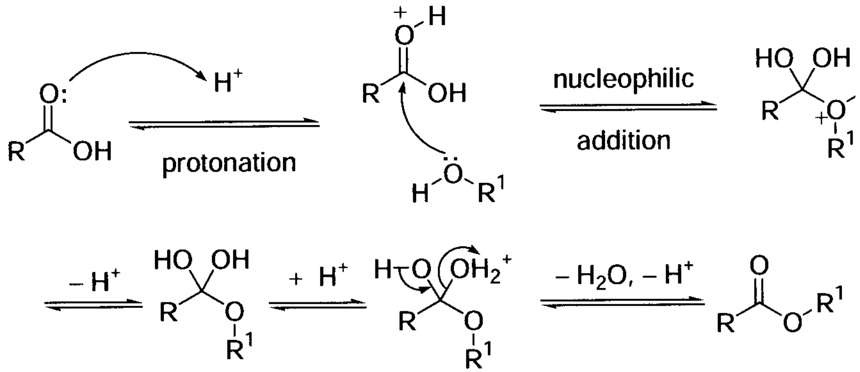
Fischer–Speier esterification

Often known as "Fischer esterification", protic acid-catalyzed esterification of an acid and an alcohol.





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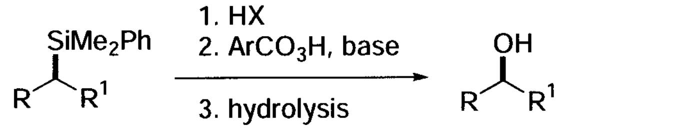
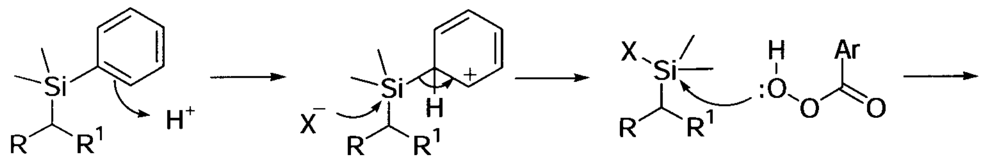
Fleming oxidation

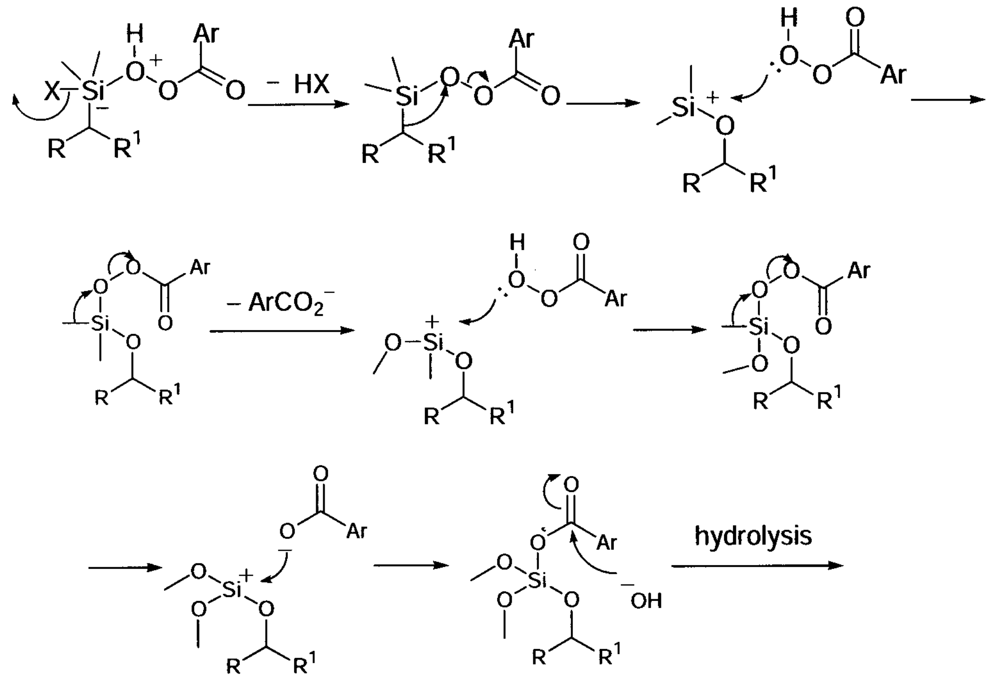
Cf. Tamao–Kumada oxidation

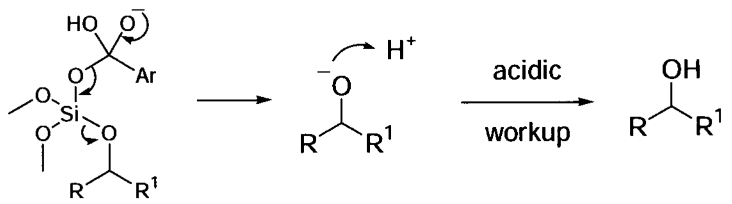


retention of configuration



the β-carbocation is stabilized by the silicon group





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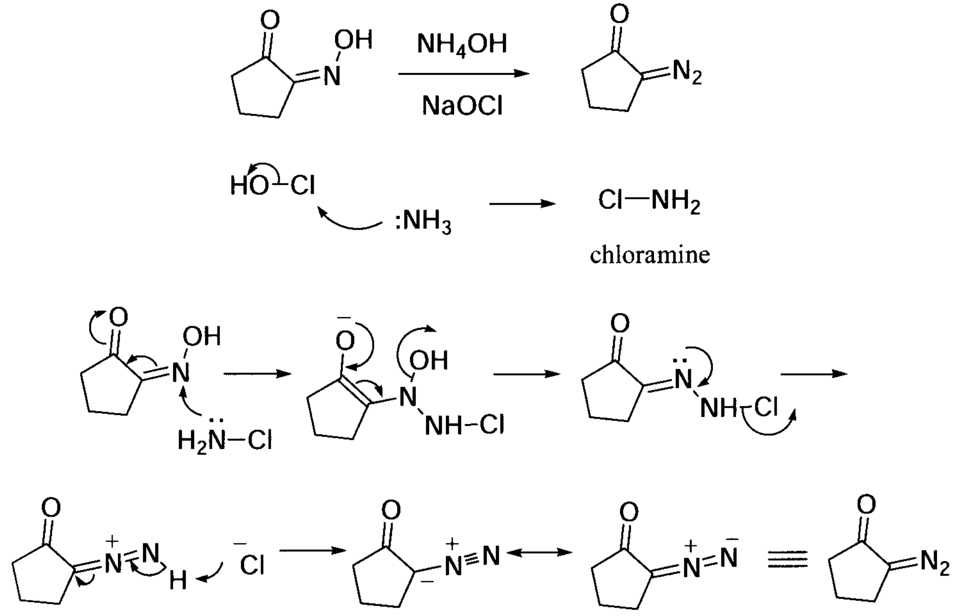
Forster reaction

Diazoketone formation from α-oximinoketones.



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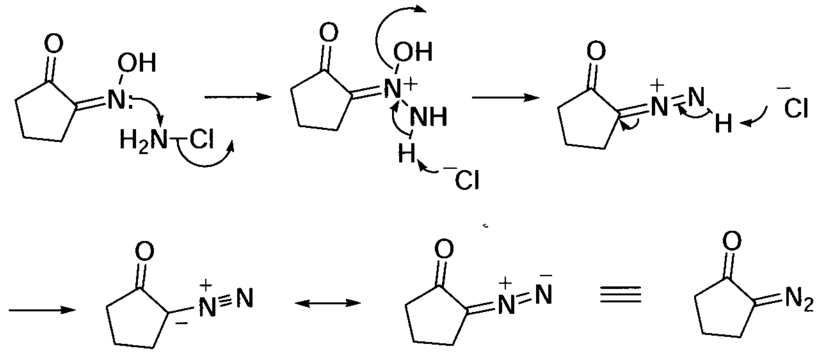

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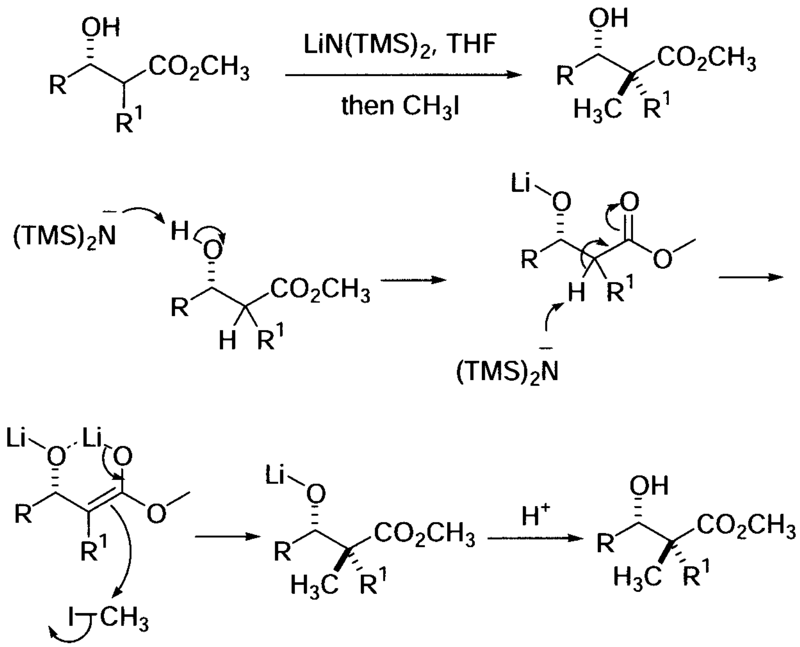
Frater–Seebach alkylation

Asymmetric alkylation of β-hydroxylesters.



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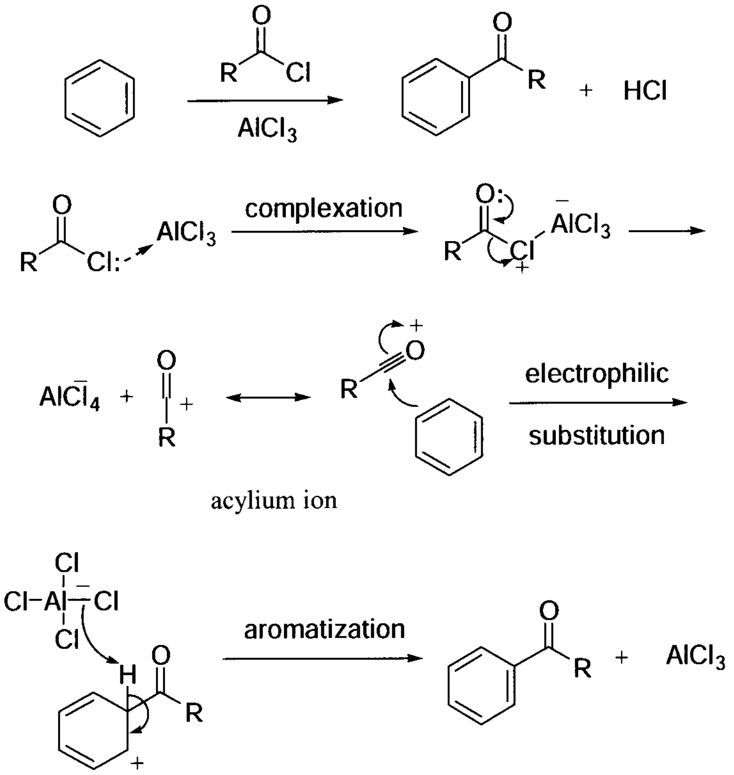
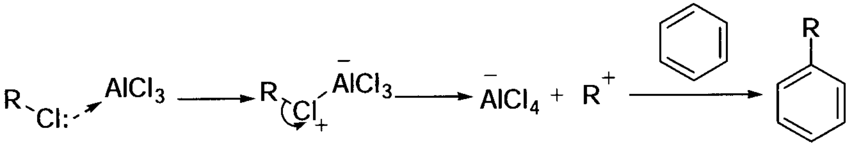
Friedel–Crafts reaction

Friedel–Crafts *acylation* reaction:



Friedel–Crafts *alkylation* reaction:



alkyl cation

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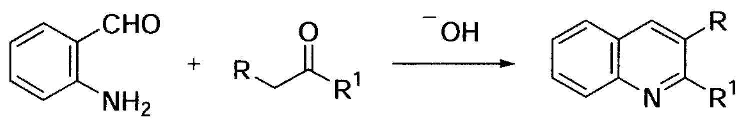
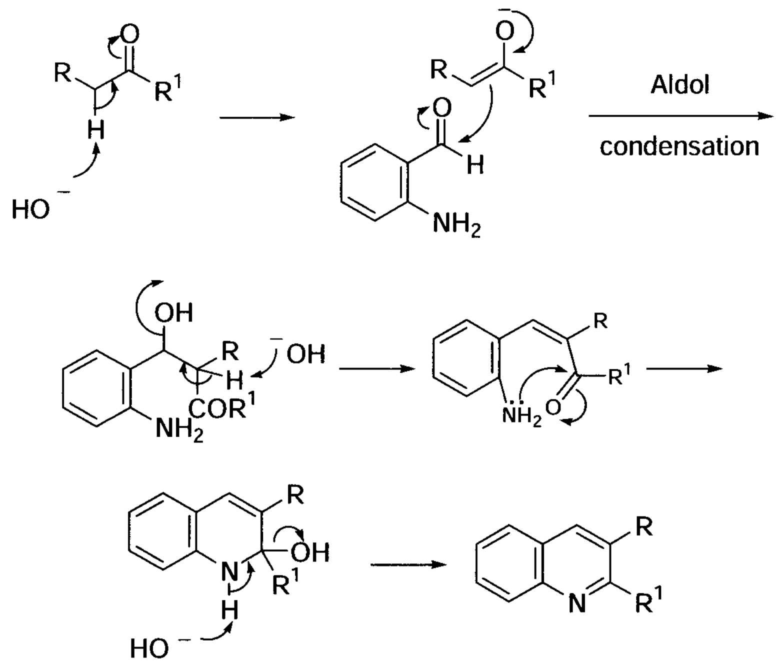
Friedländer synthesis

Quinoline synthesis from the condensation of *o*-aminobenzaldehyde with aldehyde or ketone in the presence of NaOH.





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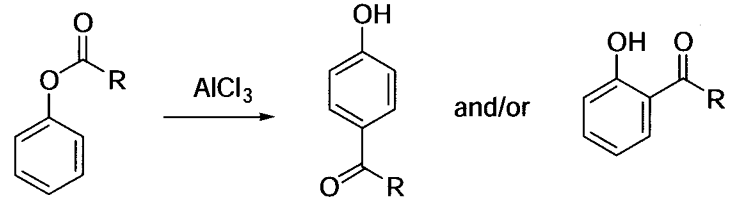
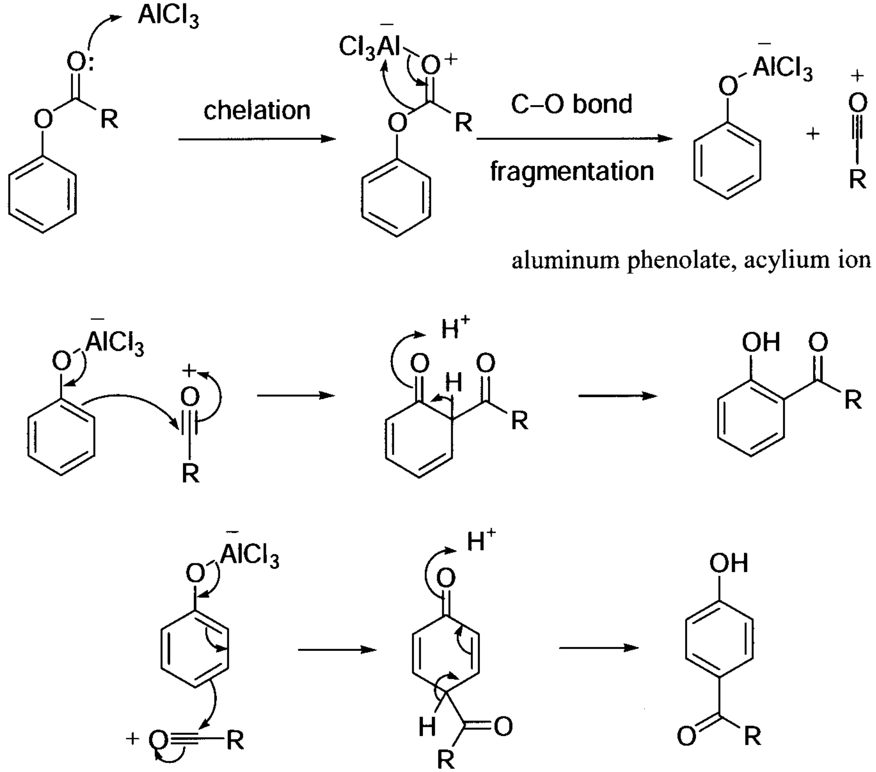
Fries rearrangement





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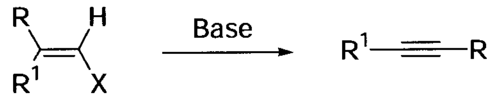
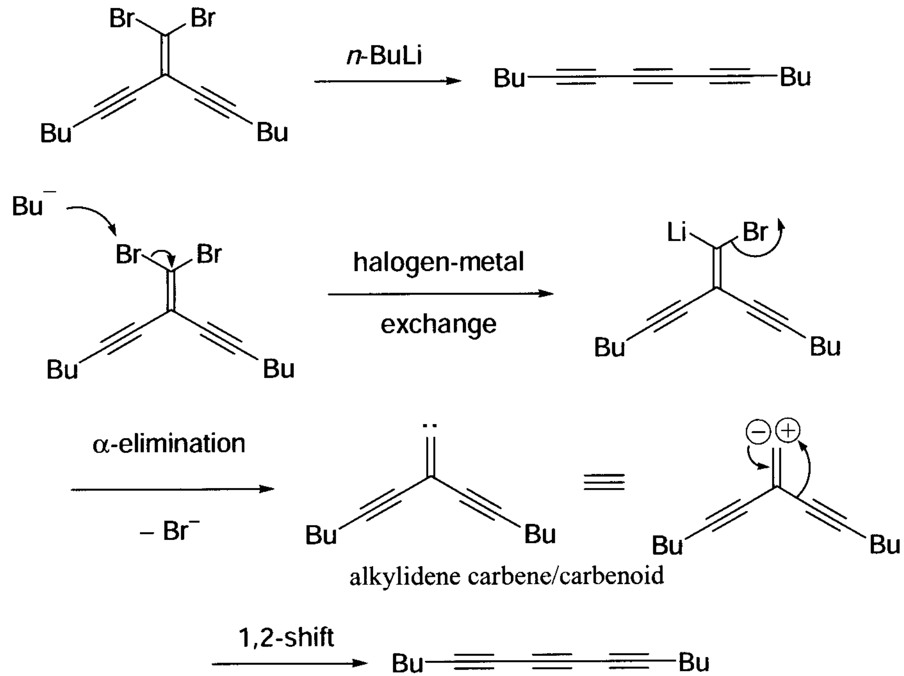
Fritsch–Buttenberg–Wiechell rearrangement



e.g. a variant:



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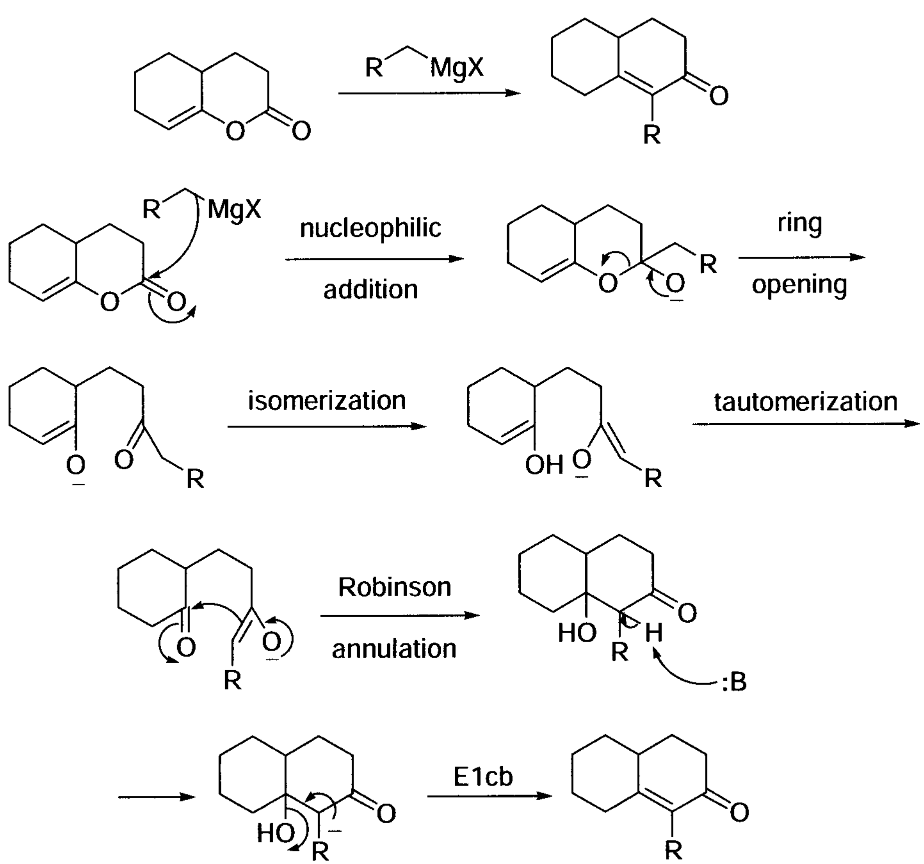
Fujimoto–Belleau reaction



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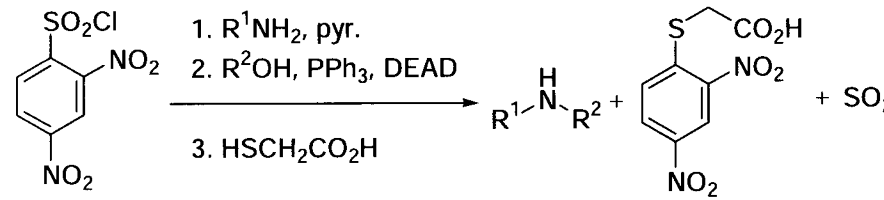
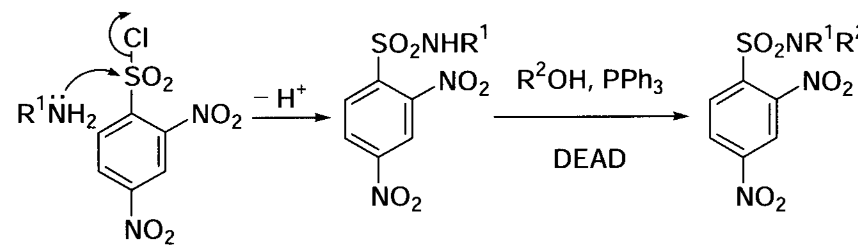
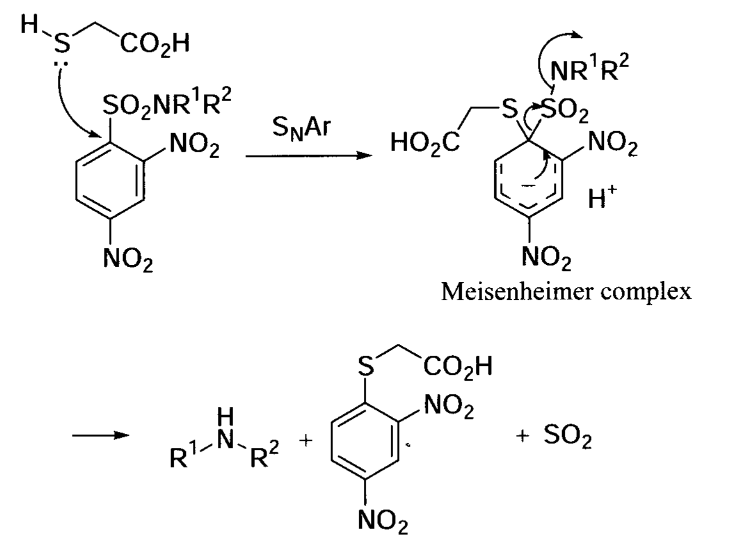
Fukuyama amine synthesis





See Mitsunobu reaction (page 238) for the mechanism.



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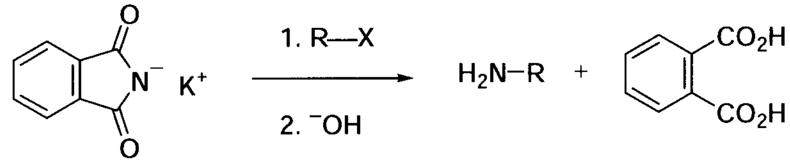
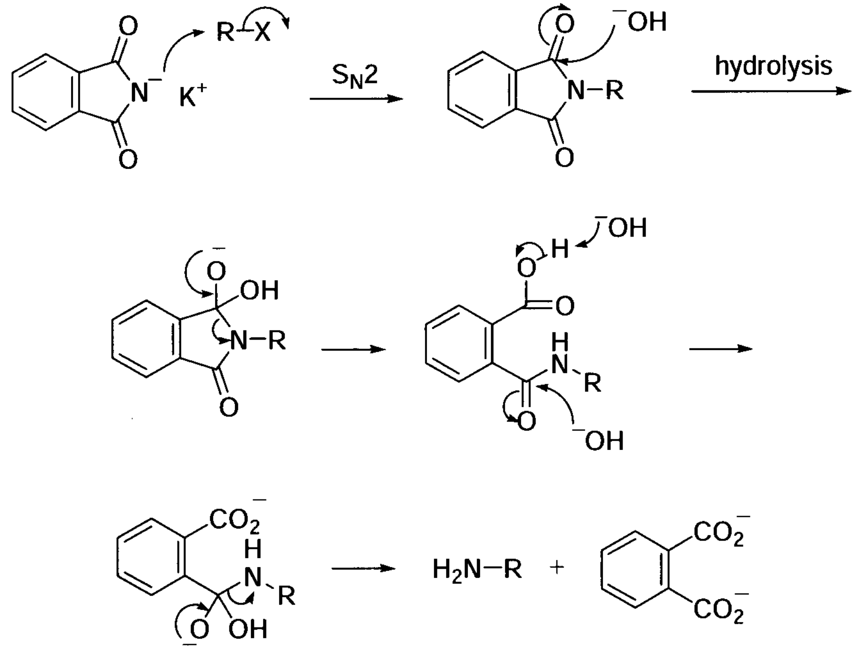
Gabriel synthesis

Synthesis of primary amines using potassium phthalimide and alkyl halides.





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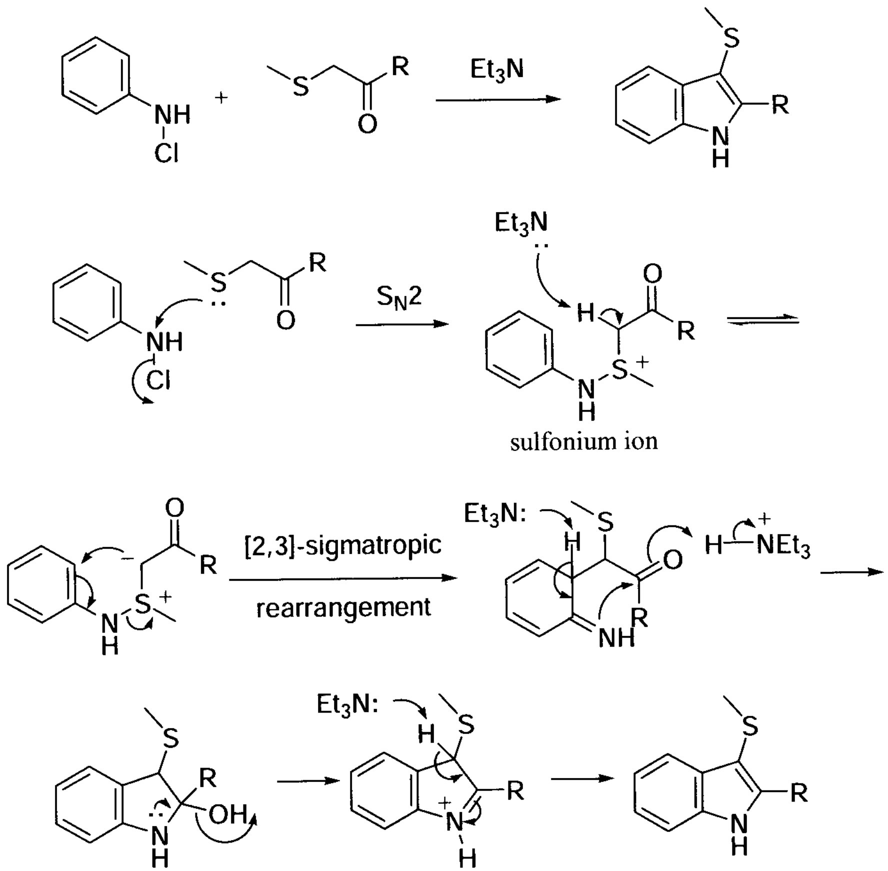
Gassman indole synthesis



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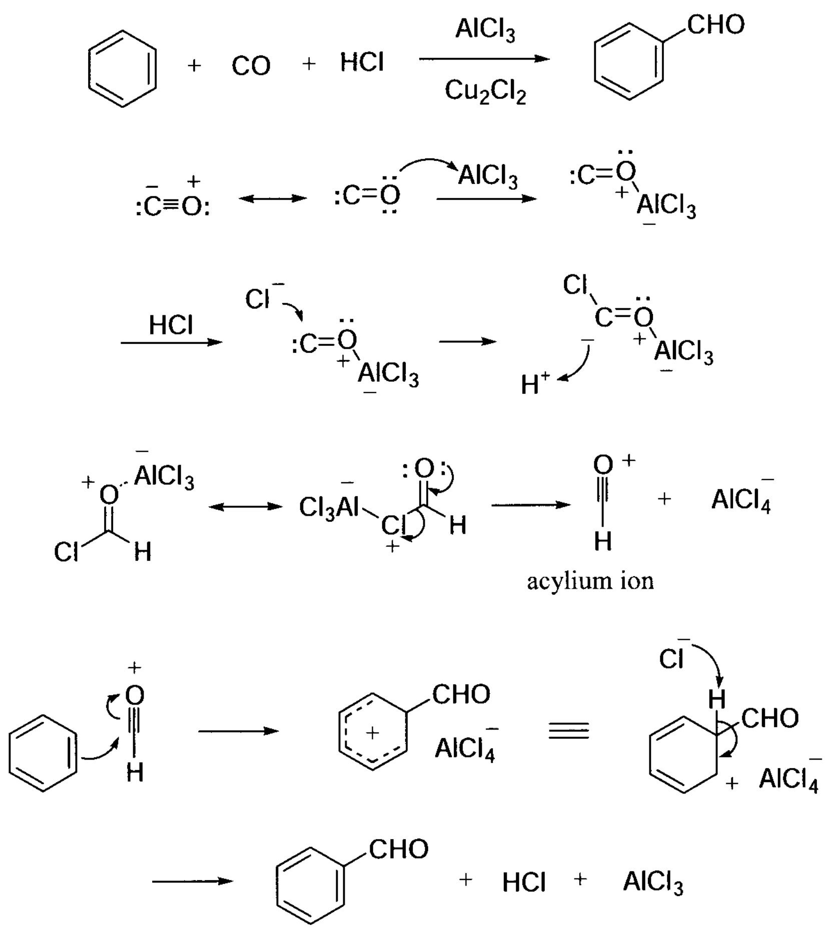
Gattermann–Koch reaction



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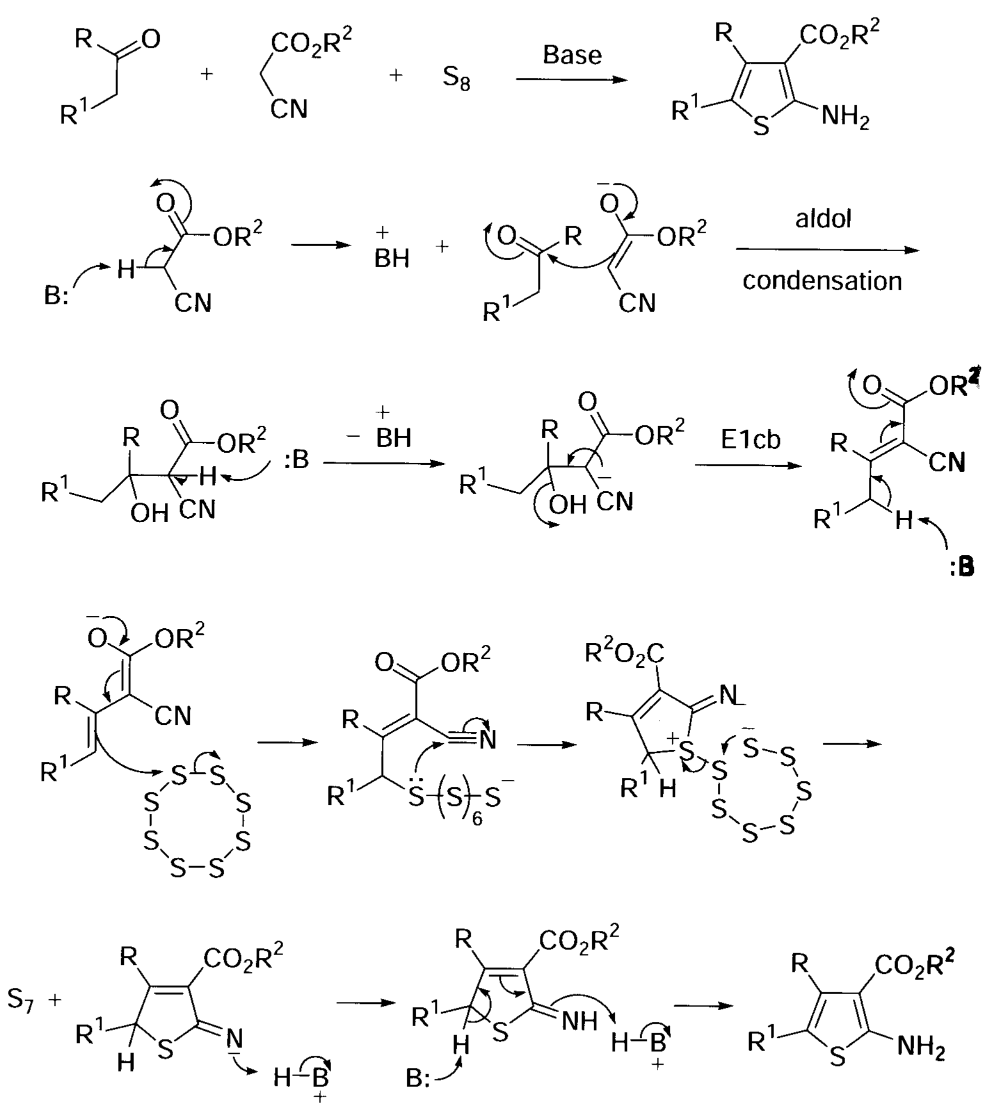
Gewald aminothiophene synthesis



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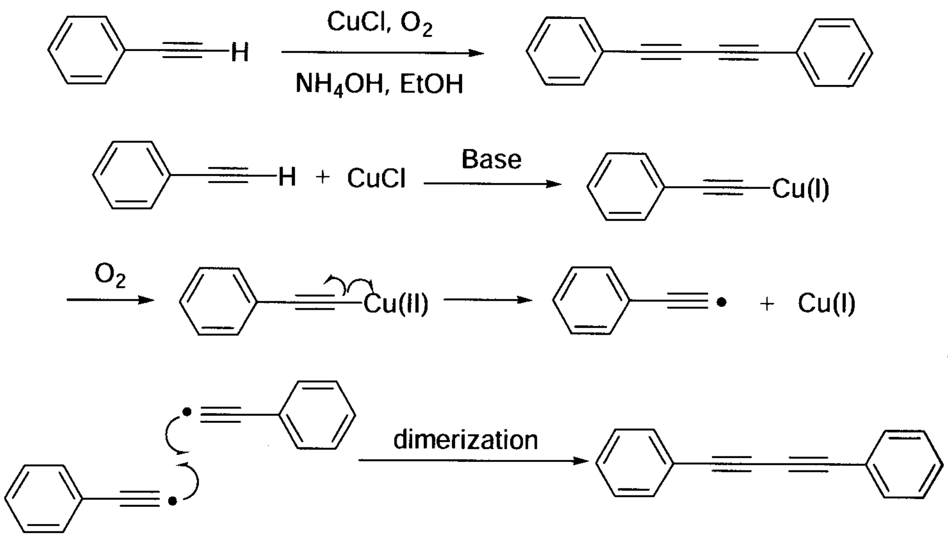
Glaser coupling

Oxidative homocoupling of terminal alkynes using copper catalyst.



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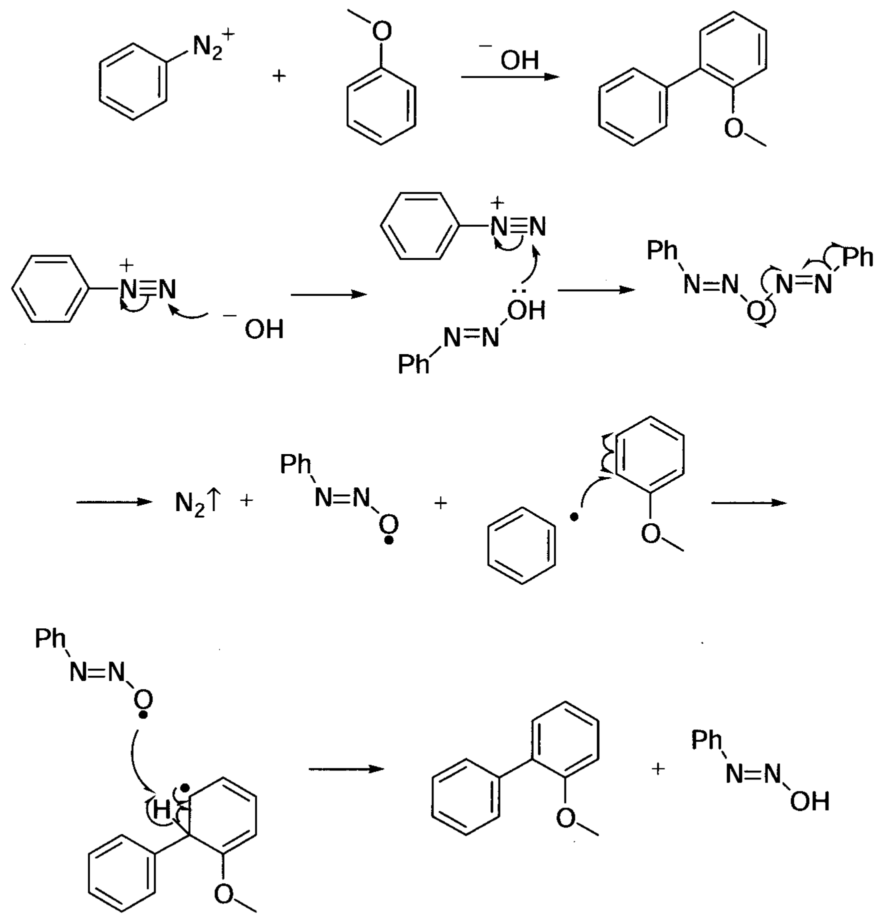
Gomberg–Bachmann reaction



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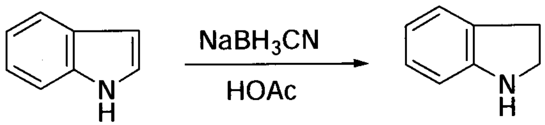
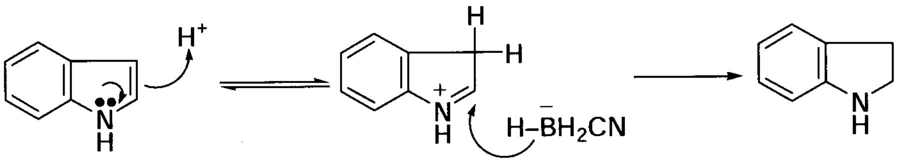
Gribble indole reduction

Reduction of the indole double bond using sodium cyanoborohydride in glacial acetic acid. The use of sodium borohydride leads to reduction and *N*-alkylation.





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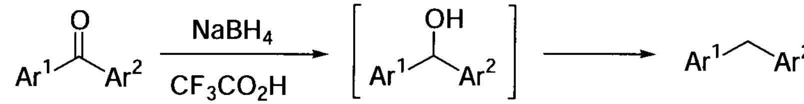
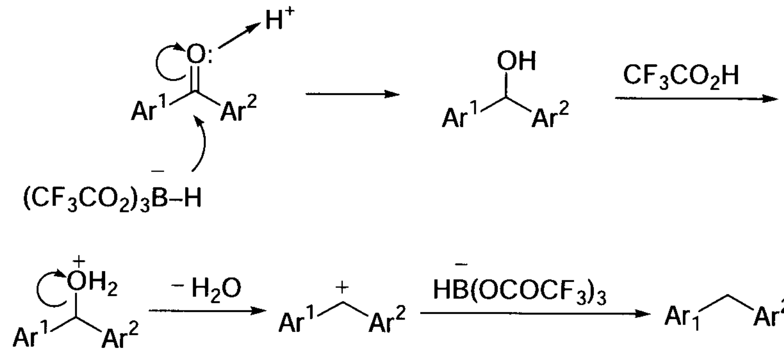
Gribble reduction of diaryl ketones

Reduction of diaryl ketones and diarylmethanols to diarylmethanes using sodium borohydride in trifluoroacetic acid. Also applicable to diheteroaryl ketones and alcohols.





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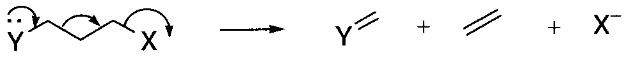
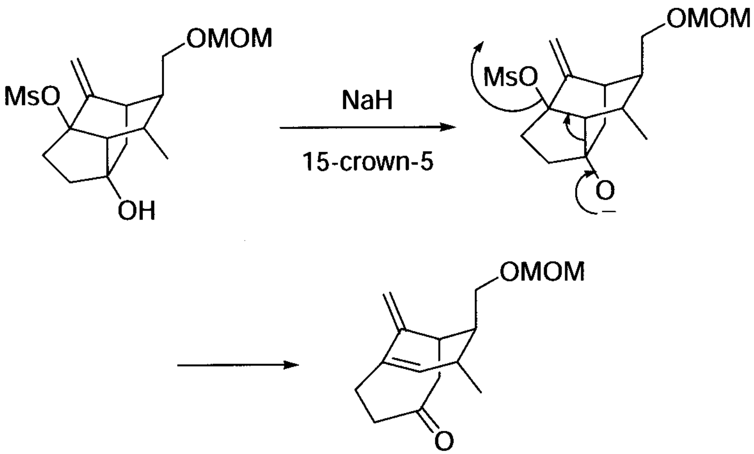
Grob fragmentation

General scheme:



$X = OH_2^+$, OTs, I, Br, Cl; $Y = O^-$, NR_2

e.g.:



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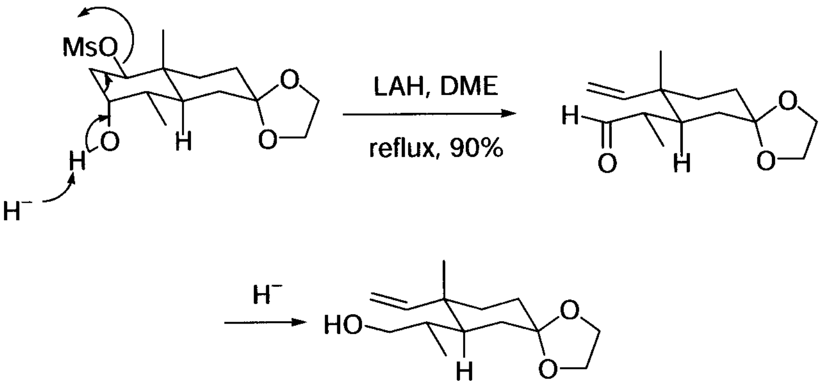

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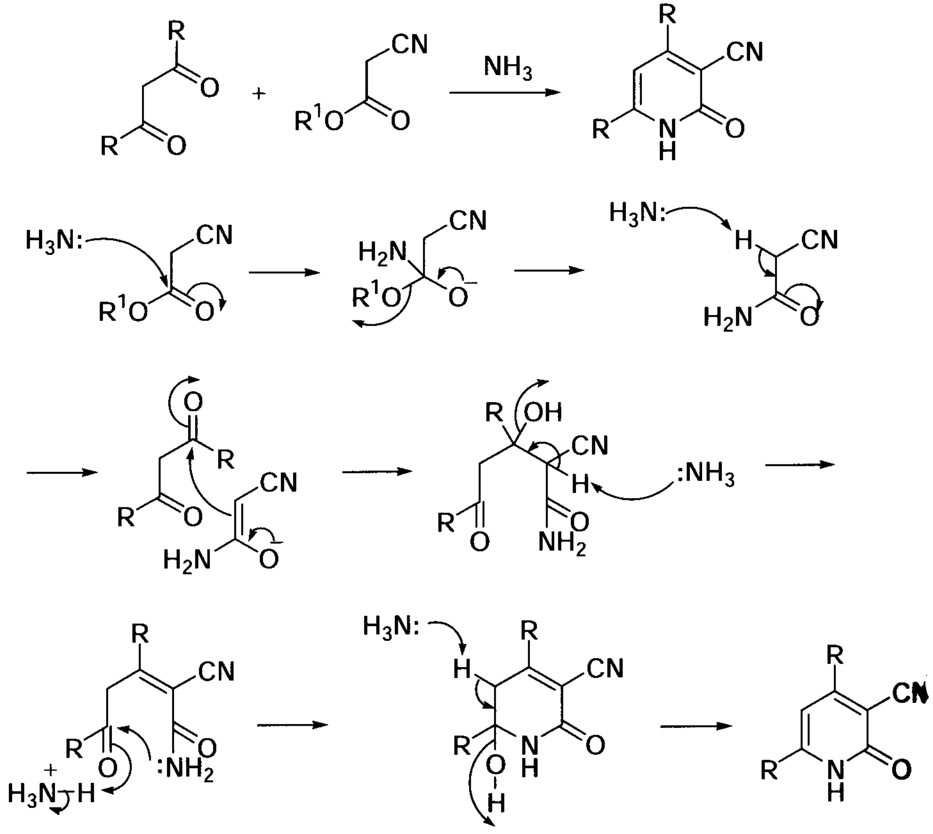
Guareschi–Thorpe condensation



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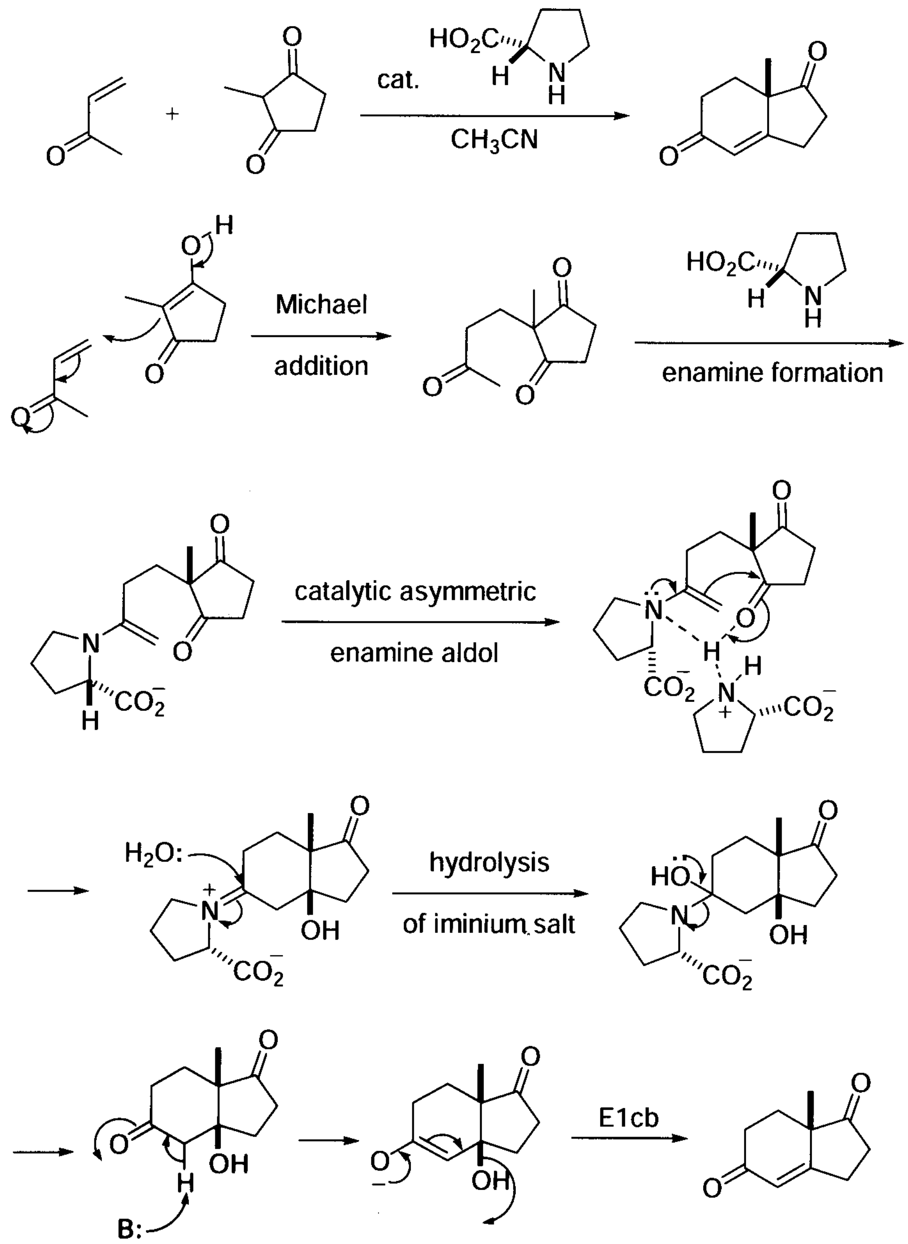
Hajos–Wiechert reaction

Asymmetric Robinson annulation catalyzed by (*S*)-(–)-proline.



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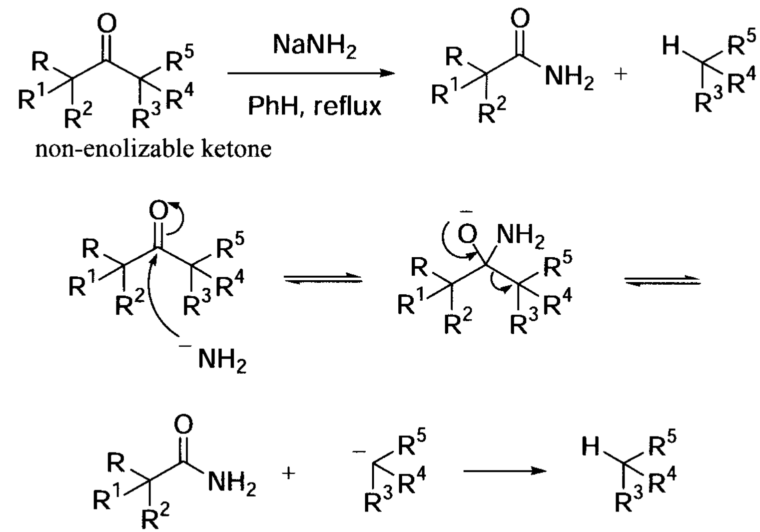
Haller–Bauer reaction

Base-induced cleavage of non-enolizable ketones leading to carboxylic acid derivative and a neutral fragment in which the carbonyl group is replaced by a hydrogen.



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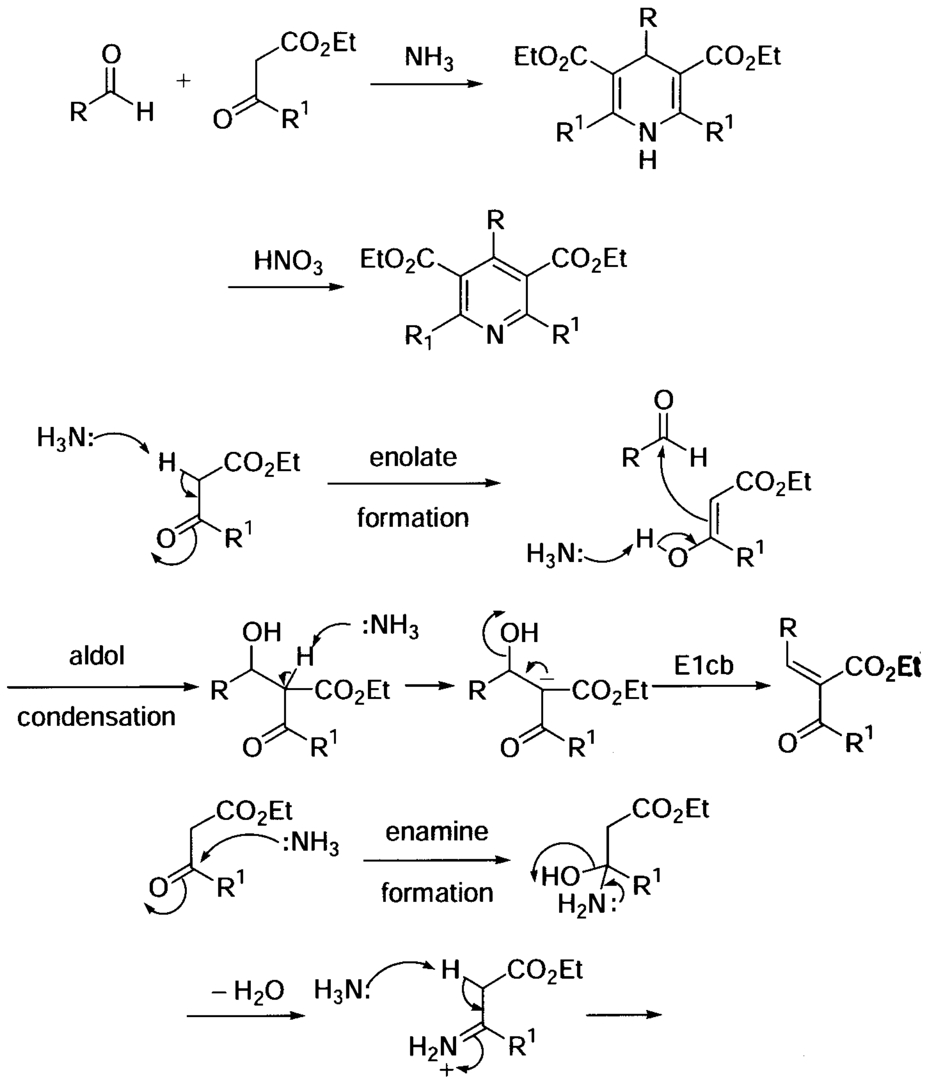
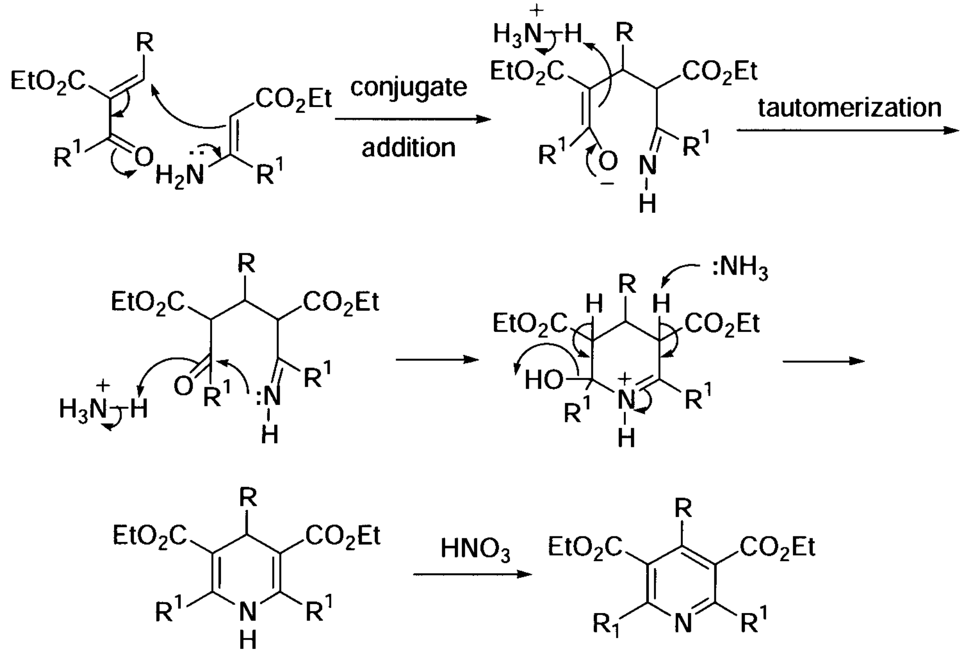
Hantzsch pyridine synthesis





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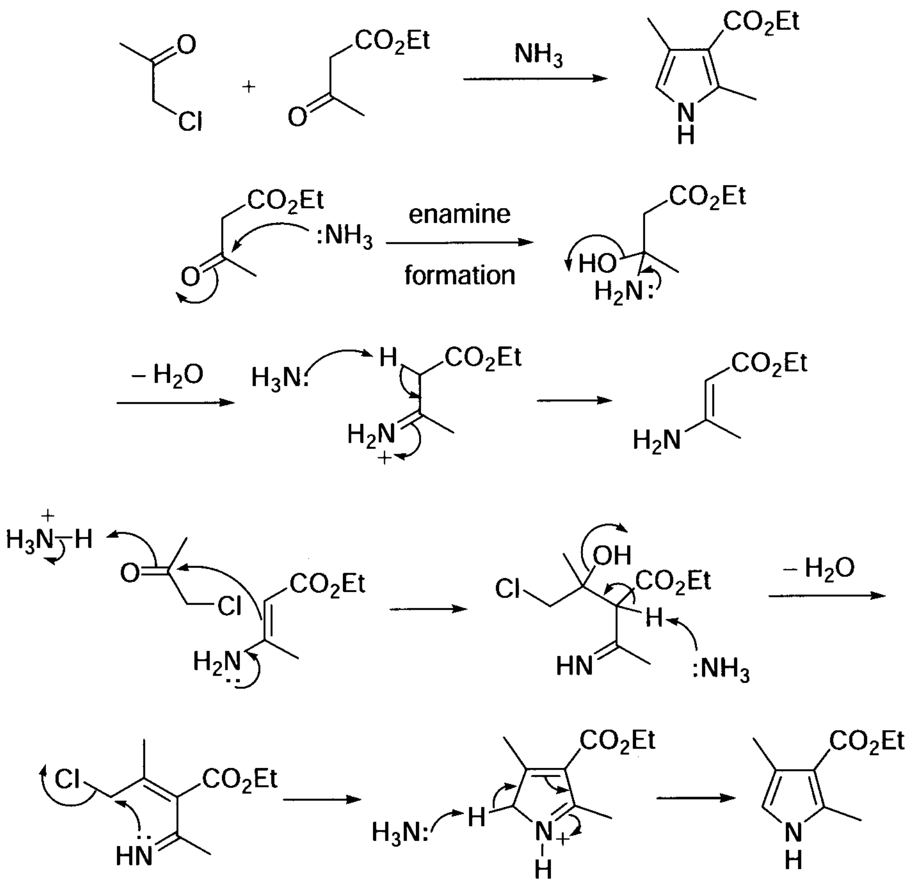
Hantzsch pyrrole synthesis



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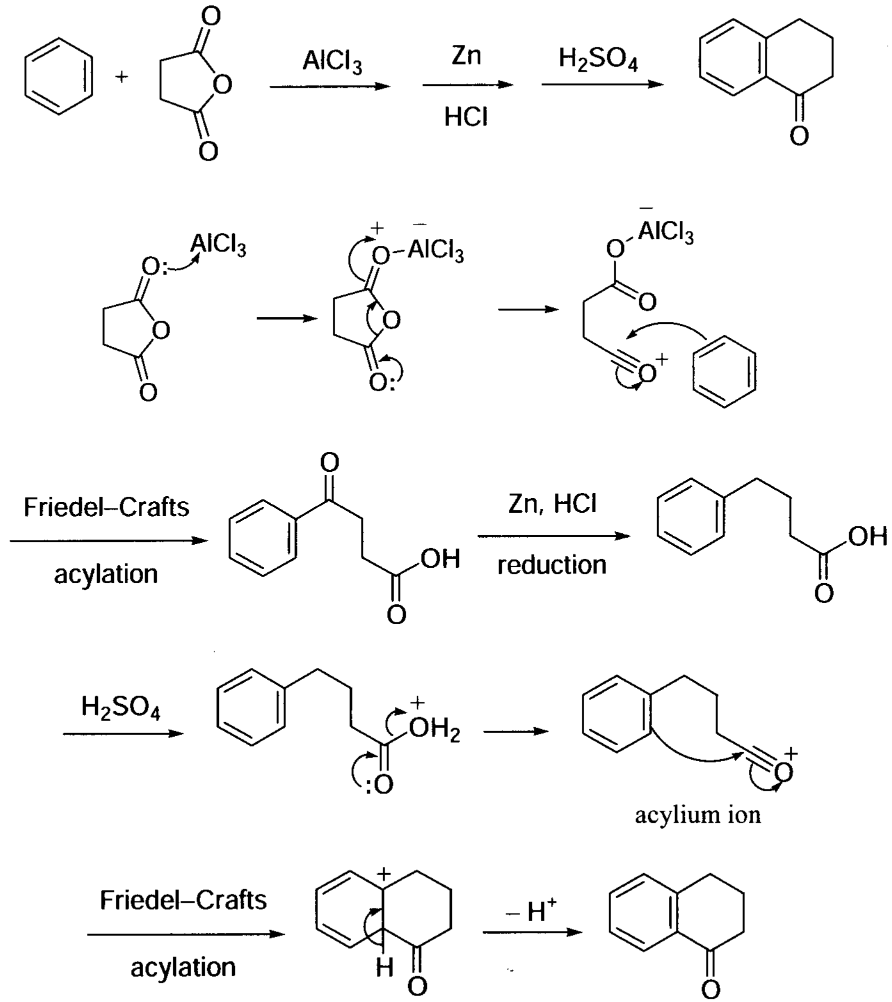
Haworth reaction



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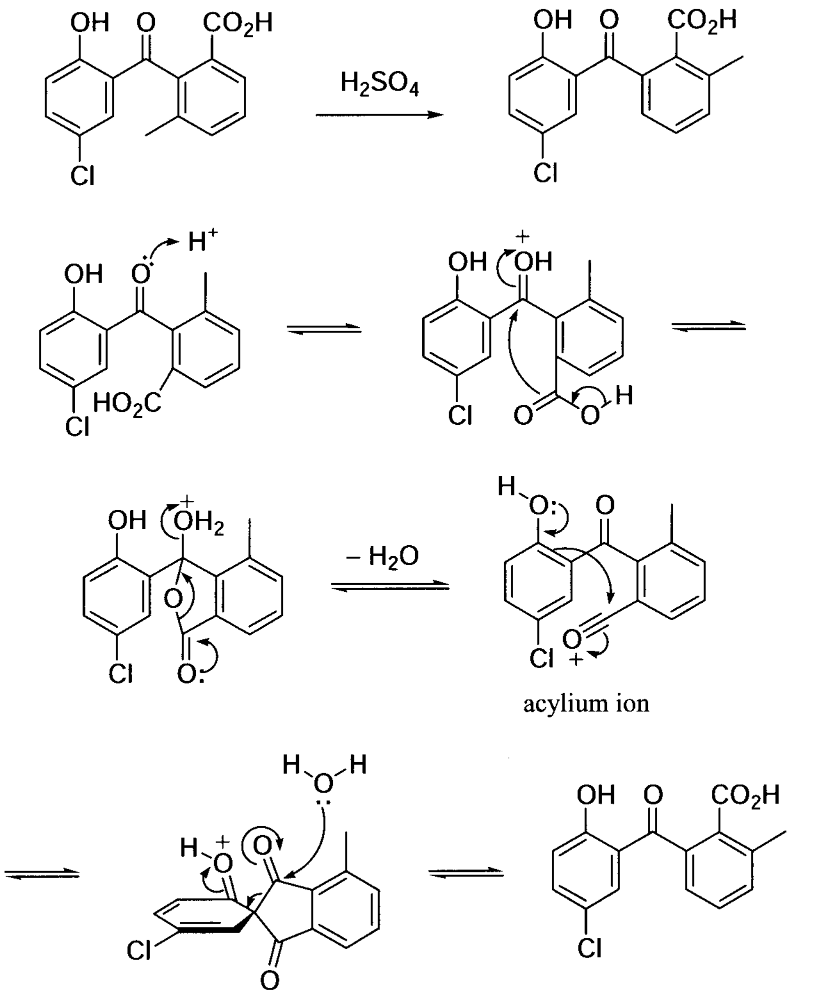
Hayashi rearrangement



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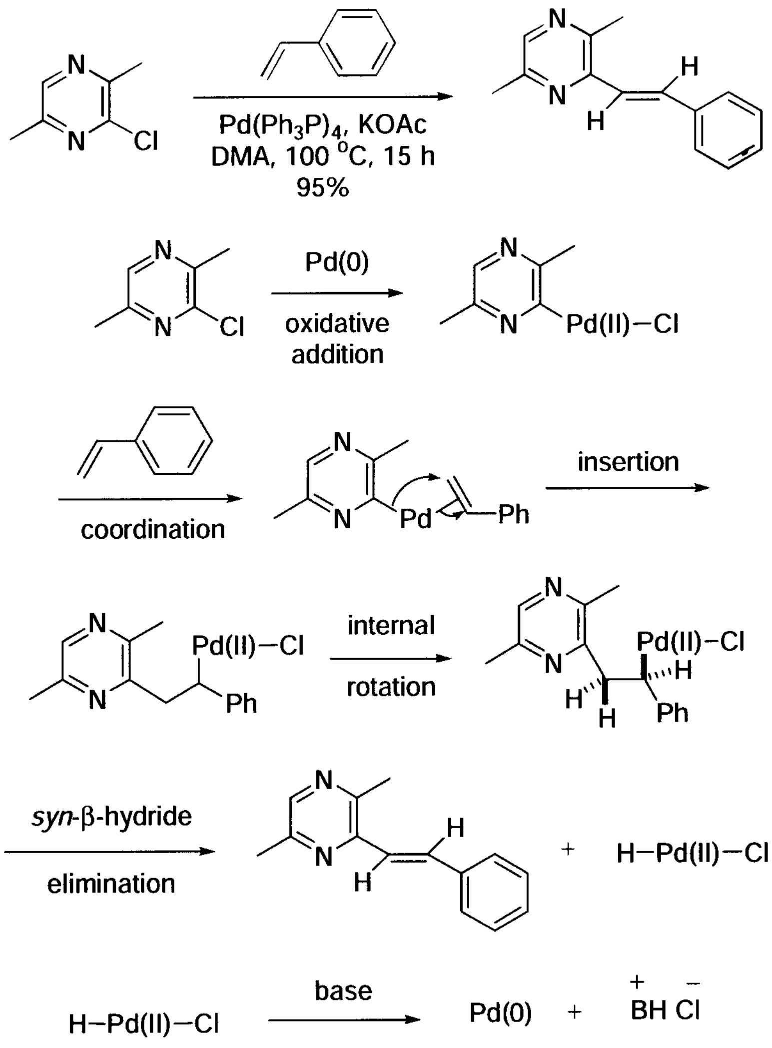
Heck reaction

Palladium-catalyzed coupling between organohalides or triflates with olefins.



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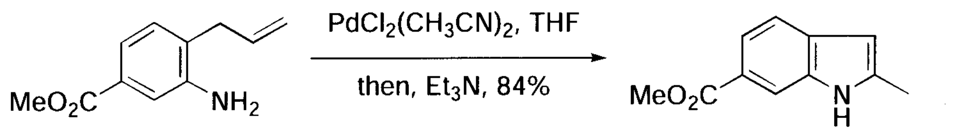
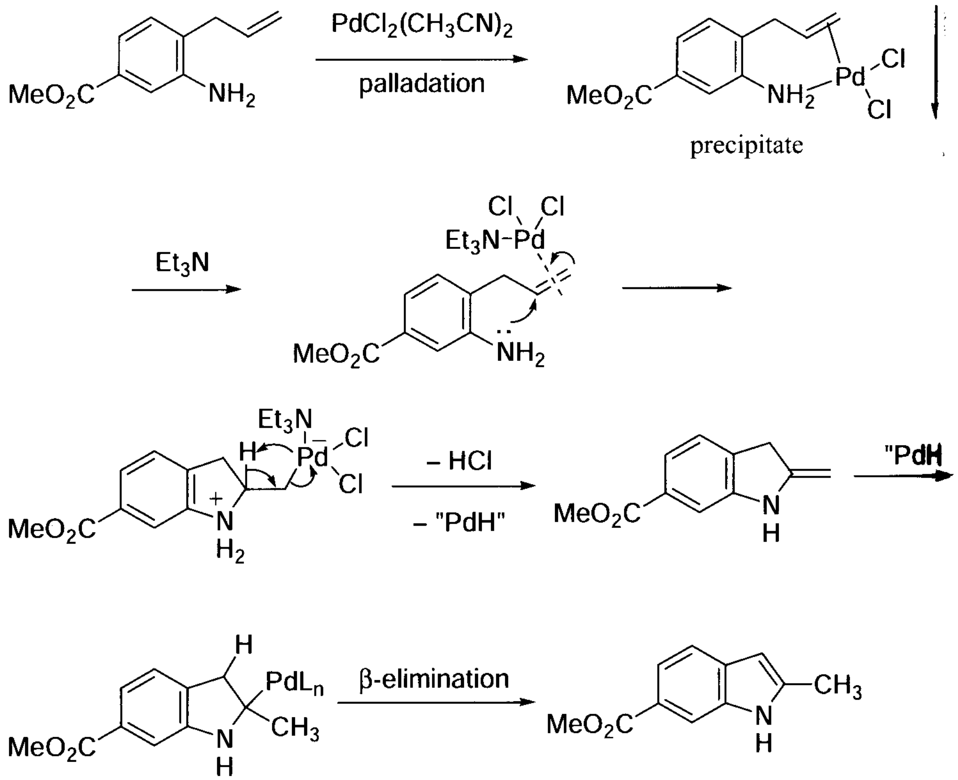
Hegedus indole synthesis

Stoichiometric Pd(II)-mediated oxidative cyclization of alkenyl anilines to indoles. *Cf.* Wacker oxidation.





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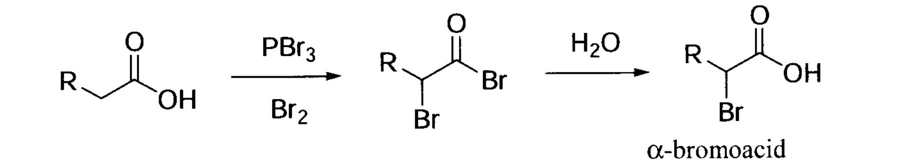
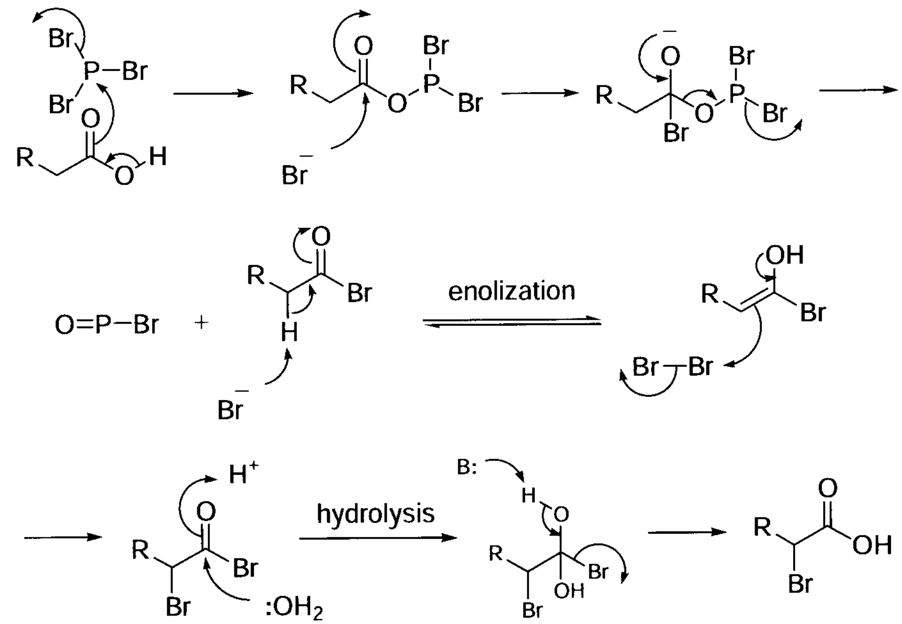
Hell–Volhardt–Zelinsky reaction

α-Bromination of carboxylic acids using Br_2/PBr_3.





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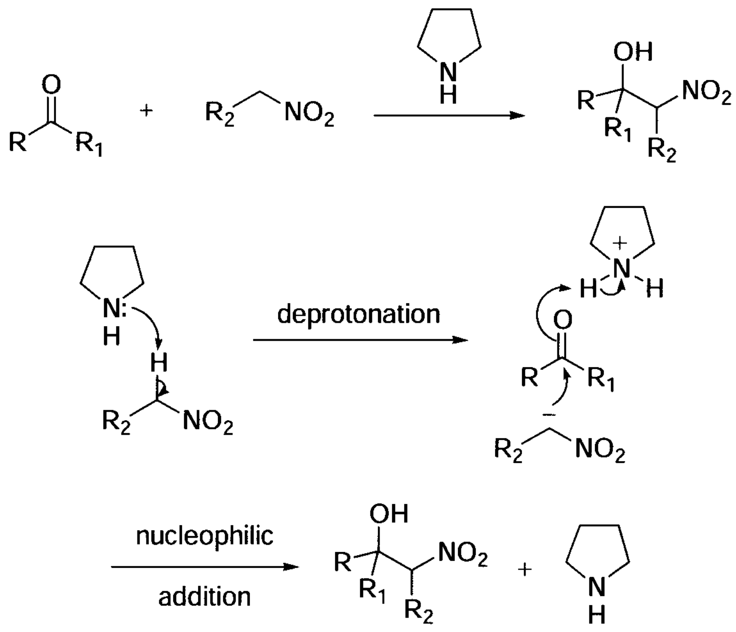
Henry reaction (nitroaldol reaction)



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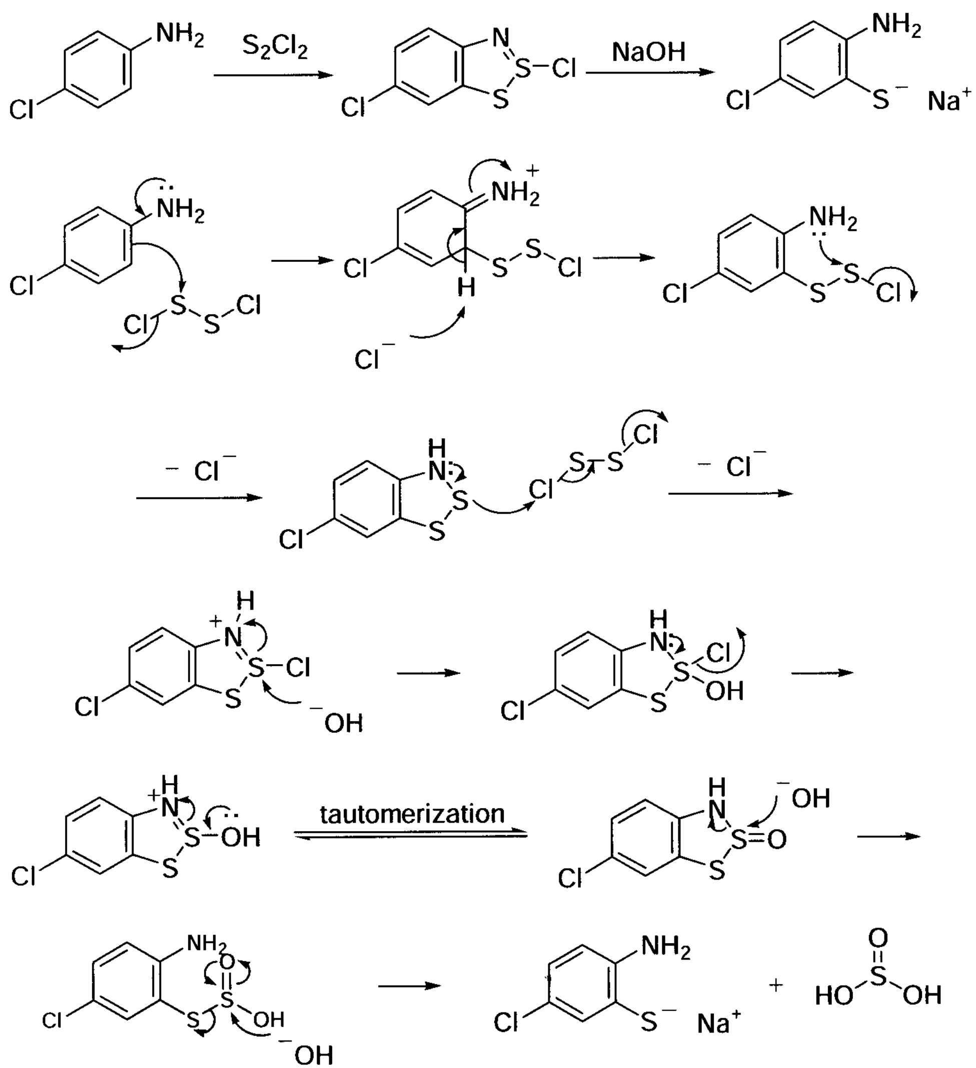
Herz reaction



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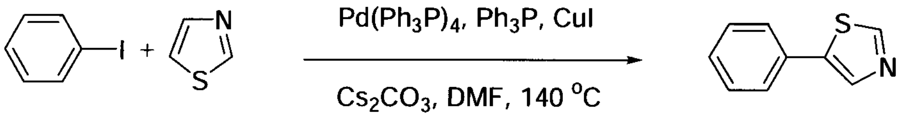
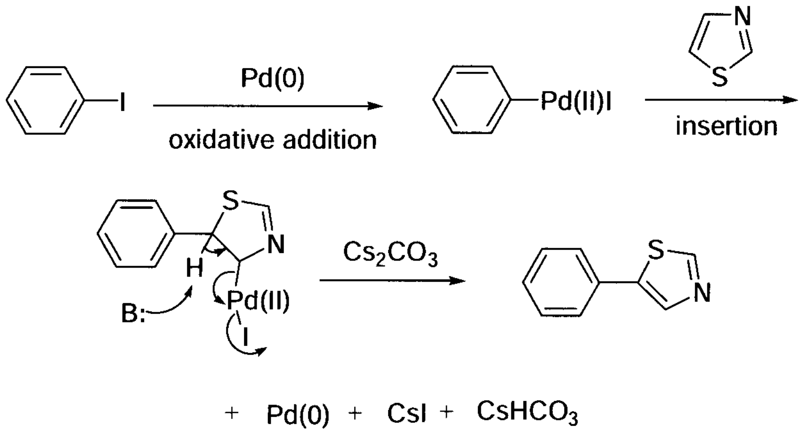
Heteroaryl Heck reaction

Intermolecular or intramolecular Heck reaction that occurs onto a heteroaryl recipient.





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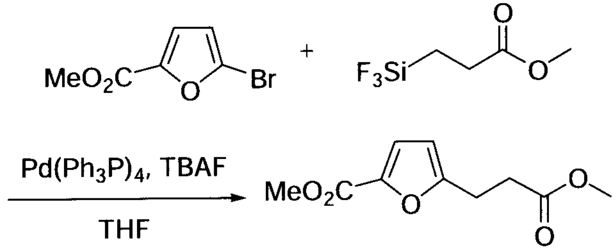
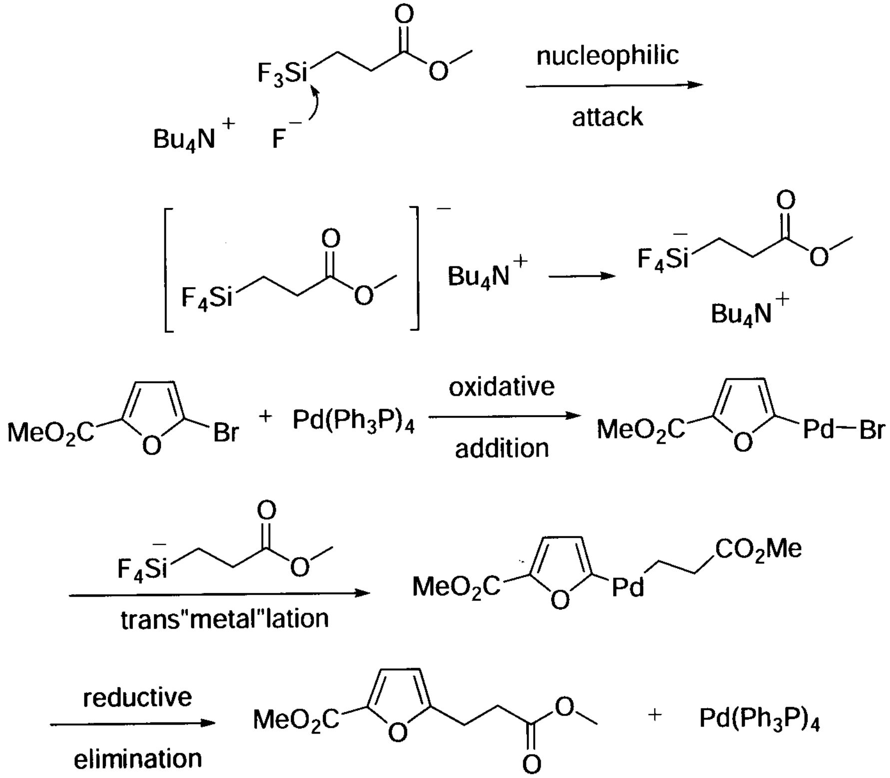
Hiyama cross-coupling reaction

Palladium-catalyzed cross-coupling reaction of organosilicons with organic halides, triflates, *etc.* in the presence of an activating agent such as fluoride or hydroxide (transmetallation is reluctant to occur without the effect of an activating agent). For the catalytic cycle, see the Kumada coupling on page 208.





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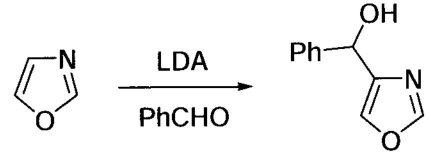
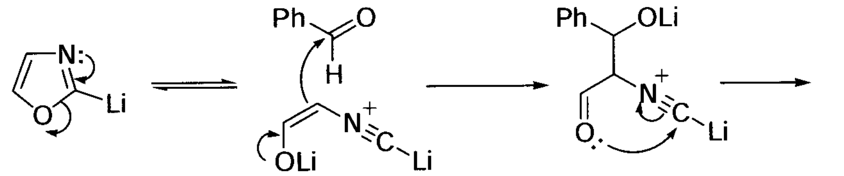
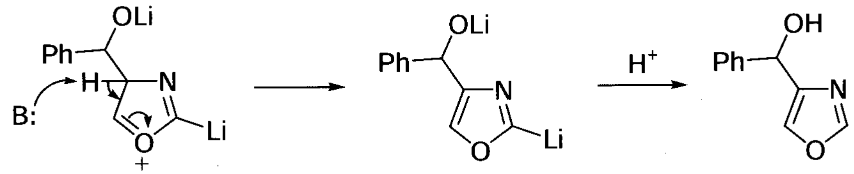
Hodges–Vedejs metallation of oxazoles

Metallation of an oxazole followed by treatment with benzaldehyde results in a 4-substituted oxazole as the major product [1]:

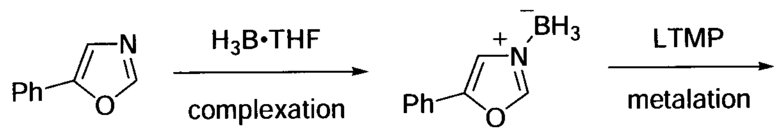




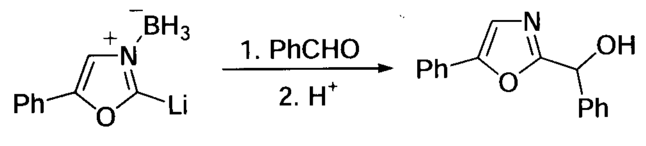
2-lithiooxazole



However, the ring-opening process can be prevented by addition of boranes [3]:



LTMP = lithium tetramethylpiperidine



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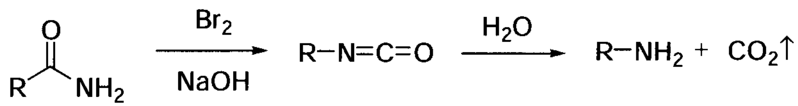
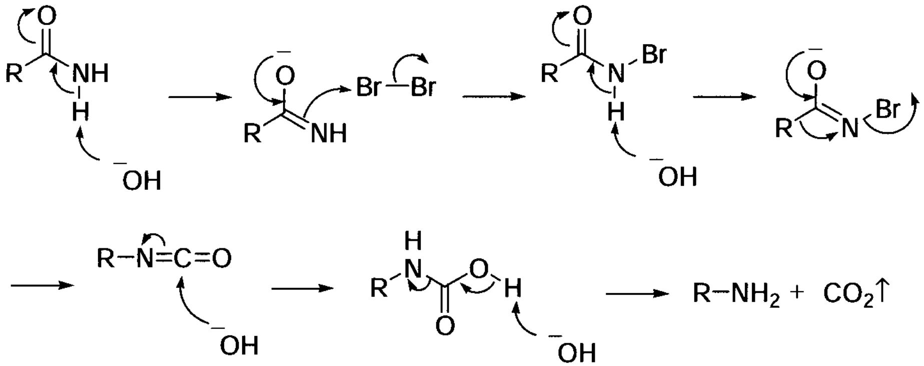
Hofmann rearrangement (Hofmann degradation reaction)





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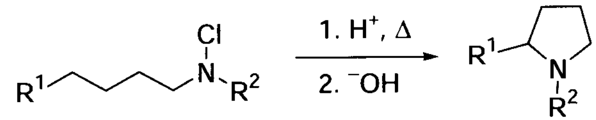
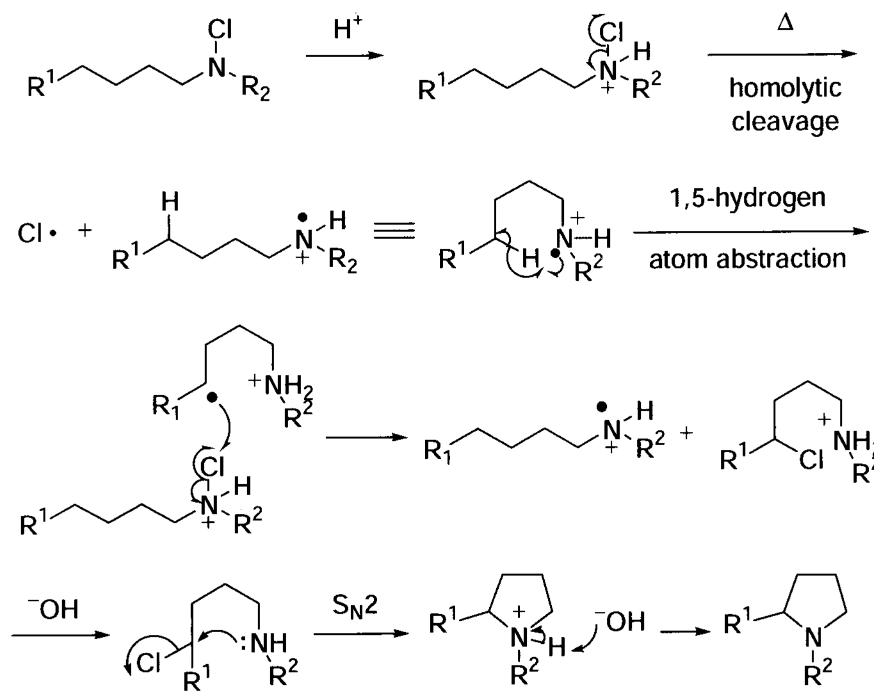
Hofmann–Löffler–Freytag reaction





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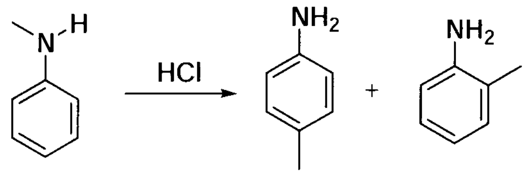
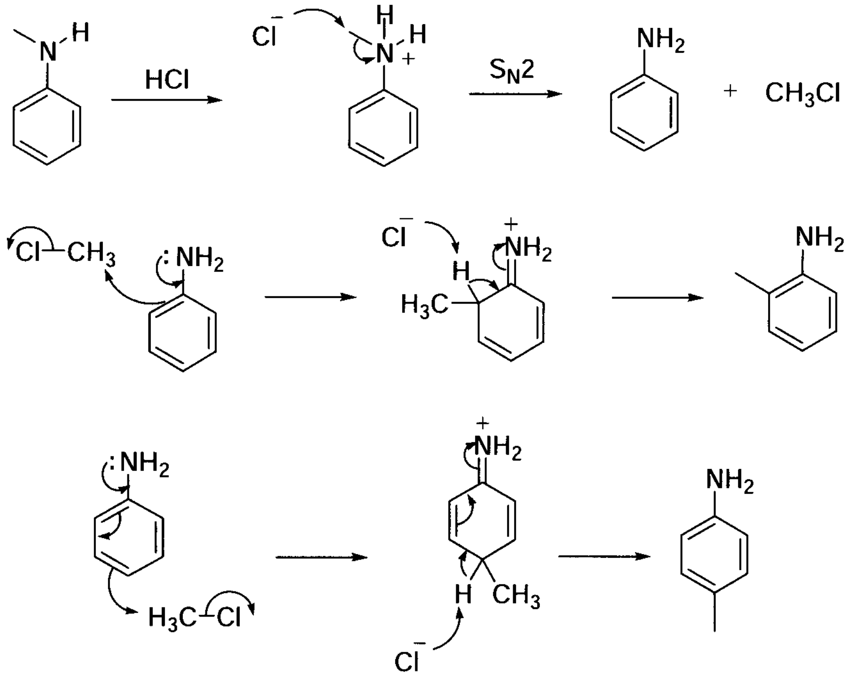
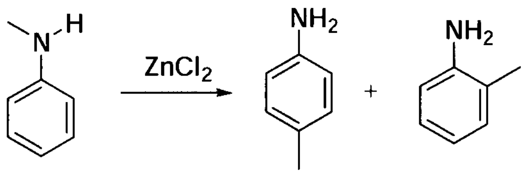
Hofmann–Martius reaction





Reilly–Hickinbottom rearrangement is a variation of the Hofmann–Martius reaction in which a Lewis acid is used instead of a protic acid. The reaction follows an analogous pathway:



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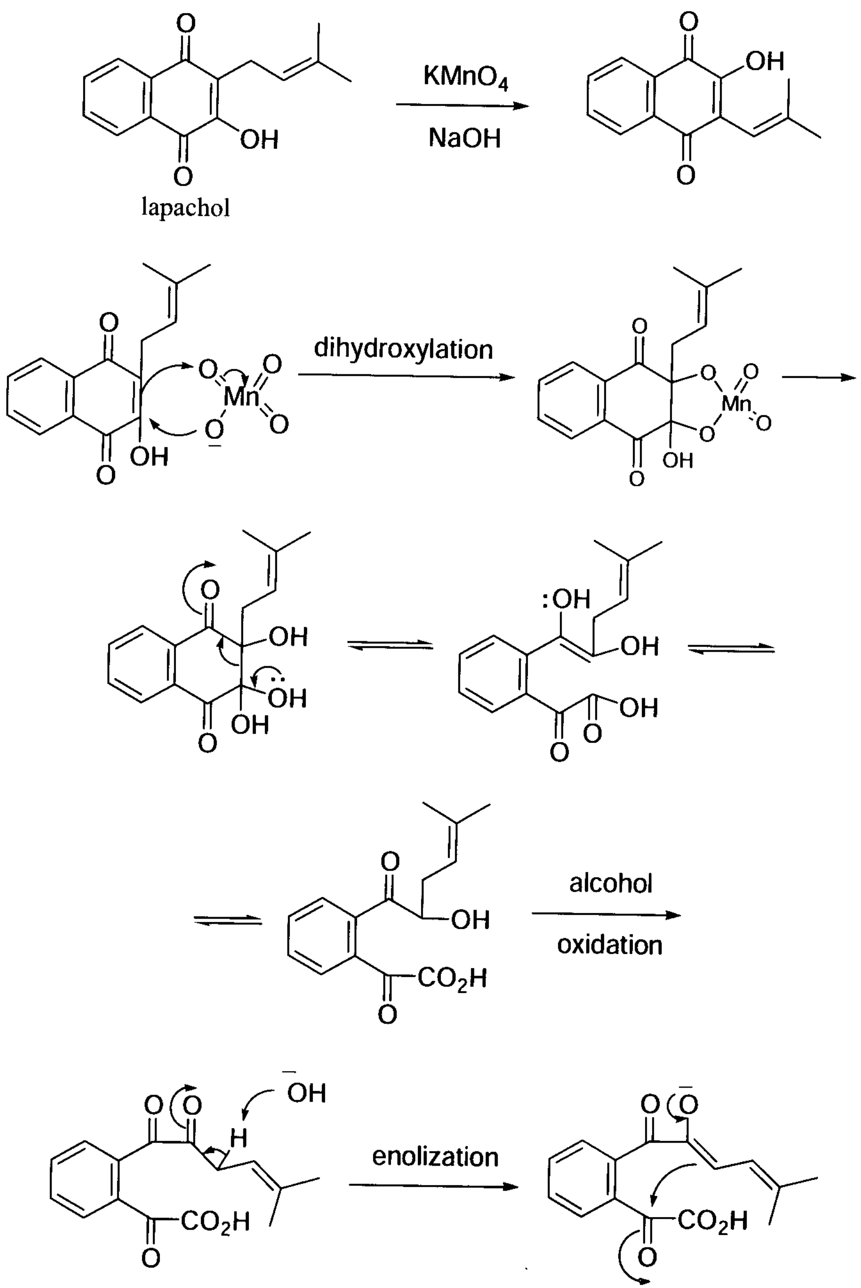
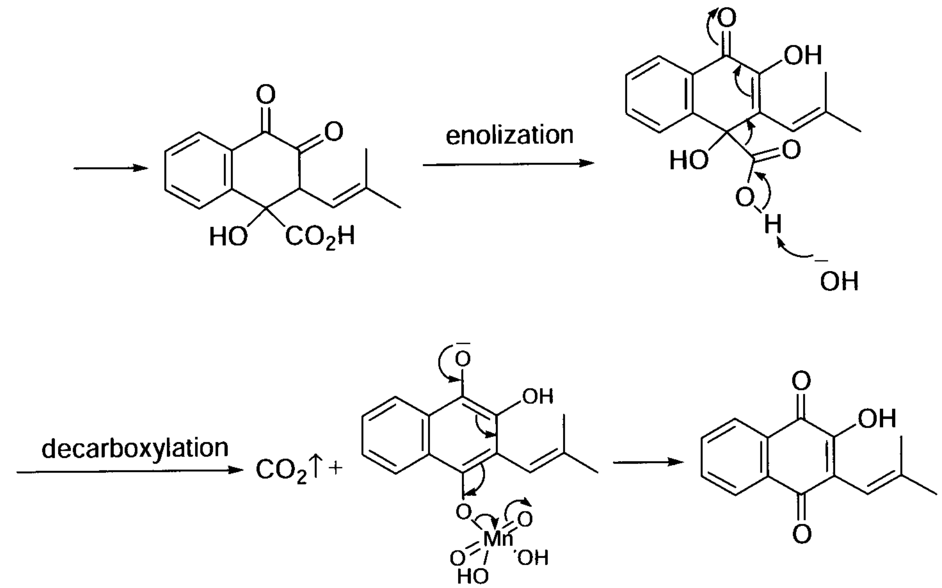
Hooker oxidation





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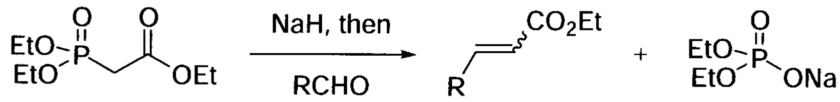
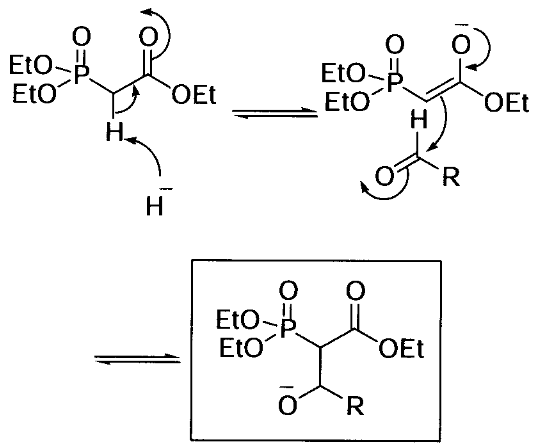
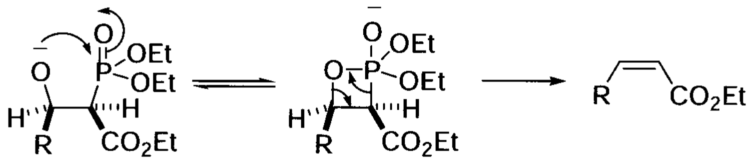
Horner–Wadsworth–Emmons reaction

Olefin formation from aldehydes and phosphonates. Workup is more advantageous than the corresponding Wittig reaction because the phosphate by-product can be washed away with water.

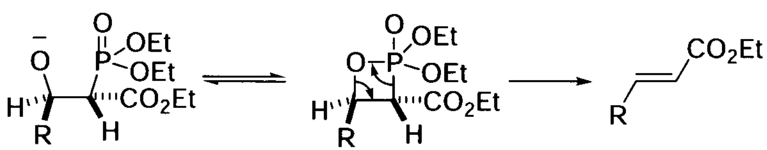




erythro (kinetic) or *threo* (thermodynamic)



erythro, kinetic adduct



threo, thermodynamic adduct

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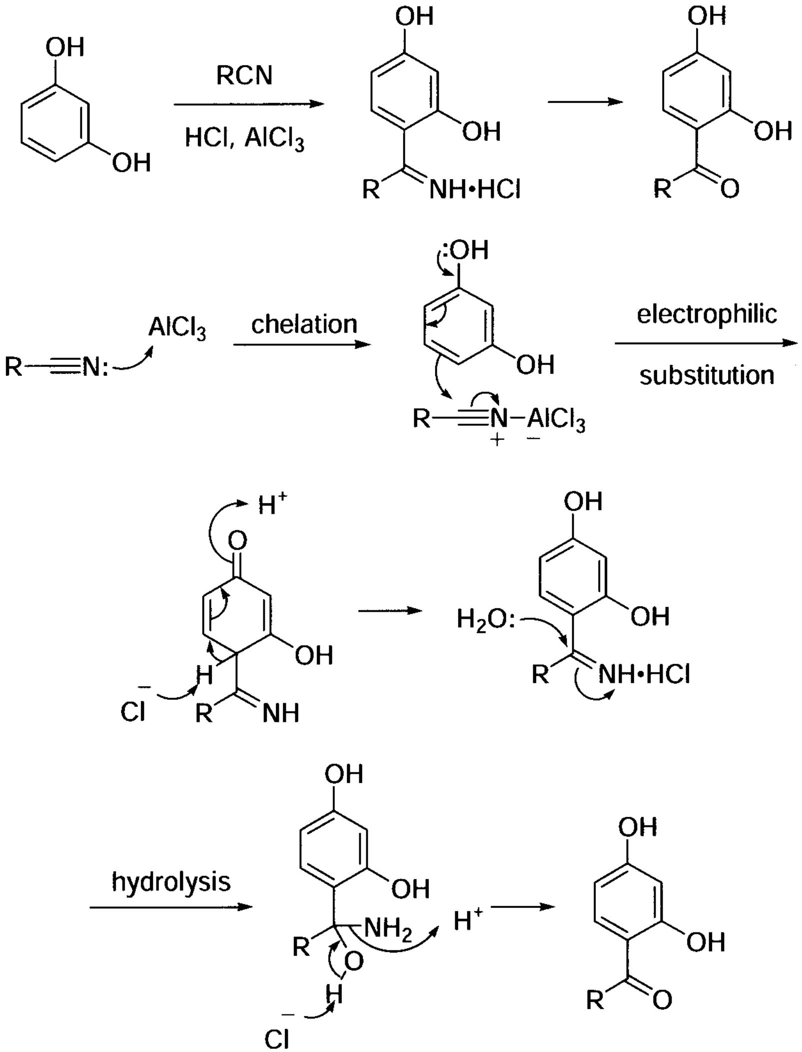
Houben–Hoesch reaction

Acid-catalyzed acylation of phenols using nitriles.



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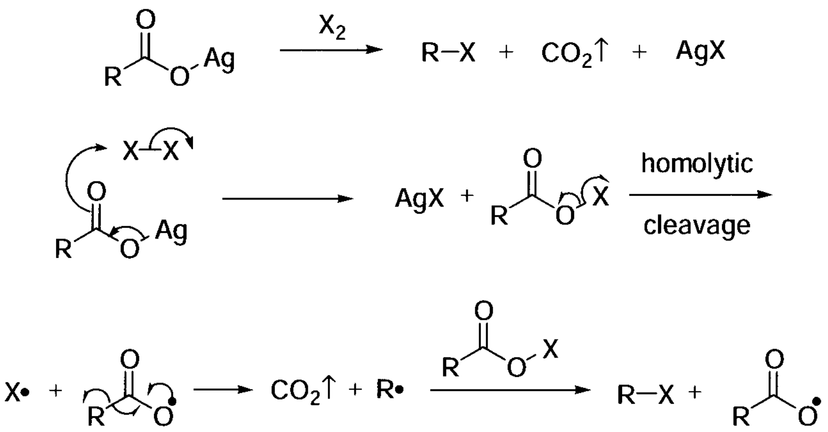
Hunsdiecker reaction



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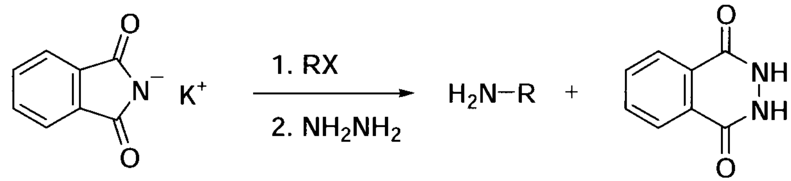
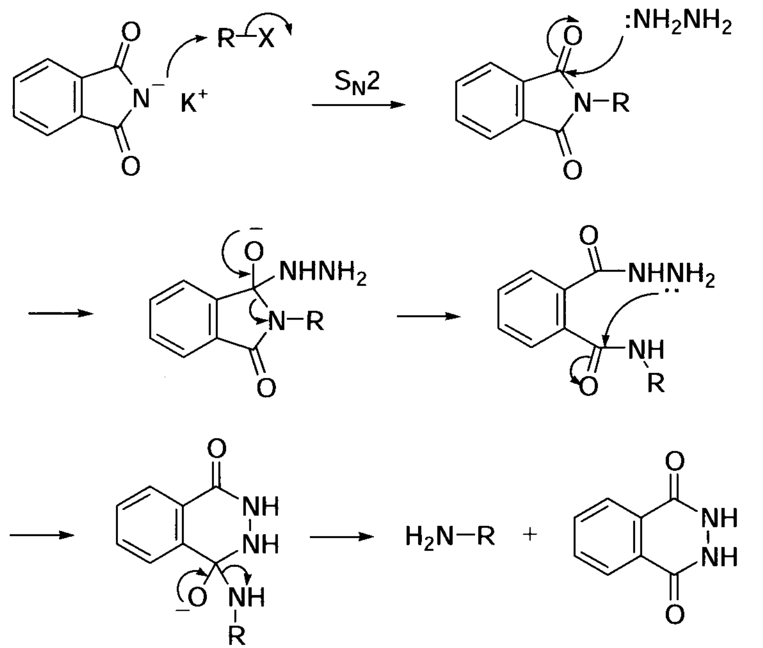
Ing–Manske procedure

A variant of Gabriel amine synthesis where hydrazine is used to release the amine from the corresponding phthalimide:





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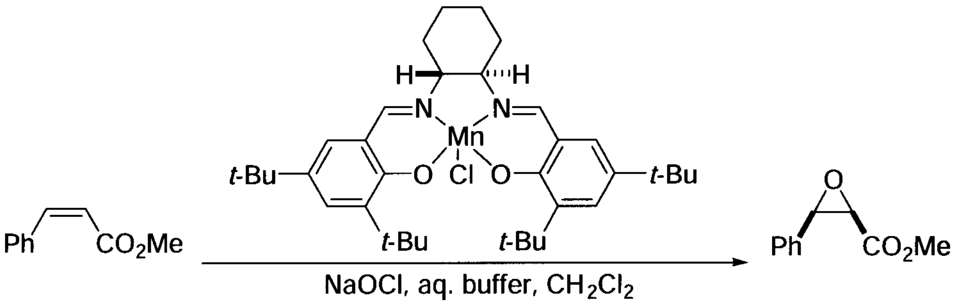
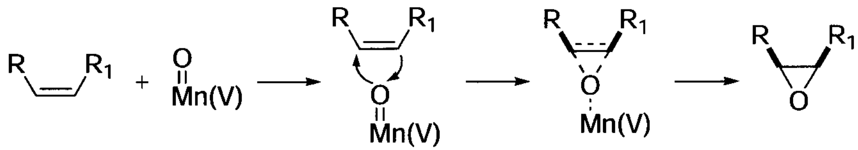
Jacobsen–Katsuki epoxidation

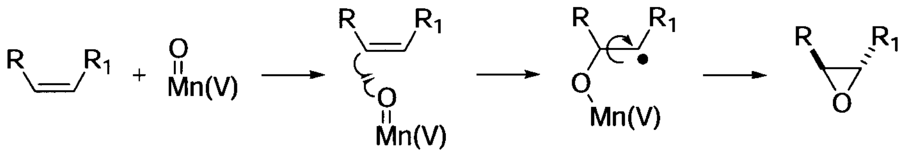
Mangnese(III)-catalyzed asymmetric epoxidation of (*Z*)-olefins.



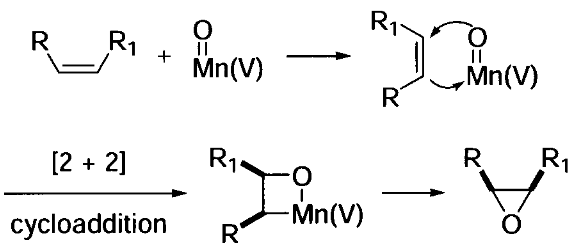
1. Concerted oxygen transfer (*cis*-epoxide):



2. Oxygen transfer *via* radical intermediate (*trans*-epoxide):



3. Oxygen transfer *via* manganaoxetane intermediate (*cis*-epoxide):



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2. Irie, R.; Noda, K.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* **1991**, *32*, 1055.
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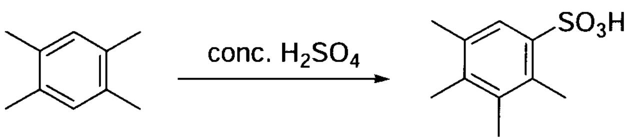
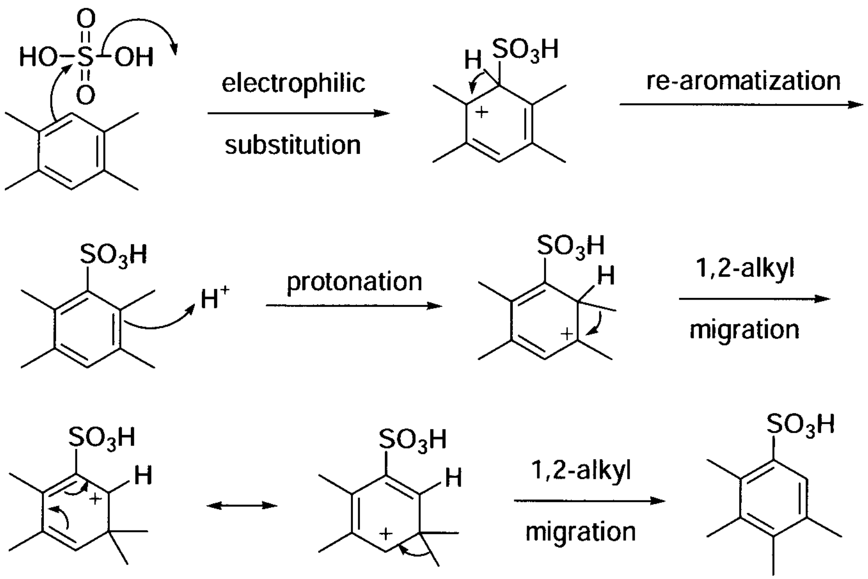
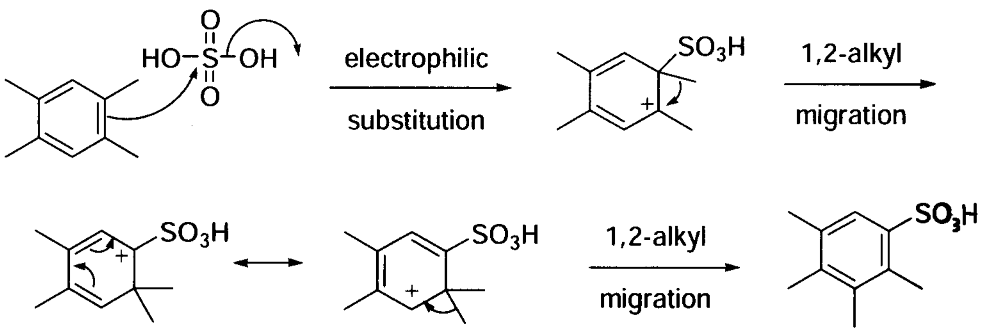
Jacobsen rearrangement



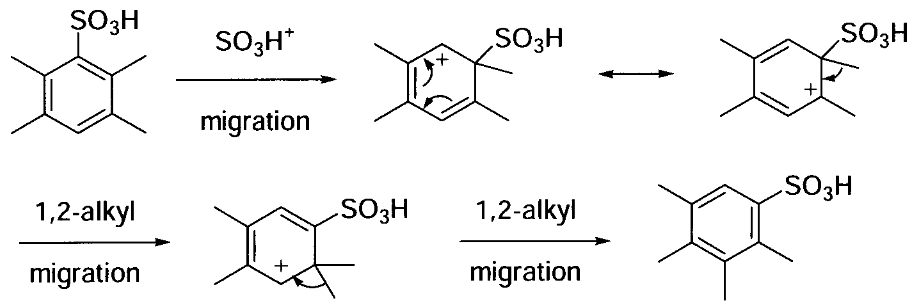
Mechanism 1:



Mechanism 2:



Mechanism 3:



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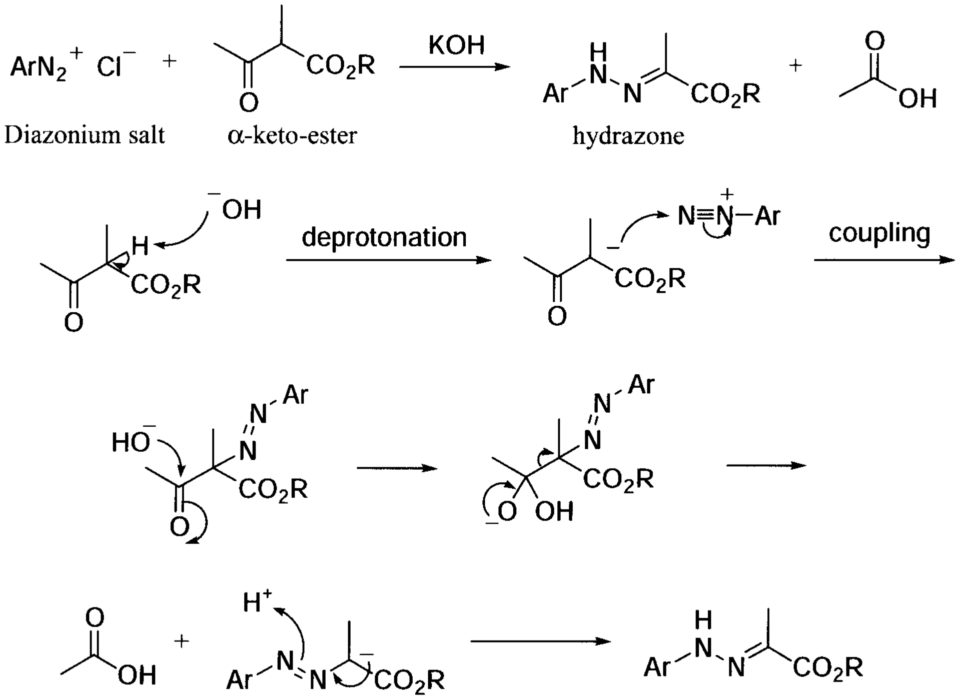
Japp–Klingemann hydrazone synthesis



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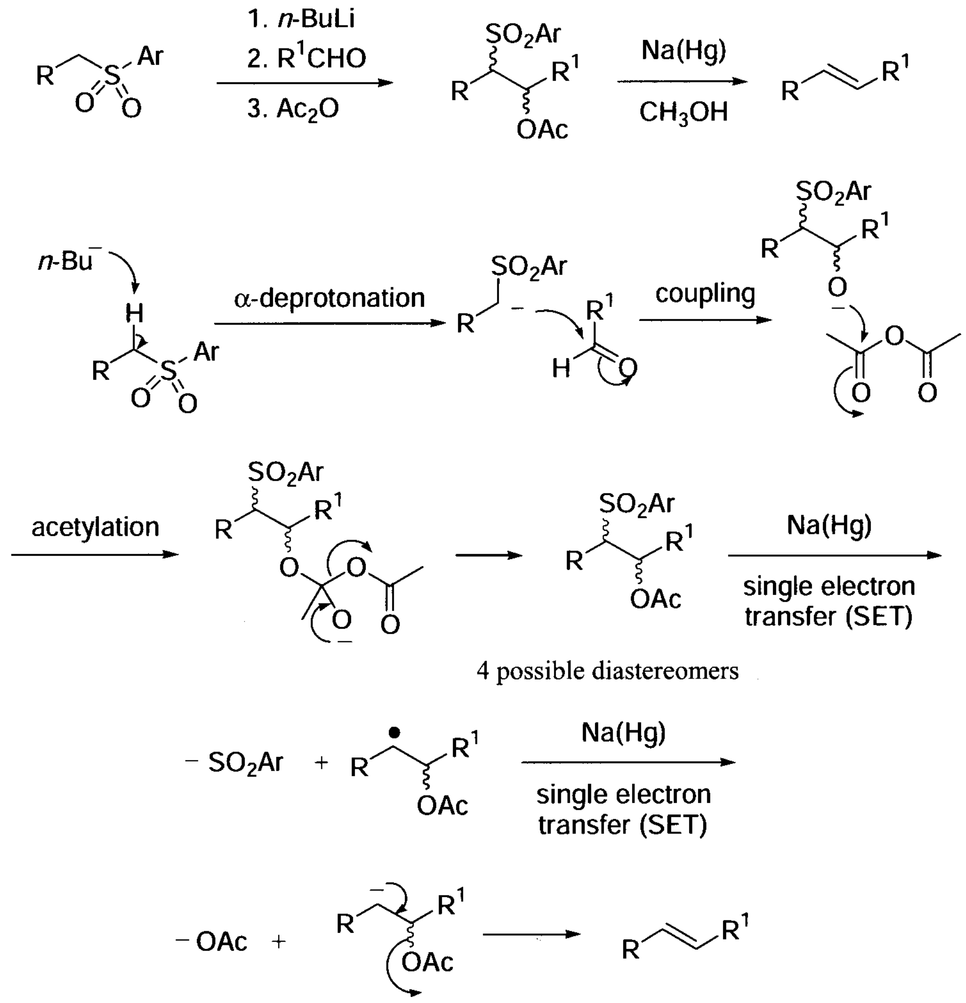
Julia–Lythgoe olefination

(*E*)-Olefins from sulfones and aldehydes.



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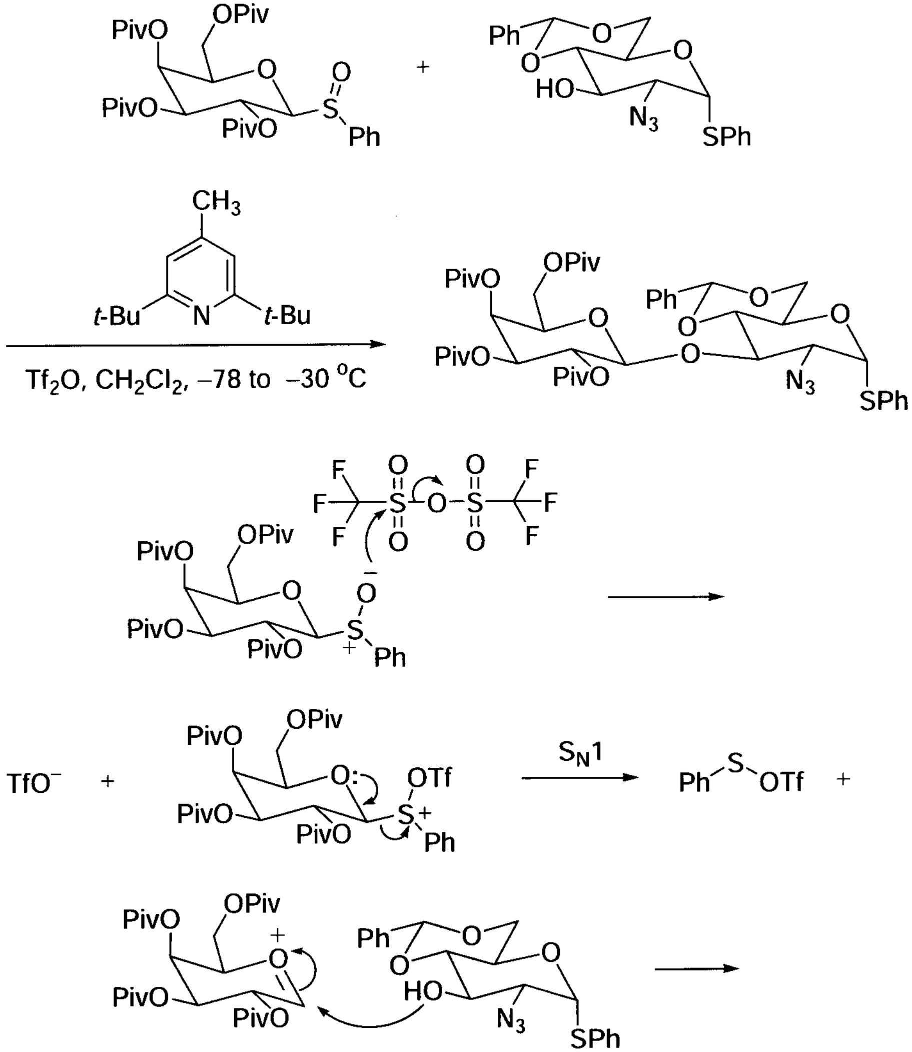
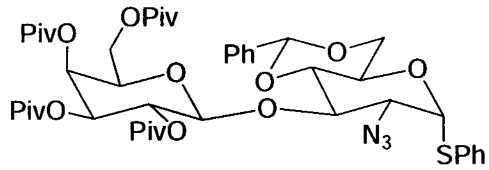
Kahne glycosidation

Diastereoselective glycosidation of a sulfoxide at the anomeric center as the glycosyl acceptor. The sulfoxide activation is achieved using Tf_2O.



oxonium ion



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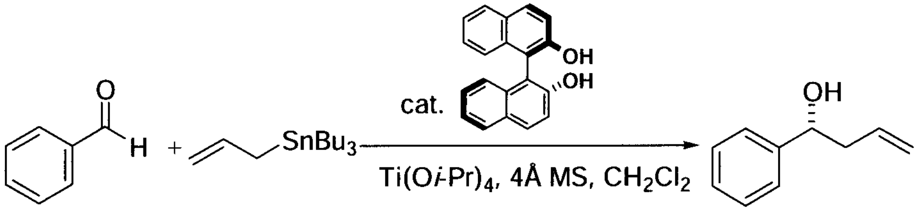
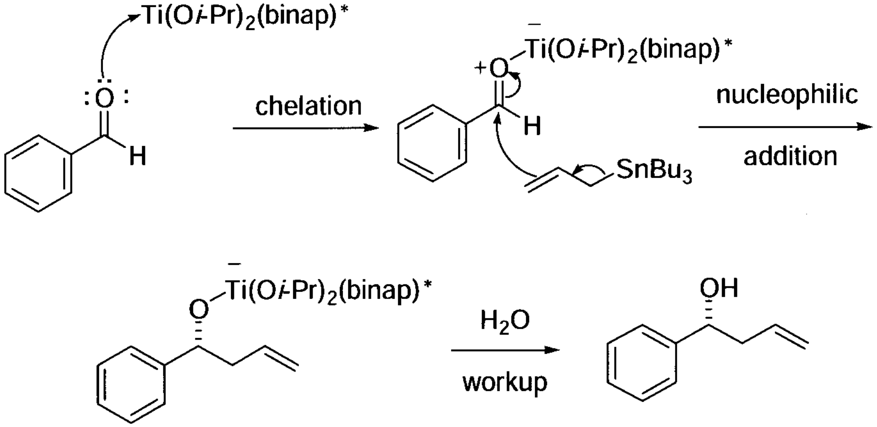
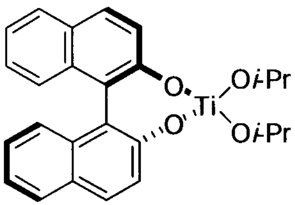
Keck stereoselective allylation

Asymmetric allylation of aldehydes with allylstannane in the presence of a Lewis acid and catalytic chiral BINAP (or other chiral ligands).





The enantioselectivity is imparted by the steric bias of the chiral ligands which displace *iso*-propoxide of titanium *iso*-propoxide. Therefore, the chiral Lewis acid becomes Ti(O*i*-Pr)$_2$(binap), which is substitutionally labile:



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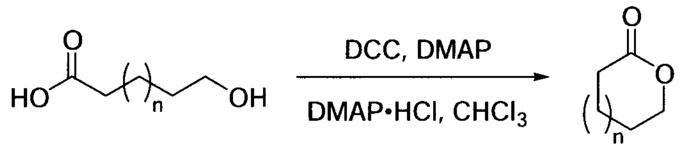
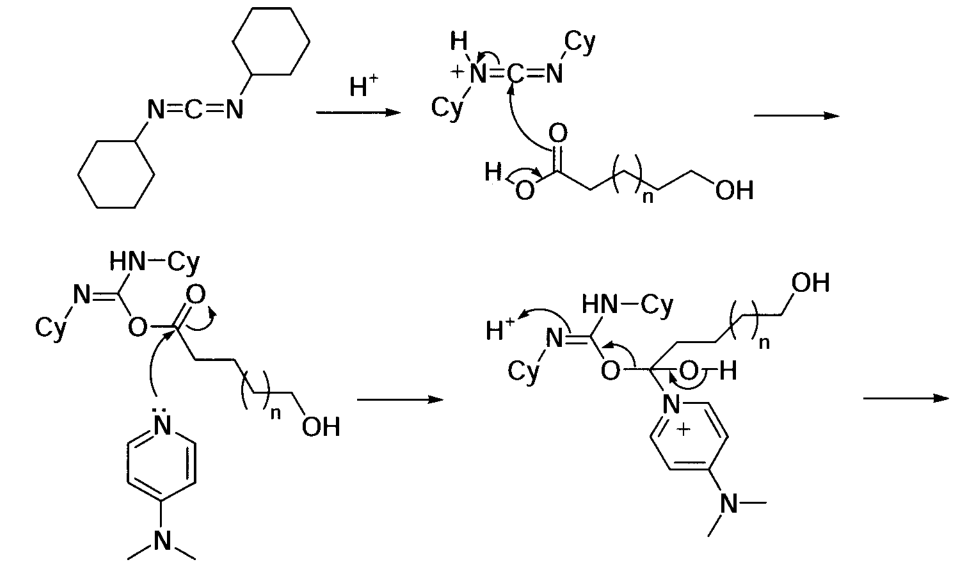
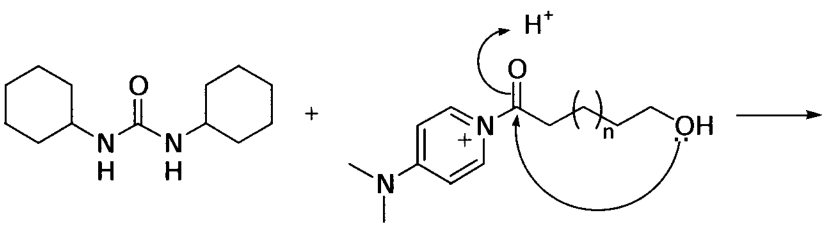
Keck macrolactonization

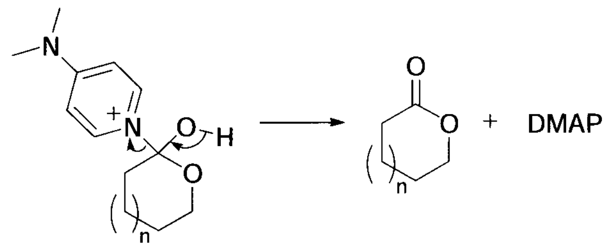




dimethylaminopyridine (DMAP)



1,3-dicyclohexylurea



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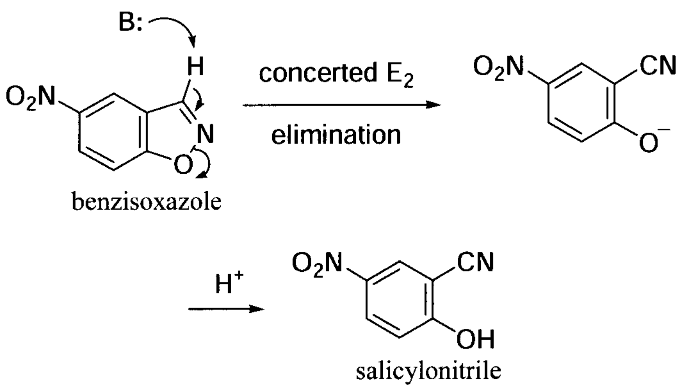
Kemp elimination

Treatment of benzisoxazole results in the ring-opening product, salicylonitrile.



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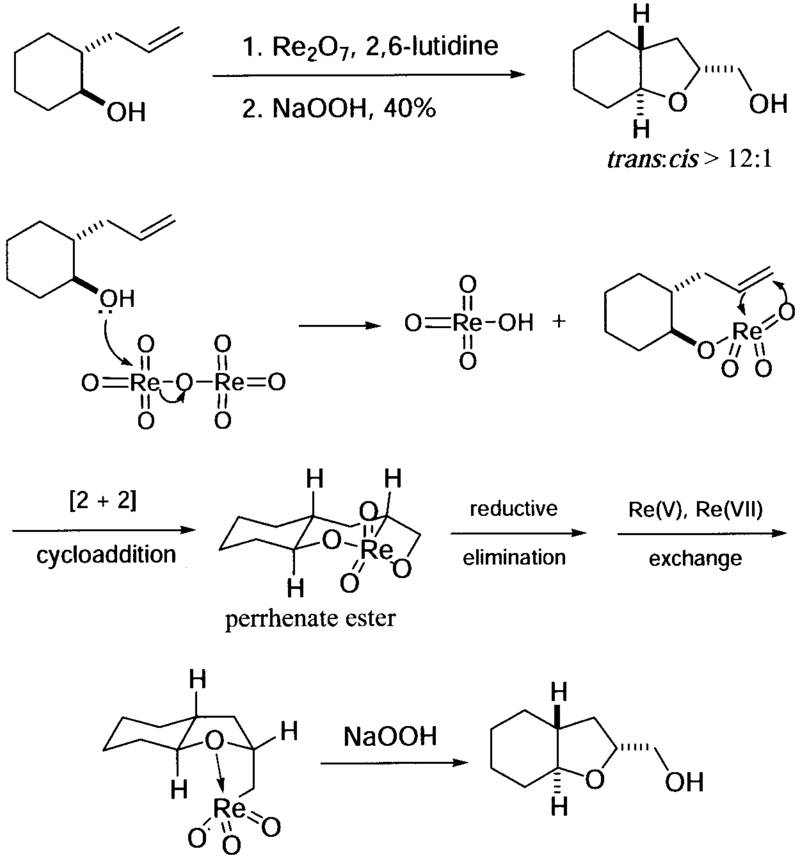
Kennedy oxidative cyclization

Asymmetric synthesis of tetrahydrofuran by treatment of a δ-hydroxyolefin with Re_2O_7.



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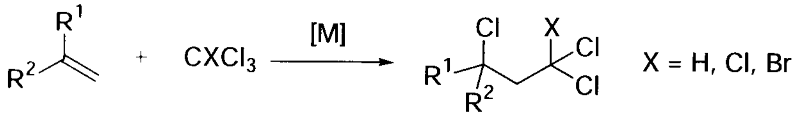
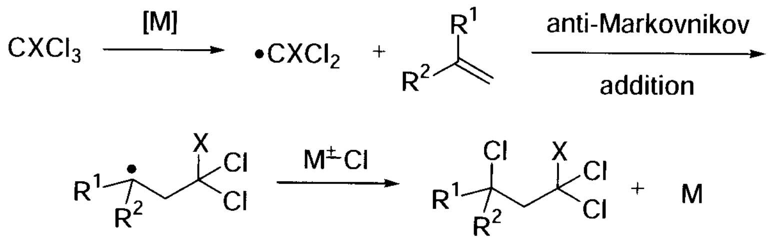
Kharasch addition reaction

Transition metal-catalyzed radical addition of $CXCl_3$ to olefins.



M   organometallic reagent containing Ru, Re, Mo, W, Fe, Al, B, Cr, Sm, *etc.*



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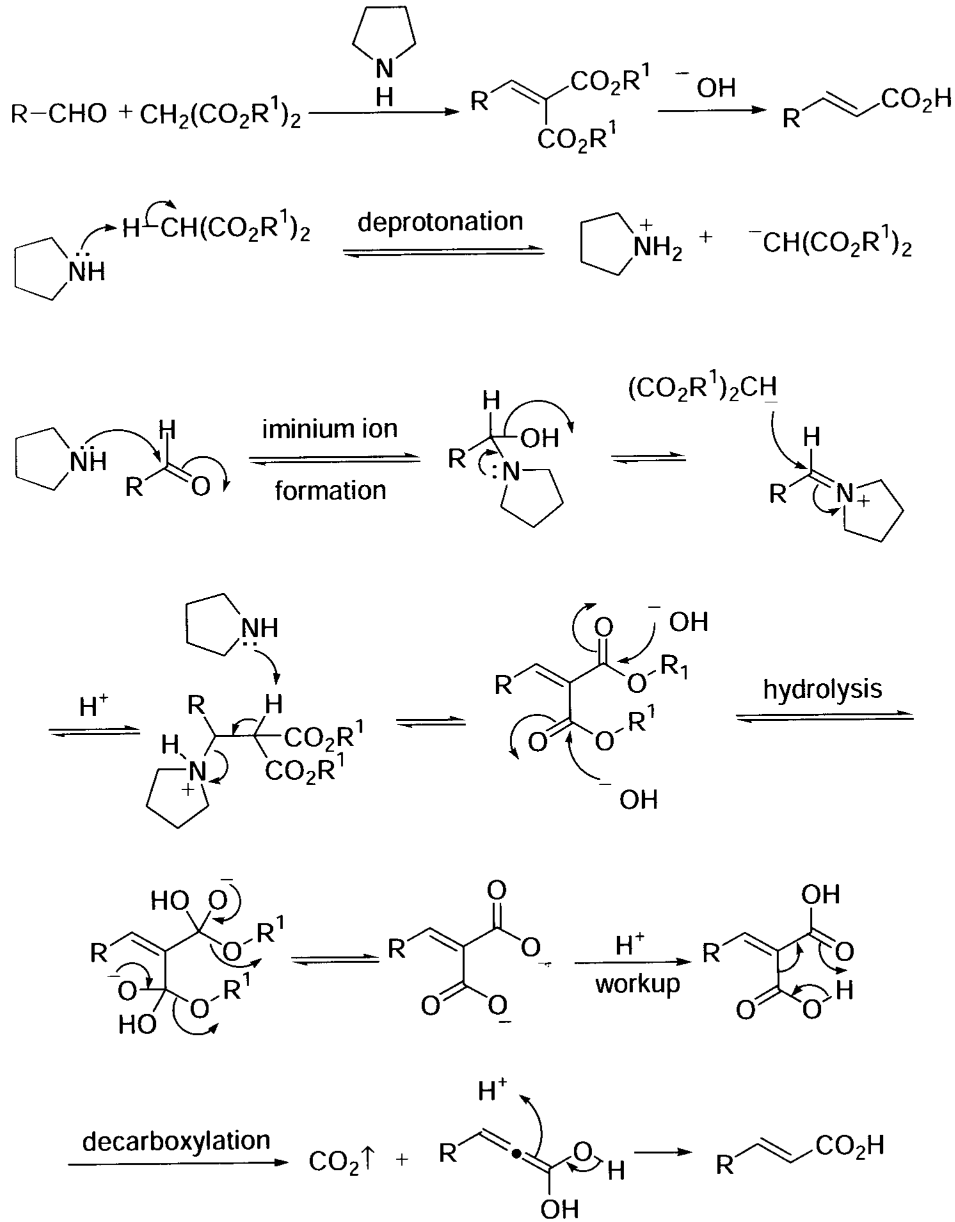
Knoevenagel condensation



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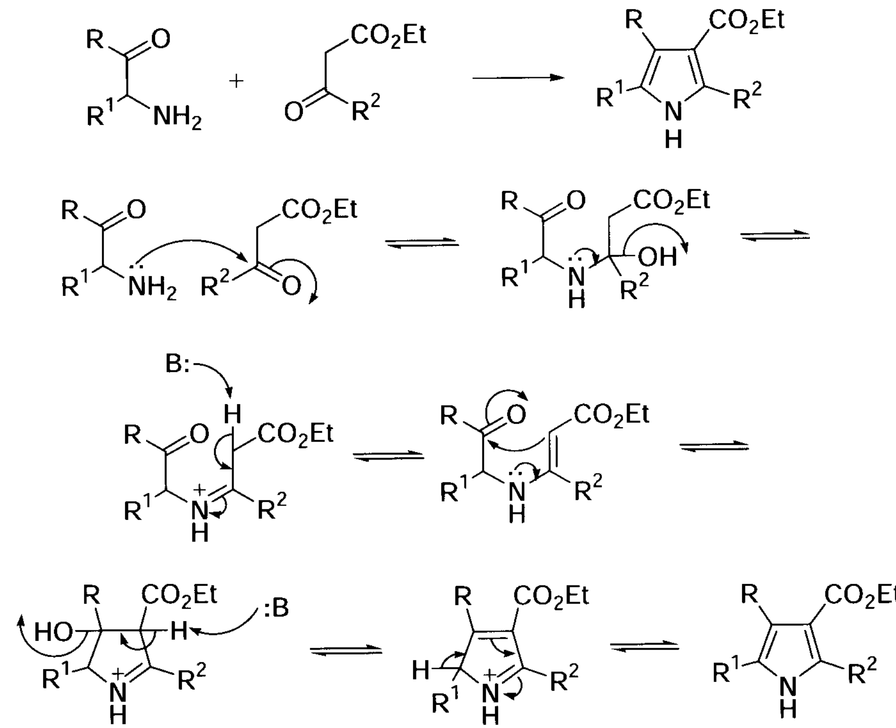
Knorr pyrrole synthesis



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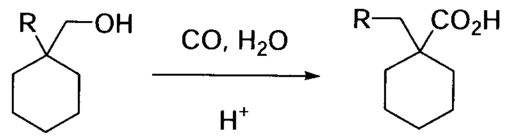
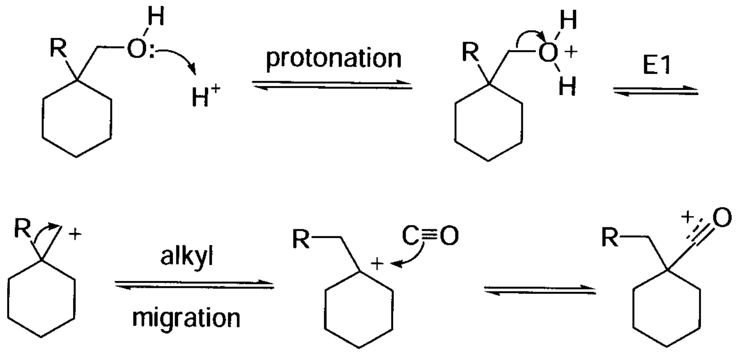
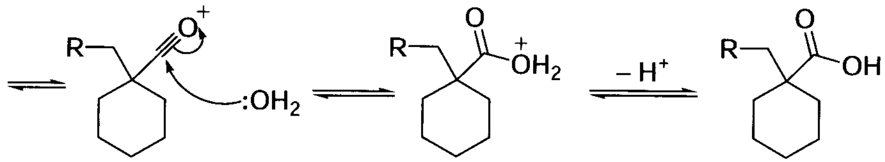
Koch carbonylation reaction (Koch–Haaf carbonylation reaction)

Strong acid-catalyzed tertiary carboxylic acid formation from alcohols or olefins and CO.





the tertiary carbocation is thermodynamically favored



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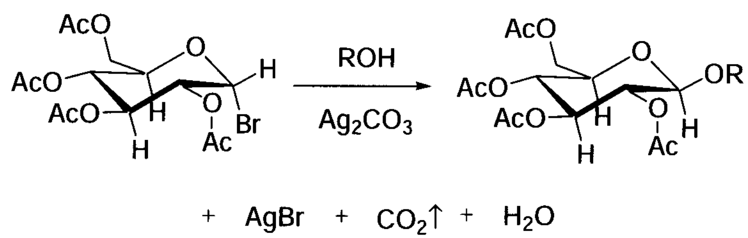
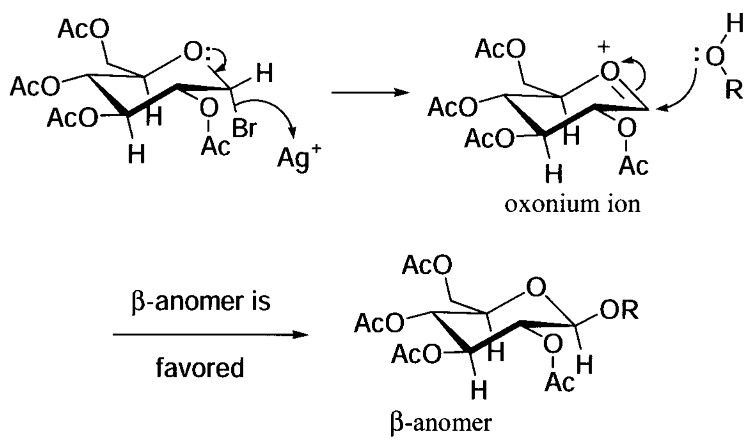
Koenig–Knorr glycosidation

Formation of the β-glycoside from α-halocarbohydrate under the influence of silver salt.





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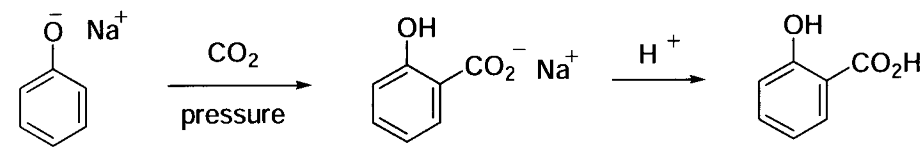
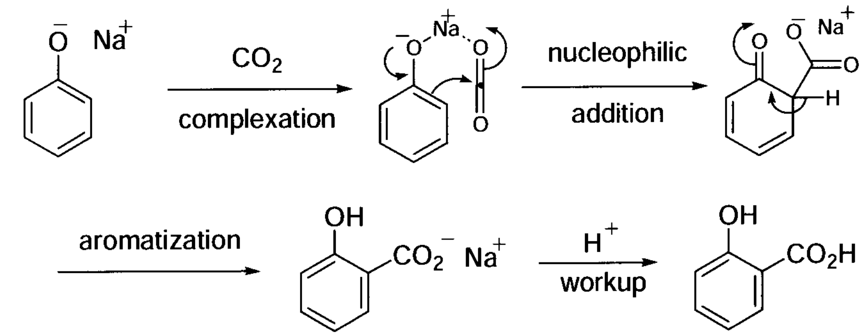
Kolbe–Schmitt reaction





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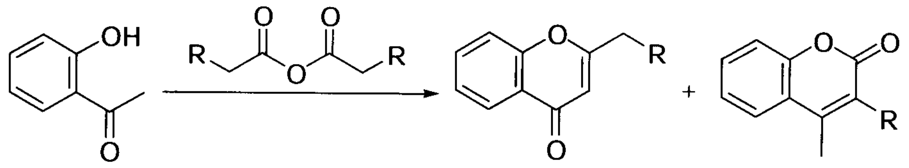
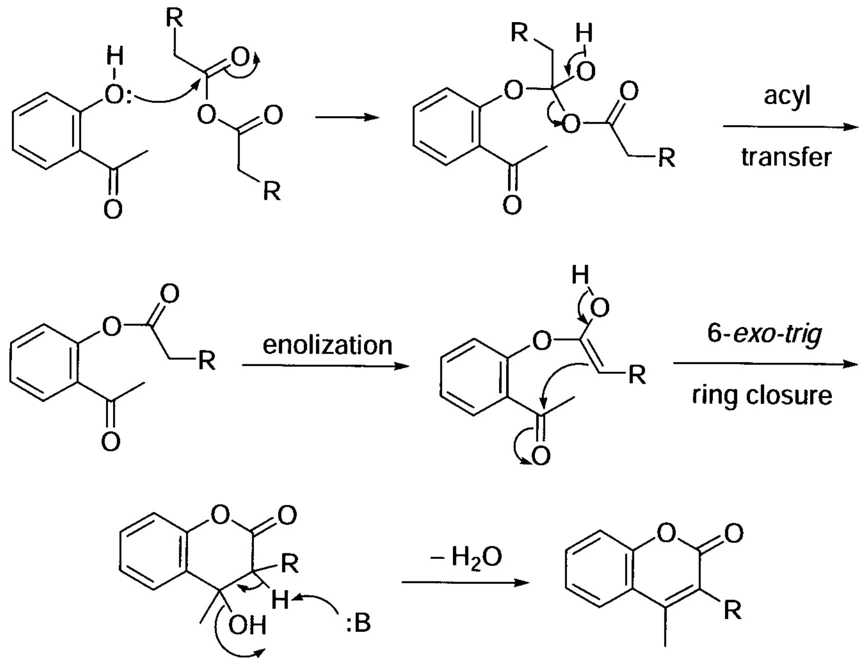
Kostanecki reaction



1 2 3

Also known as **Kostanecki–Robinson reaction**. Transformation **1**→**2** represents an **Allan–Robinson reaction** (see page 3), whereas **1**→**3** is a **Kostanecki (acylation) reaction**:



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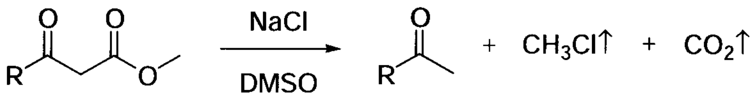
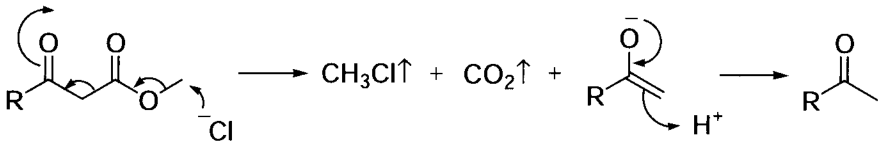
Krapcho decarboxylation

Nucleophilic decarboxylation of β-ketoesters, malonate esters, α-cyanoesters, and α-sulfonylesters.





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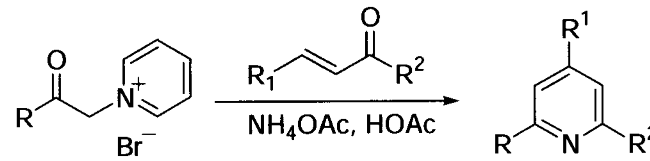
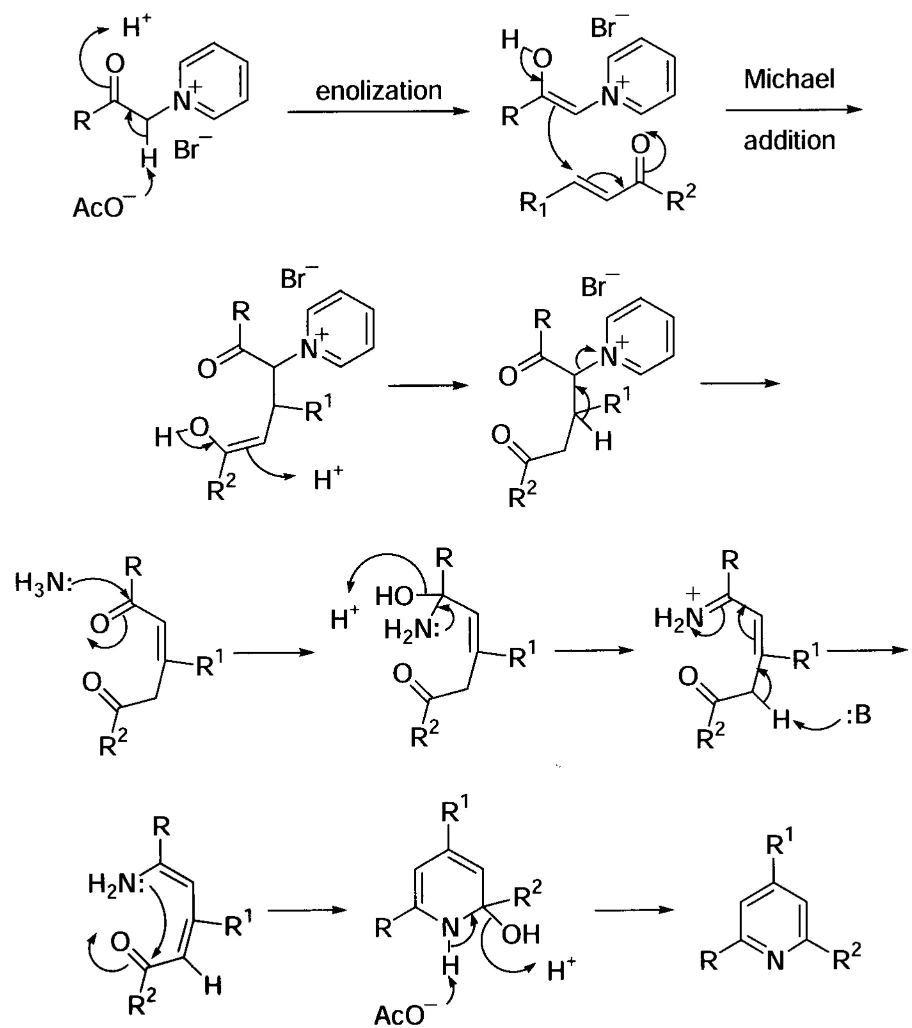
Kröhnke reaction (pyridine synthesis)





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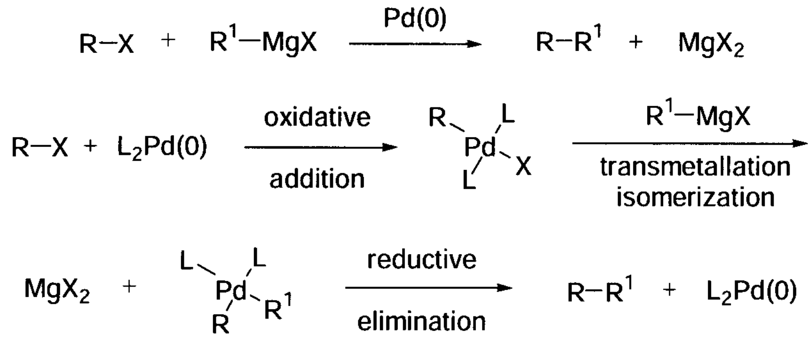
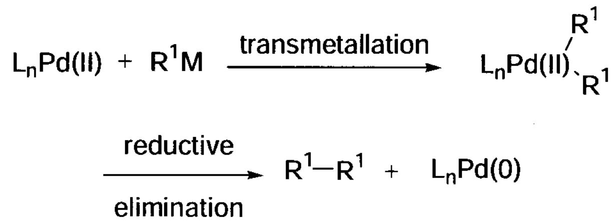
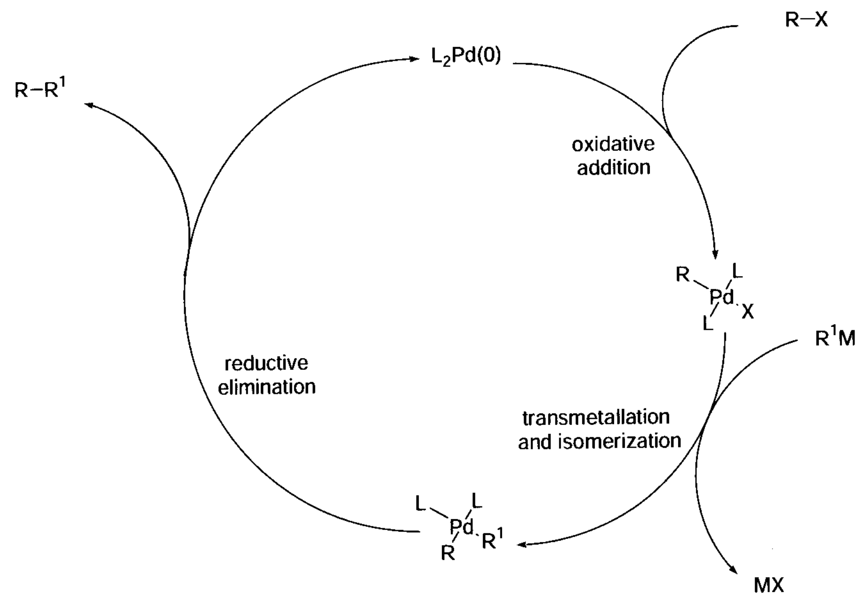
Kumada cross-coupling reaction



The Kumada cross-coupling reaction (also occasionally known as the Kharasch cross-coupling reaction) is a nickel- or palladium-catalyzed cross-coupling reaction of a Grignard reagent with an organic halide, triflate, *etc.* Along with Negishi, Stille, Hiyama, and Suzuki cross-coupling reactions, they belong to the same category of Pd-catalyzed cross-coupling reactions of organic halides, triflates and other electrophiles with organometallic reagents. These reactions follow a general mechanistic cycle as shown on the next page. There are slight variations for the Hiyama and Suzuki reactions, for which an additional activation step is required for the transmetallation to occur.

The catalytic cycle:





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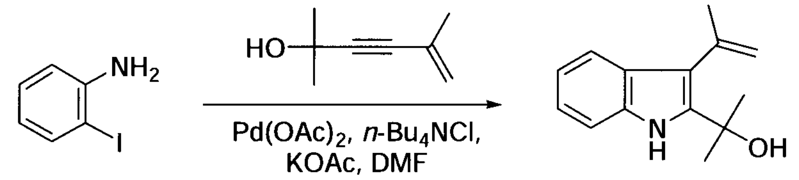
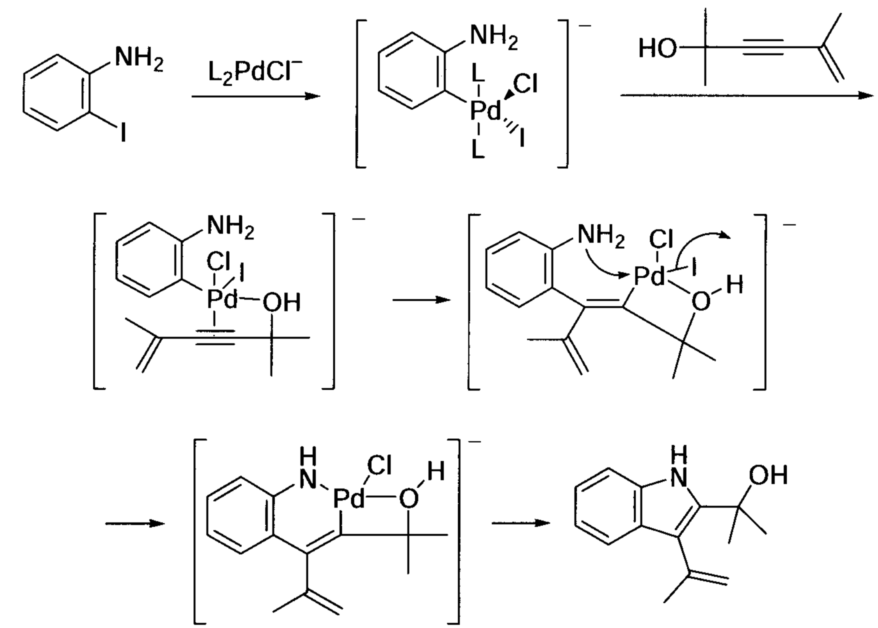
Larock indole synthesis

Indole synthesis using the palladium-catalyzed coupling reaction of an *o*-iodoaniline with a propargyl alcohol.





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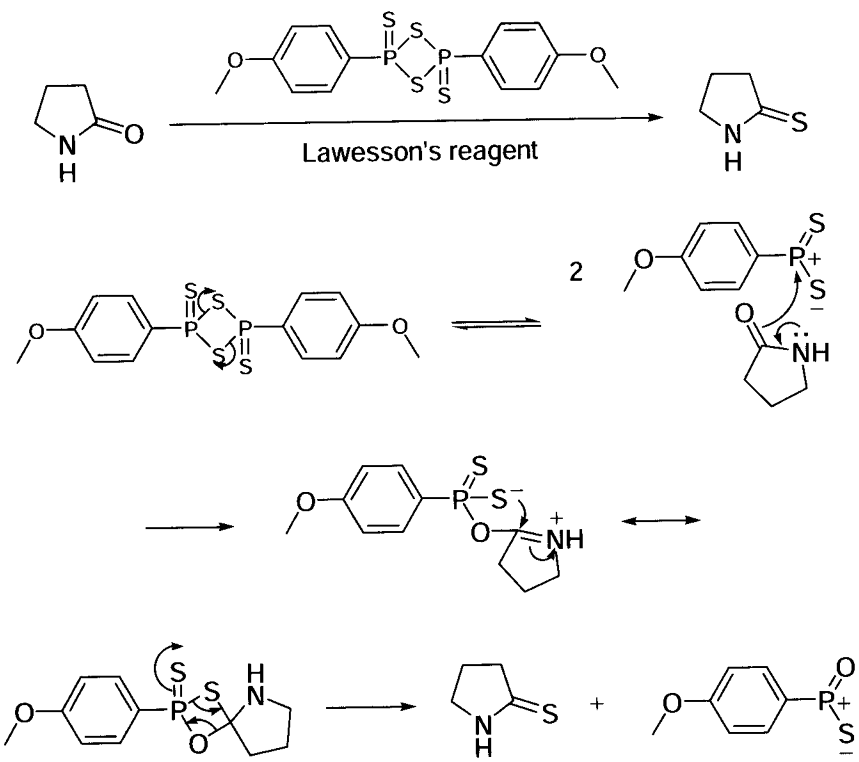
Lawesson's reagent



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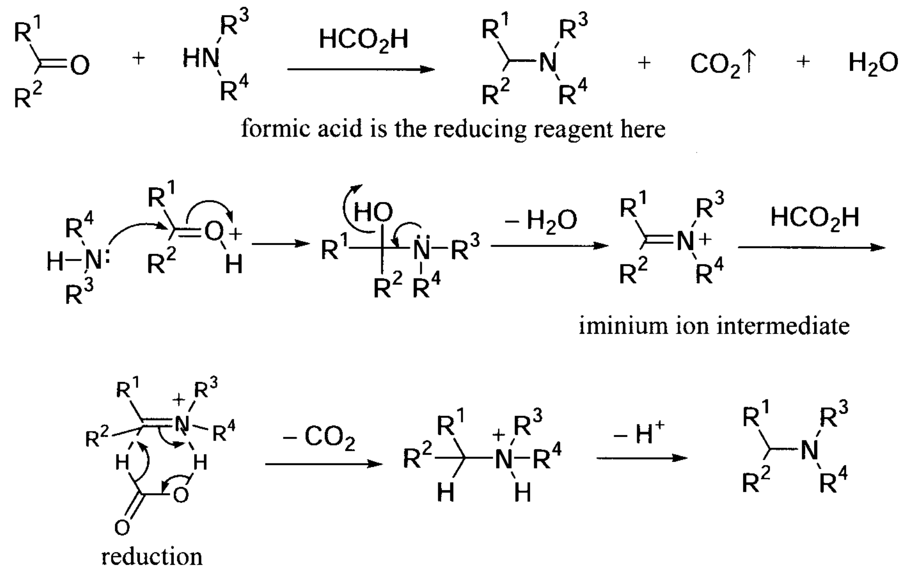
Leuckart–Wallach reaction



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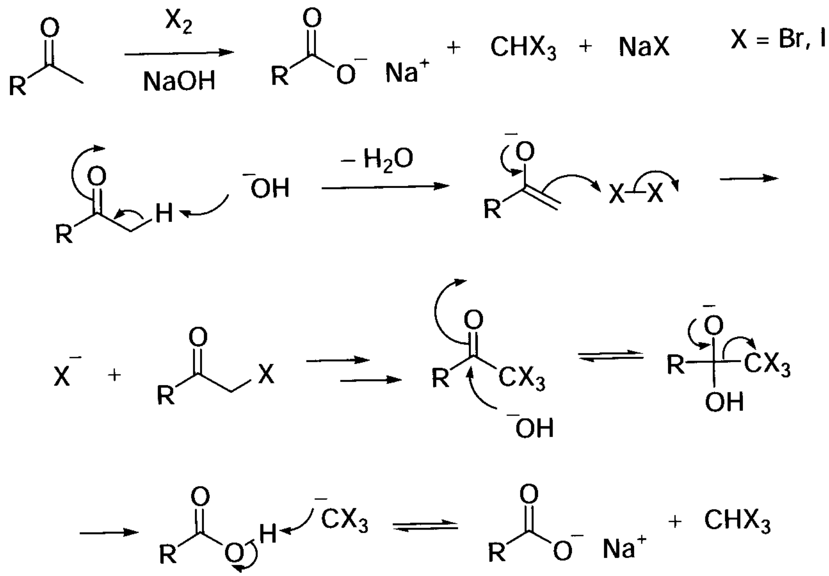
Lieben haloform reaction

Iodoform, a yellow precipitate in water, is often used for detection of methyl ketones.



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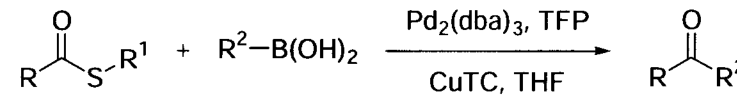
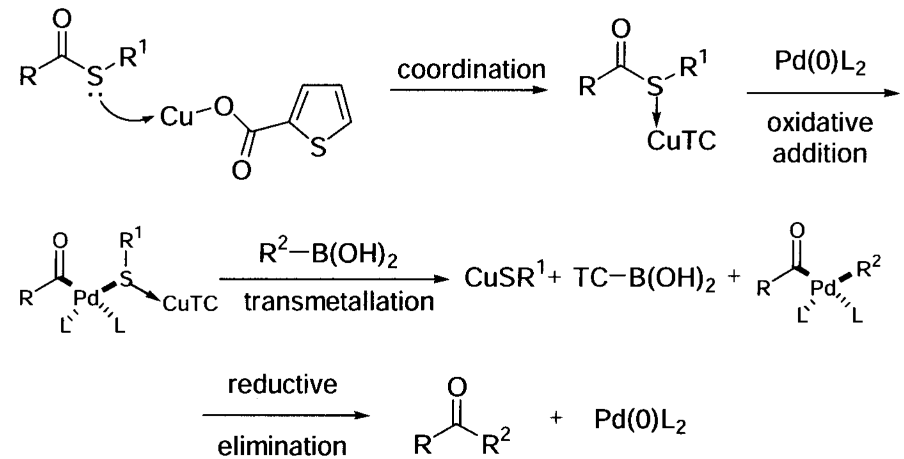
Liebeskind–Srogl coupling



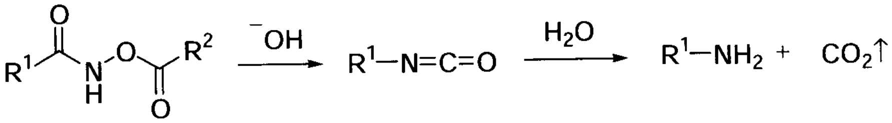
TFP = tris(2-furyl)phosphine, CuTC = copper(I) thiophene-2-carboxylate

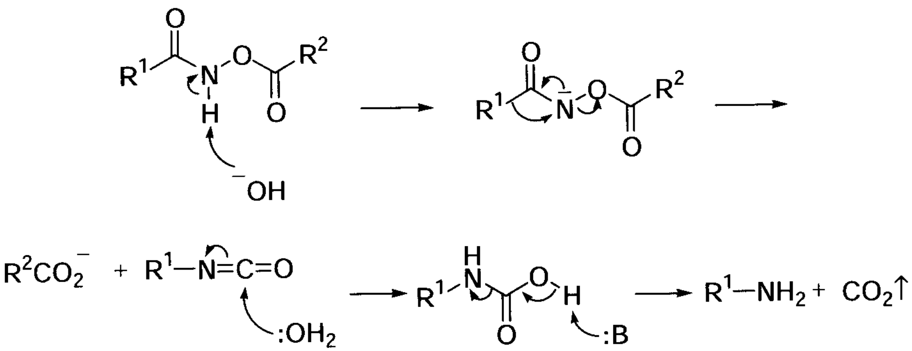


Reference

Liebeskind, L. S.; Srogl, J. *J. Am. Chem. Soc.* **2000**, *122*, 11260.

Lossen rearrangement





isocyanate intermediate

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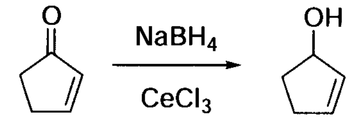
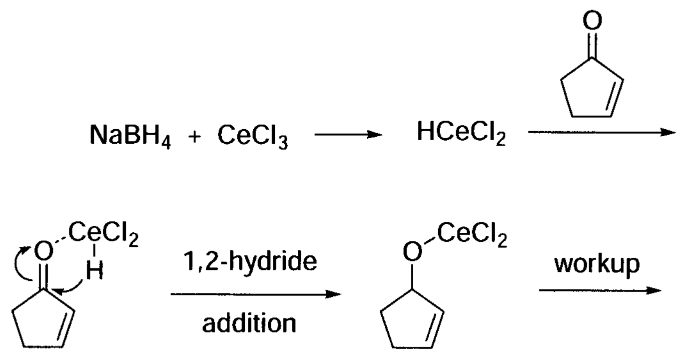
Luche reduction

1,2-Reduction of enones using $NaBH_4$–$CeCl_3$.





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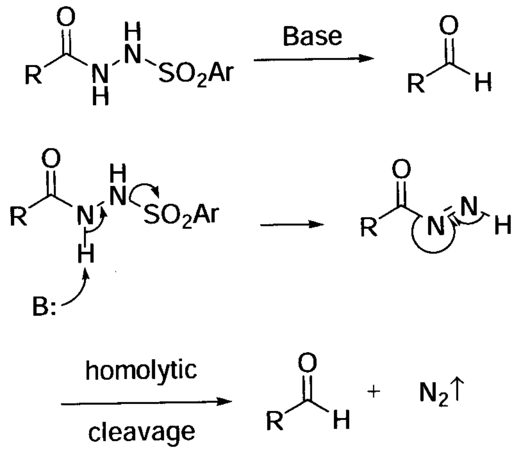
McFadyen–Stevens reduction

Treatment of acylbenzenesulfonylhydrazines with base delivers the corresponding aldehydes.



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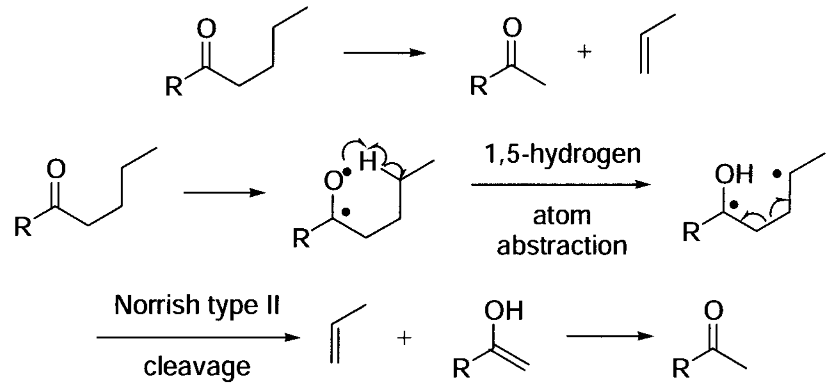
McLafferty fragmentation

Intramolecular fragmentation of carbonyls in mass spectra.



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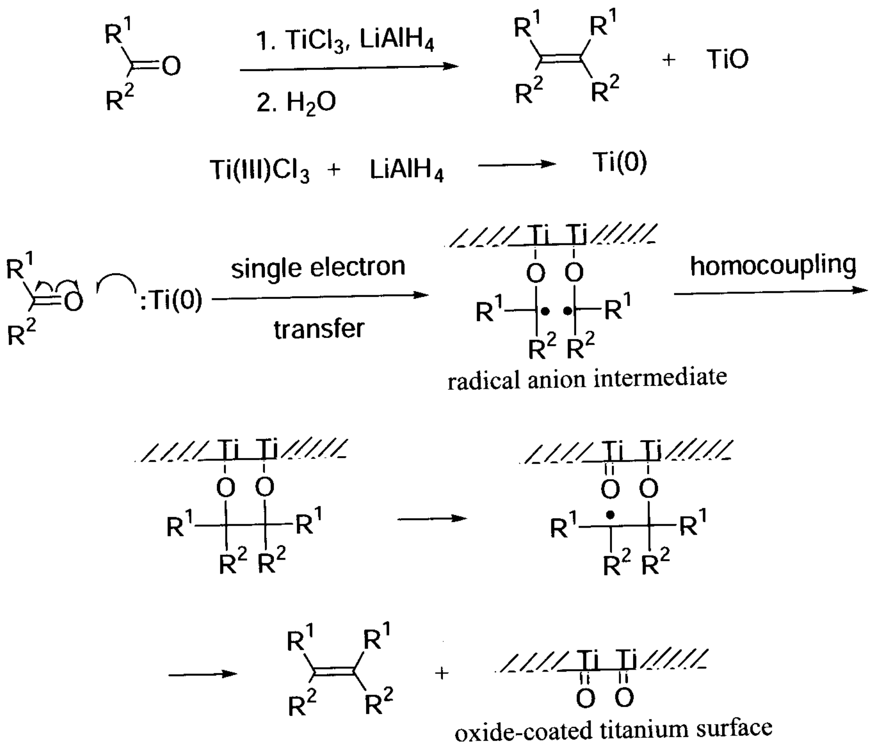
McMurry coupling

Olefination of carbonyls with $TiCl_3/LiAlH_4$.



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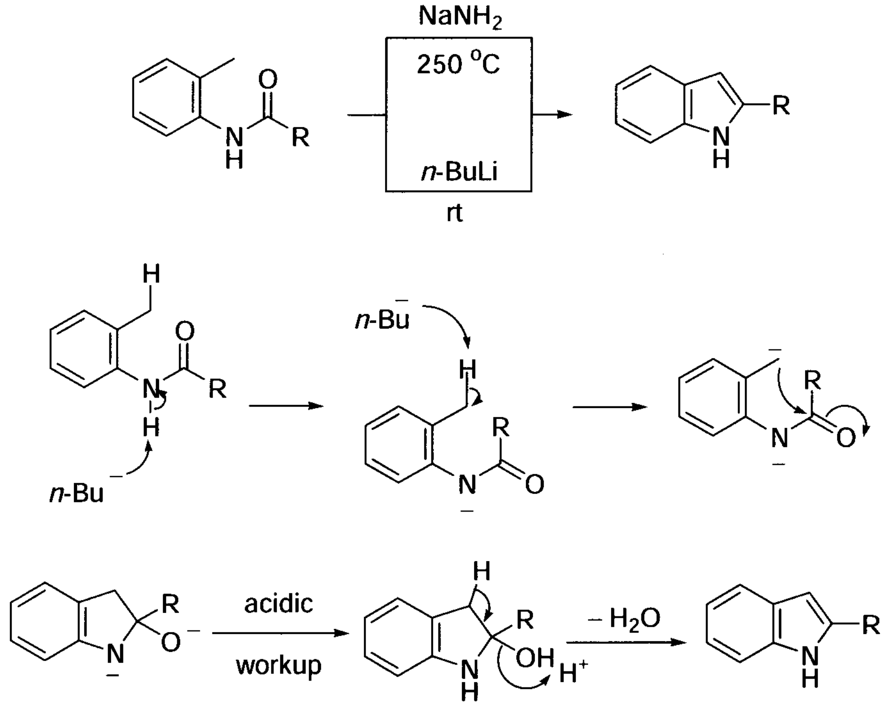
Madelung indole synthesis

Indoles from the cyclization of 2-(acylamino)-toluene using strong bases.



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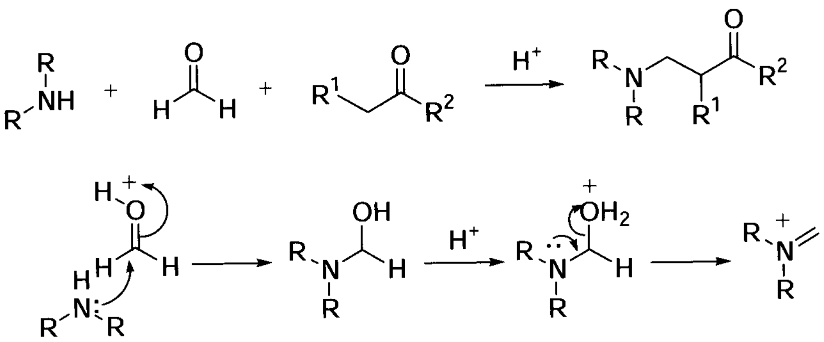
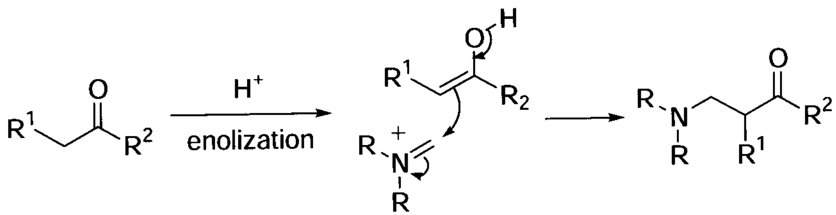
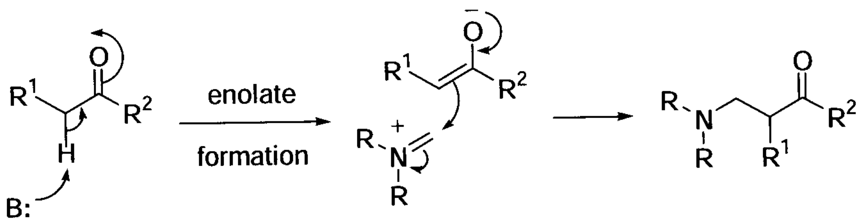
Mannich reaction



When R = H, the $^{+}NH_2$=CH_2 salt is known as **Eschenmoser's salt**



The Mannich reaction can also operate under basic conditions:



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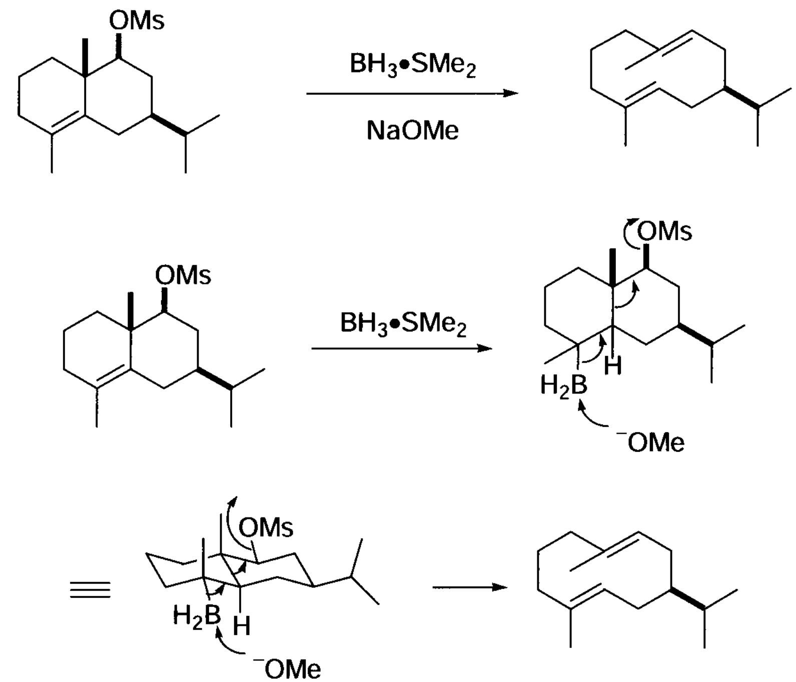
Marshall boronate fragmentation

Cf. Grob fragmentation. In fact, Marshall boronate fragmentation belongs to the Grob fragmentation category.



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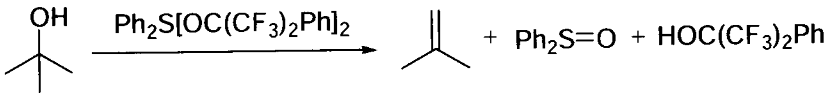
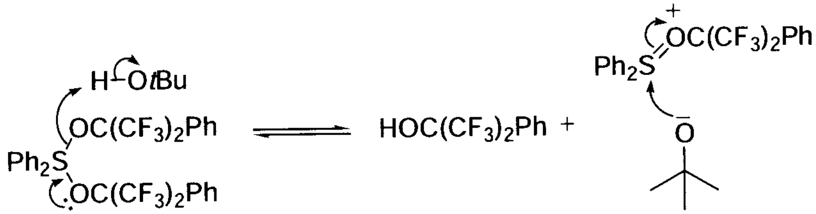
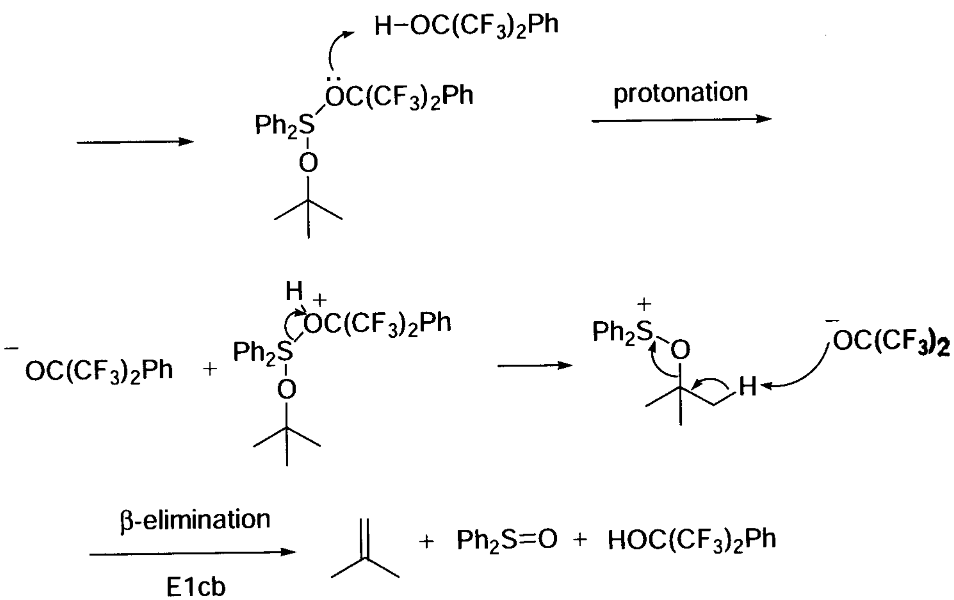
Martin's sulfurane dehydrating reagent

Cf. Burgess dehydrating reagent.





The alcohol is acidic



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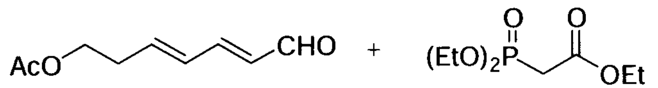
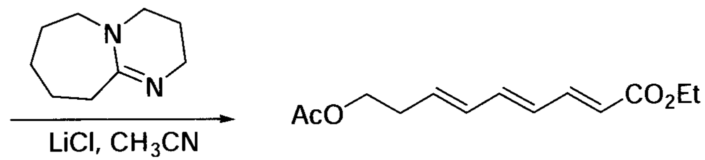
Masamune–Roush conditions

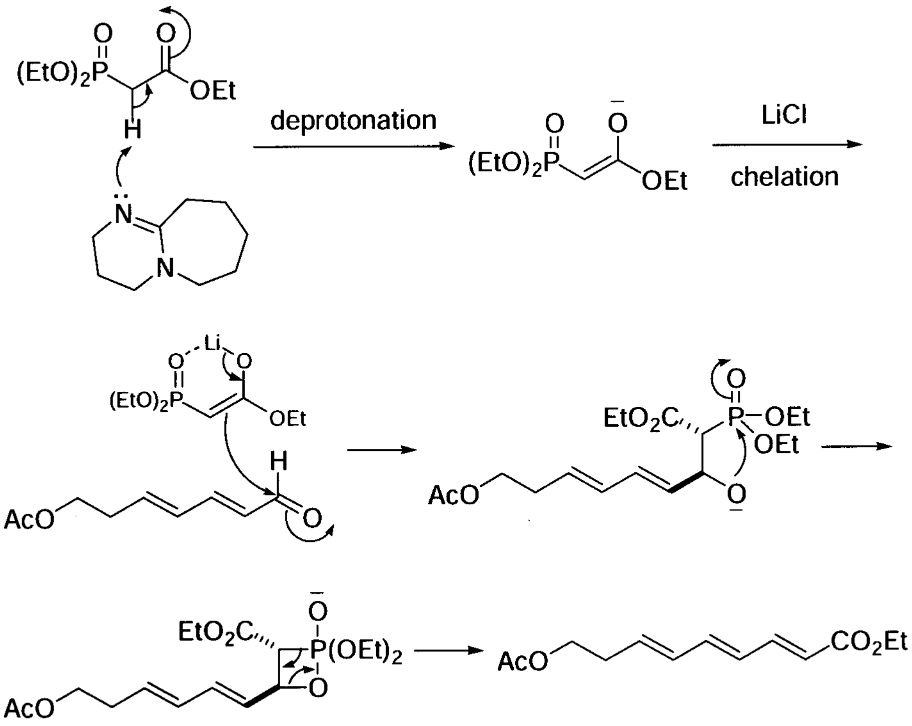
Applicable to base-sensitive aldehydes and phosphonates for the Horner–Wadsworth–Emmons reaction



α-keto or α-alkoxycarbonyl phosphonate required



1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)



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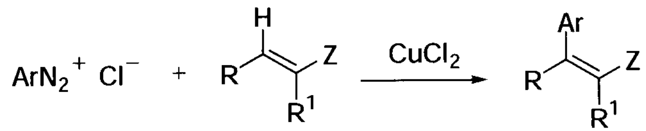
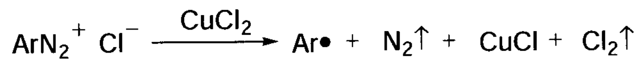
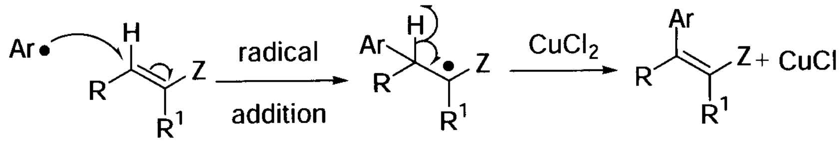
Meerwein arylation

Arylation of unsaturated compounds by diazonium salts.



Z = Ar, C=C, C=O, CN, H





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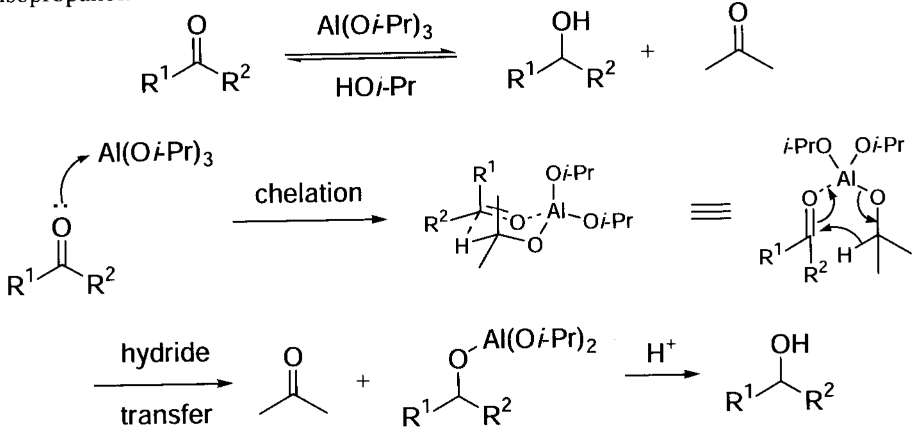
Meerwein–Ponndorf–Verley reduction

Reduction of ketones to the corresponding alcohols using Al(O*i*-Pr)$_3$ in isopropanol.



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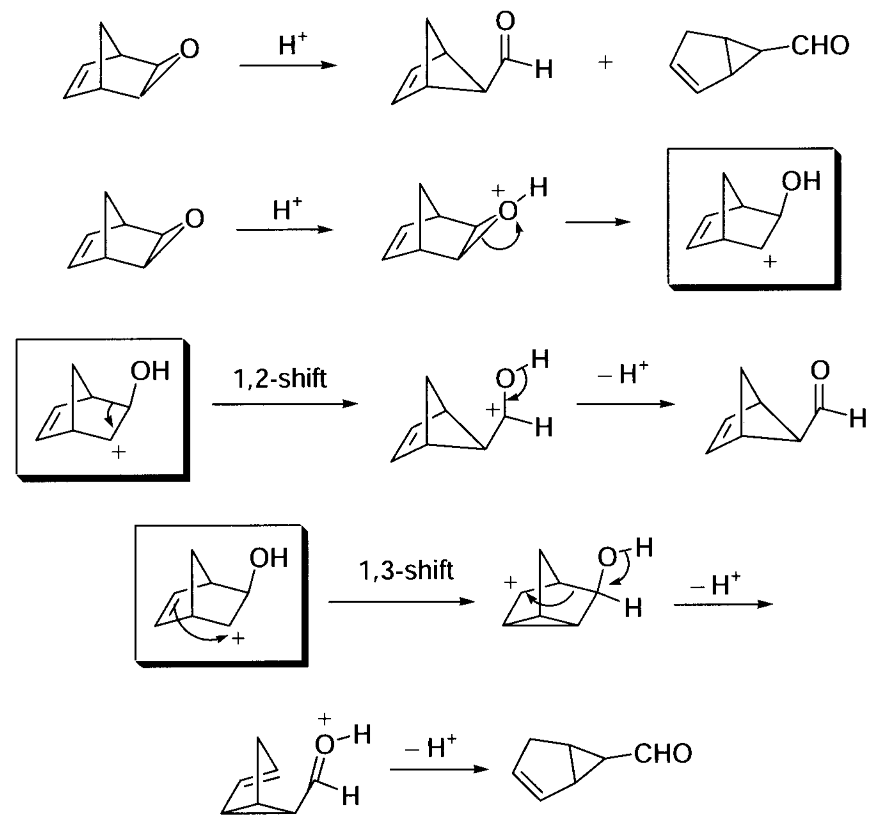
Meinwald rearrangement



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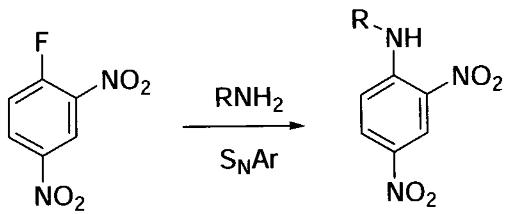
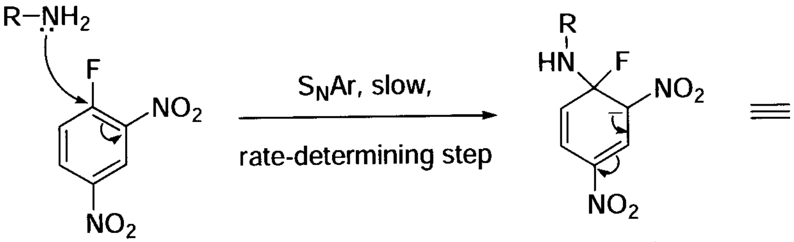
Meisenheimer complex

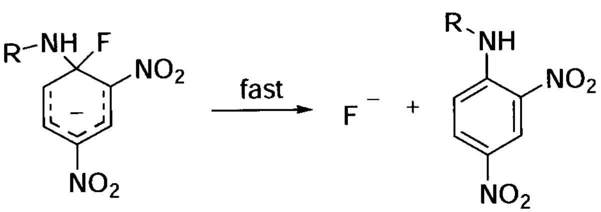
Also known as Meisenheimer–Jackson salt, the stable intermediate for certain S_NAr reactions.



Sanger's reagent



ipso attack *ipso* substitution



Meisenheimer complex (**Meisenheimer–Jackson salt**)

The reaction using Sanger's reagent is faster than using the corresponding chloro-, bromo-, and iodo-dinitrobenzene — the fluoro-Meisenheimer complex is the most stabilized because F is the most electron-withdrawing. The reaction rate does not depend upon the leaving ability of the leaving group.

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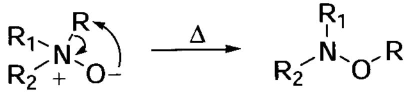
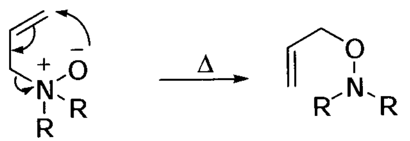
Meisenheimer rearrangement

[1,2]-sigmatropic rearrangement:



[2,3]-sigmatropic rearrangement:



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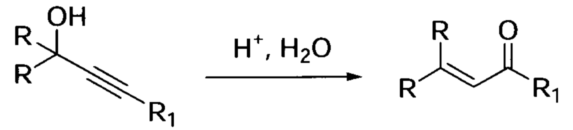
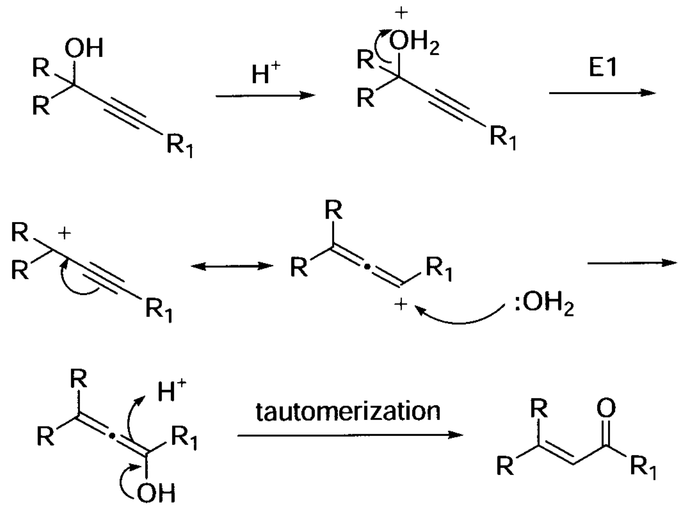
Meyer–Schuster rearrangement

The isomerization of secondary and tertiary α-acetylenic alcohols to α,β-unsaturated carbonyl groups *via* a 1,3-shift. When the acetylenic group is terminal, the products are aldehydes, whereas the internal acetylenes give ketones.
Cf. Rupe rearrangement





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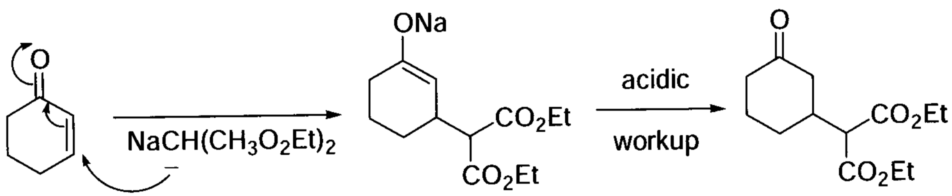
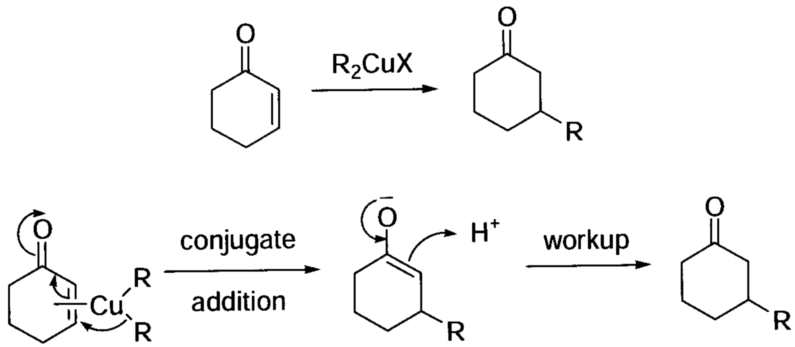
Michael addition

Conjugate addition of a carbon-nucleophile to an α,β-unsaturated system.

e.g.:



e.g.:



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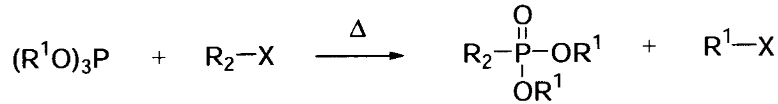
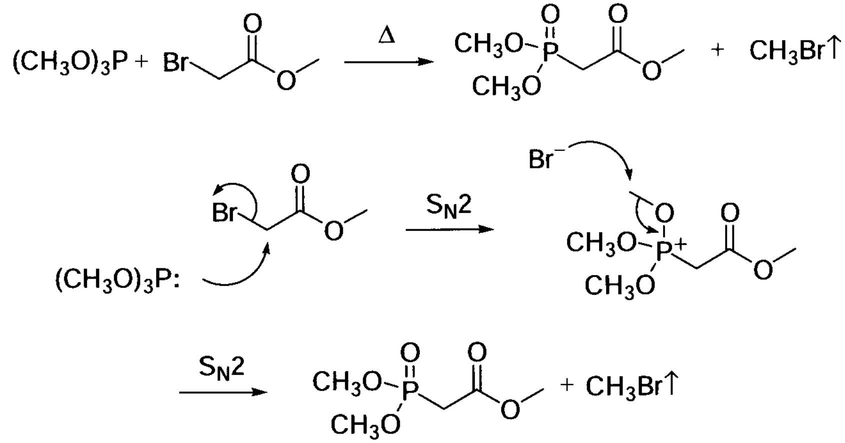
Michaelis–Arbuzov phosphonate synthesis

General scheme:



R^1 = alkyl, *etc.*; R_2 = alkyl, acyl, *etc.*; X = Cl, Br, I

e.g.:



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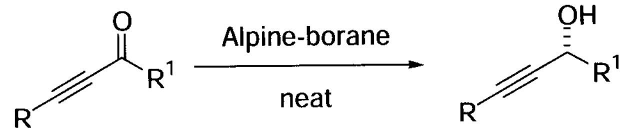
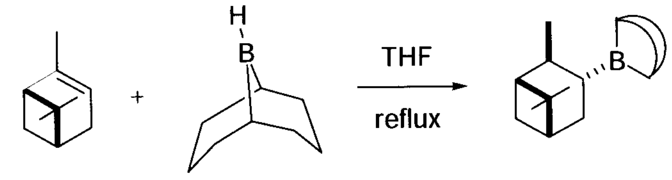
Midland reduction

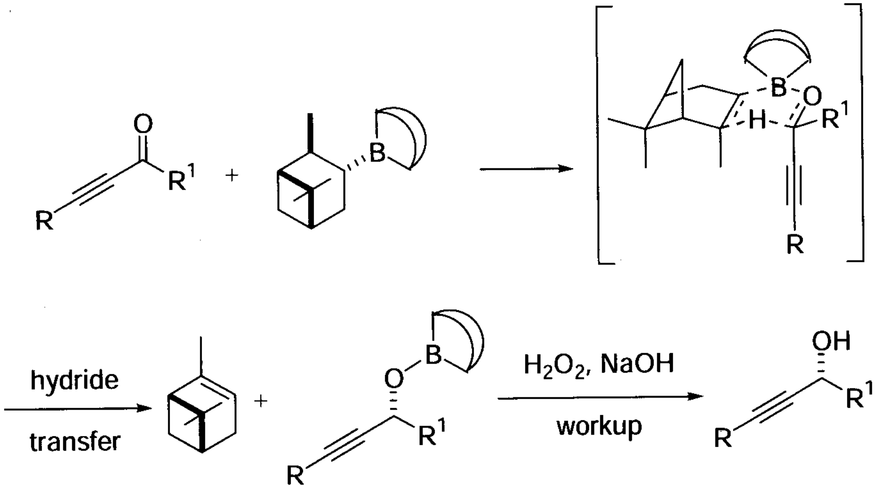
Asymmetric reduction of ketones using Alpine-borane®.
Alpine-borane® = *B*-isopinocampheyl-9-borabicyclo[3.3.1]nonane.





(1*R*)-(+)-α-pinene 9-BBN (*R*)-Alpine-borane

9-BBN = 9-borabicyclo[3.3.1]nonane



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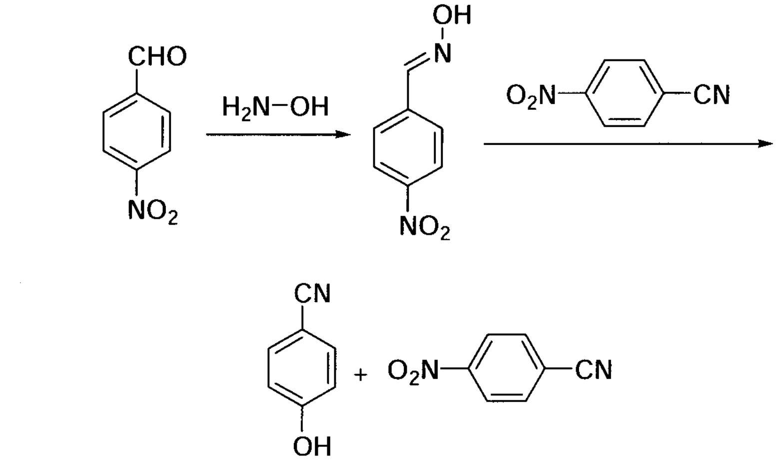
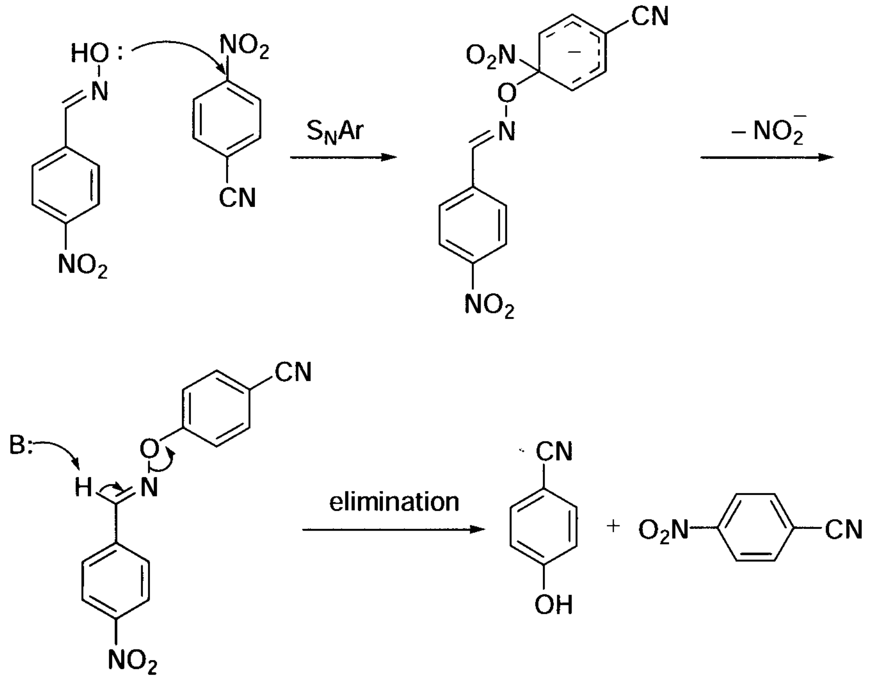
Miller–Snyder aryl cyanide synthesis

Benzonitriles from *p*-nitrobenzaldehyde and *p*-nitrobenzonitrile.





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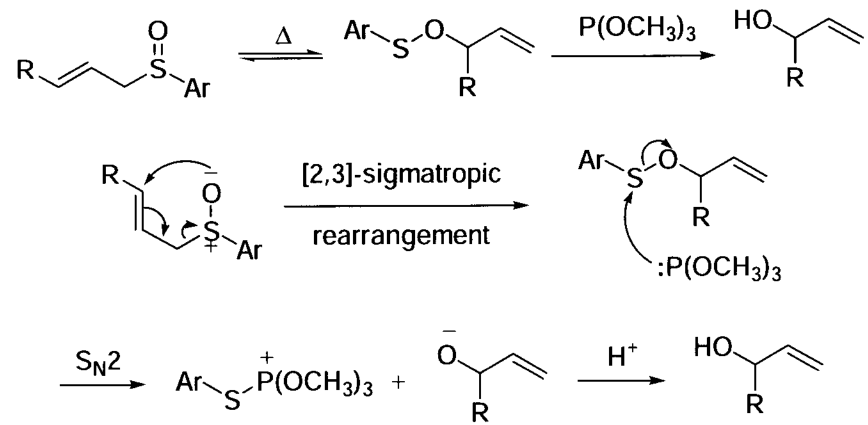
Mislow–Evans rearrangement



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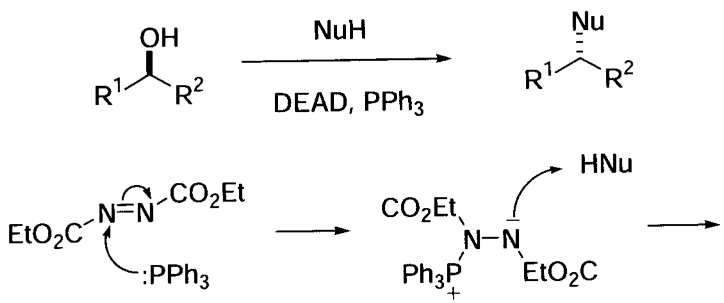
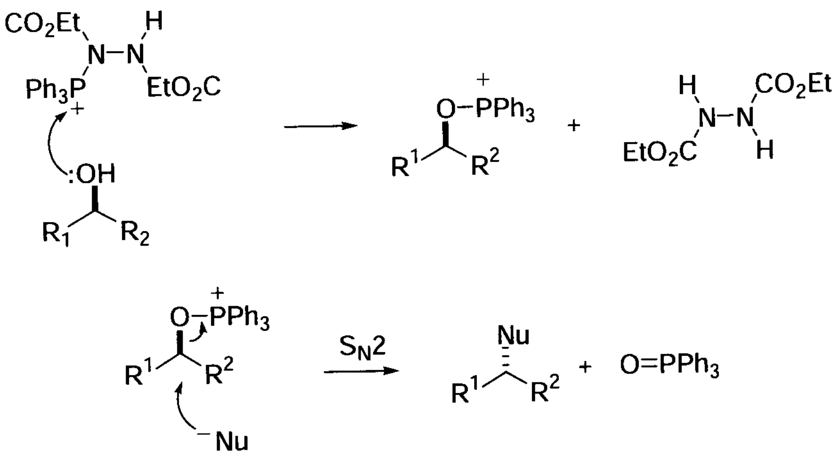
Mitsunobu reaction



DEAD, diethyl azodicarboxylate



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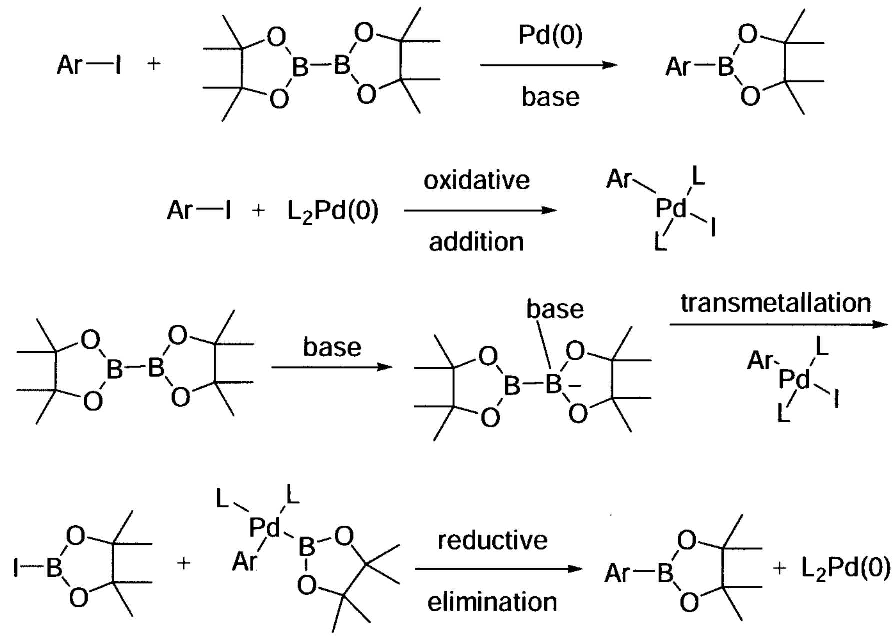
Miyaura boration reaction



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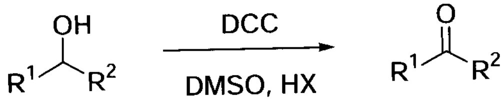
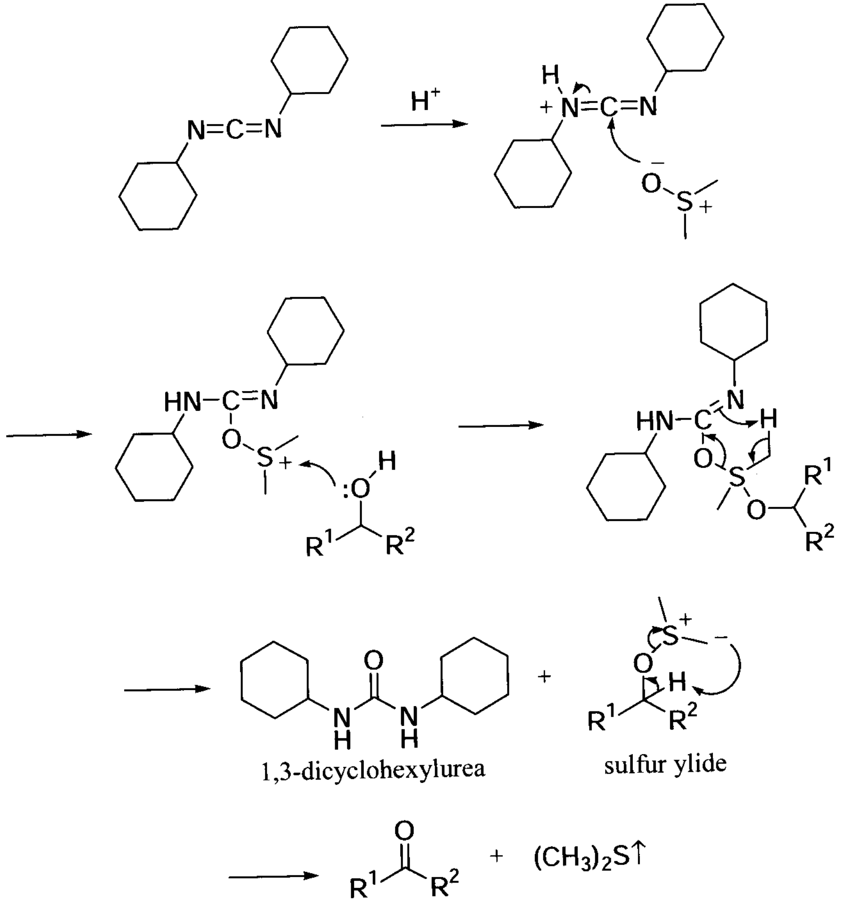
Moffatt oxidation



DCC, 1,3-dicyclohexylcarbodiimide



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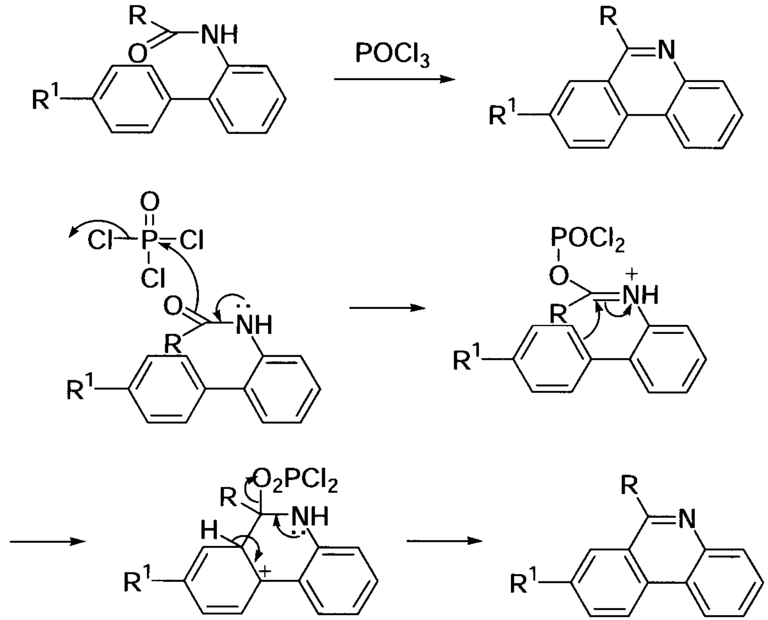
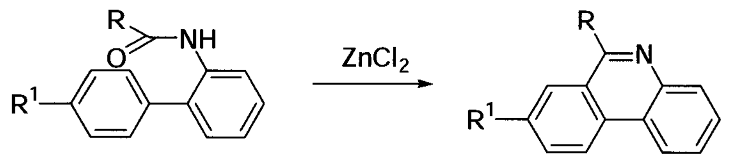
Morgan–Walls reaction (Pictet–Hubert reaction)

Morgan–Walls reaction



Pictet–Hubert reaction



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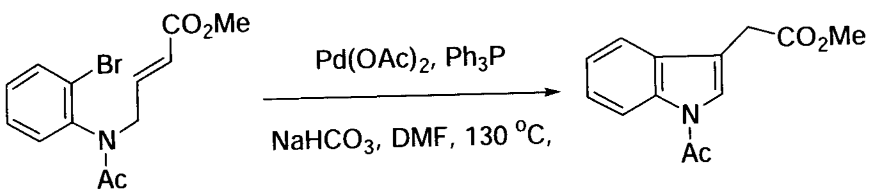
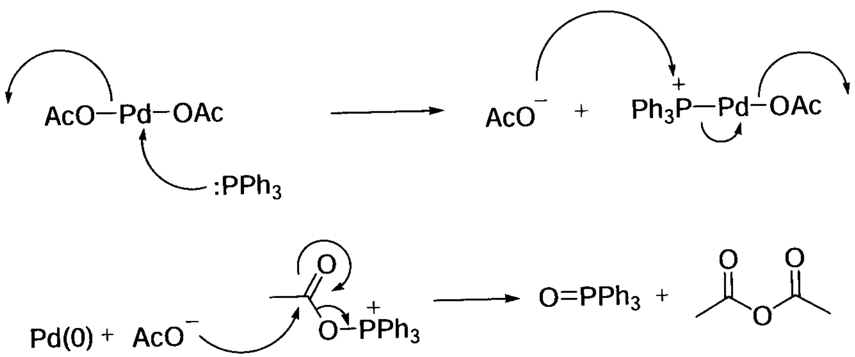
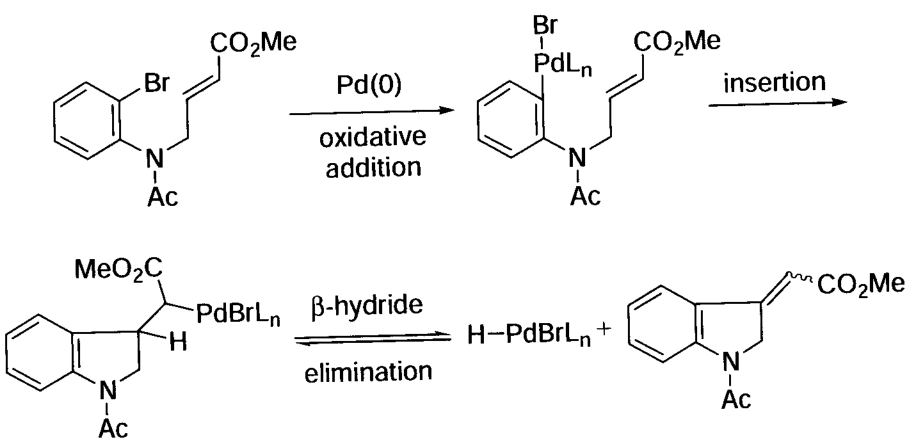
Mori–Ban indole synthesis

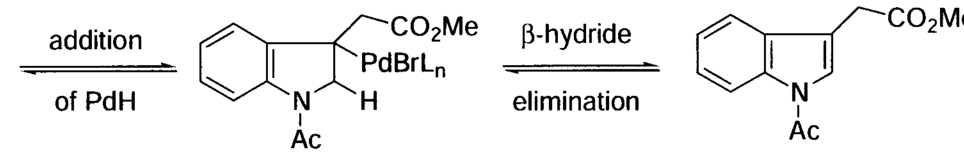


Reduction of $Pd(OAc)_2$ to Pd(0):



Mori–Ban indole synthesis:





Regeneration of Pd(0):

$$H{-}PdBrL_n + NaHCO_3 \longrightarrow Pd(0) + NaBr + H_2O + CO_2\uparrow$$

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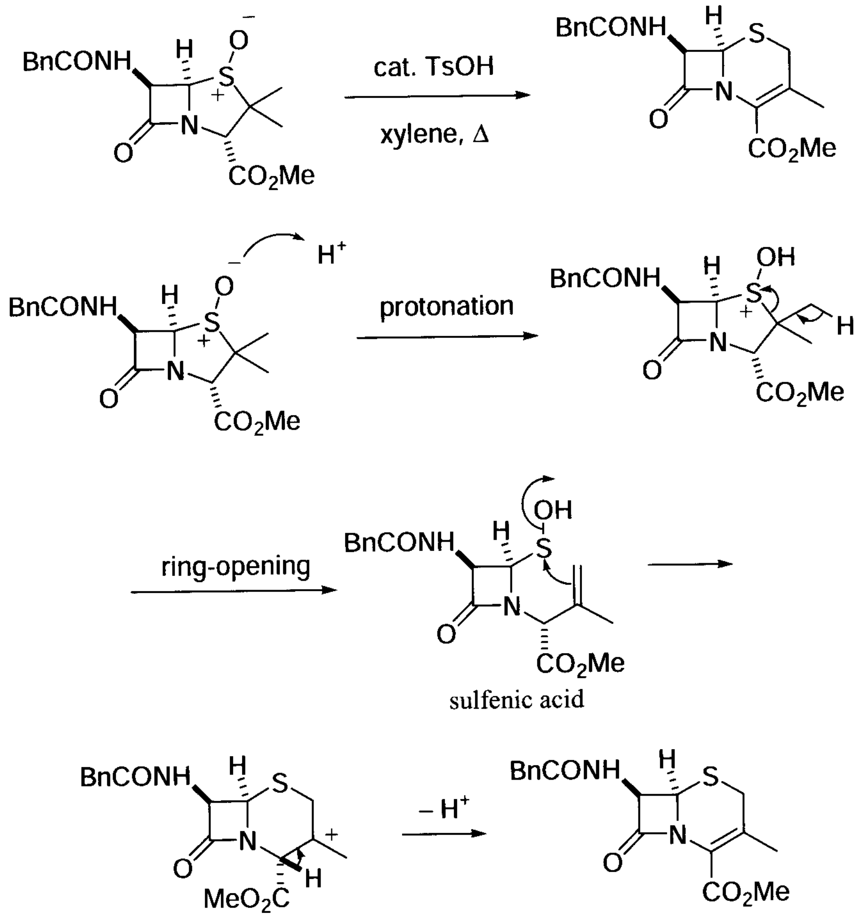
Morin rearrangement

Acid-catalyzed conversion of penicillin sulfoxides to cephalosporins. The rearrangement seems to be general for a variety of other heterocyclic sulfoxides as well.



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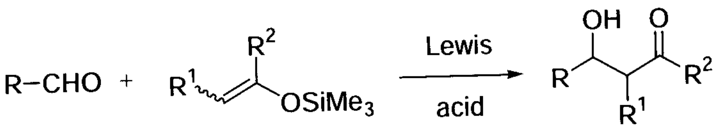
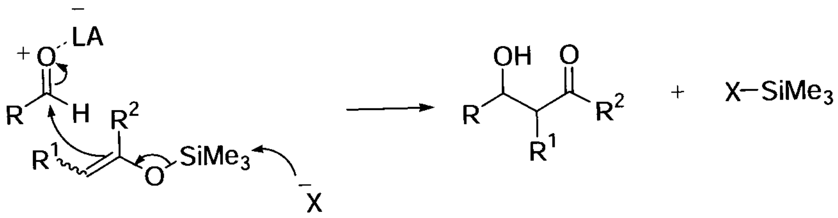
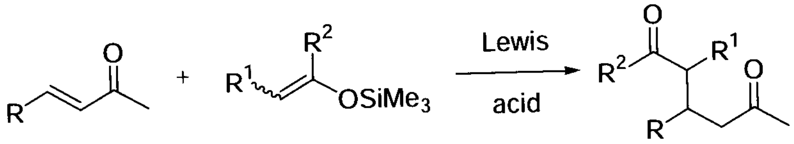
Mukaiyama aldol reaction





Mukaiyama Michael addition



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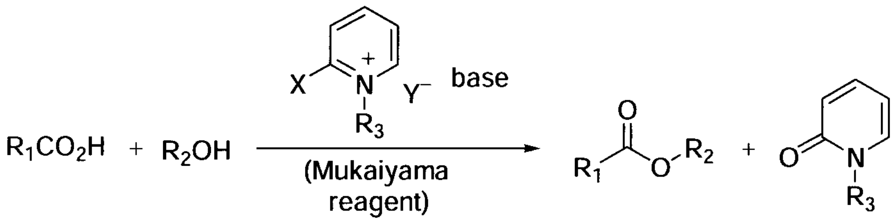
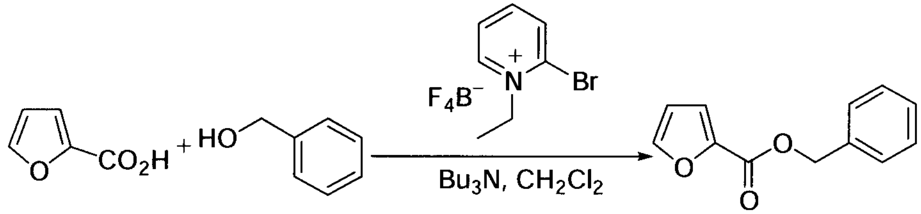
Mukaiyama esterification

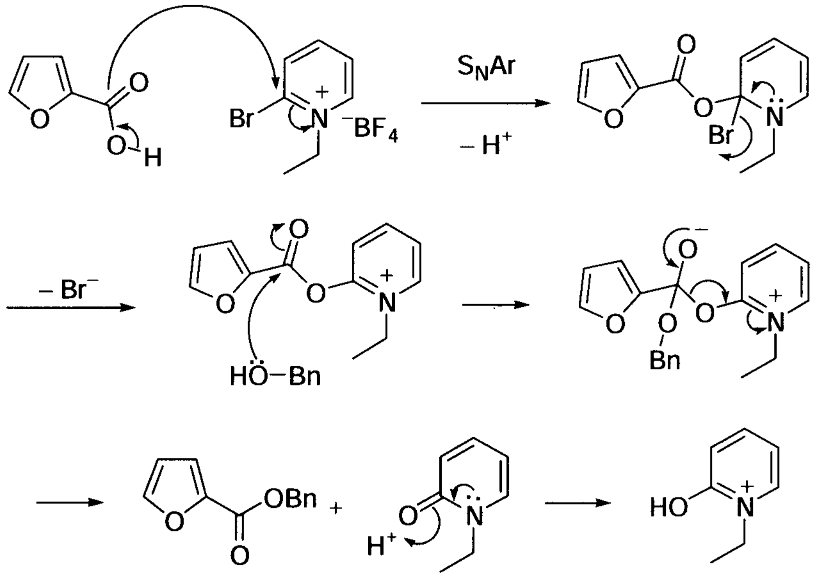
General scheme:



X = F, Cl, Br

e.g.





Amide formation using the Mukaiyama reagent follows a similar mechanistic pathway [4].

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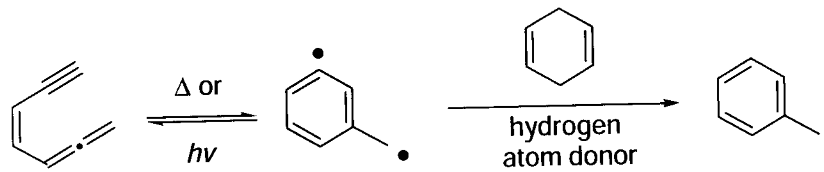
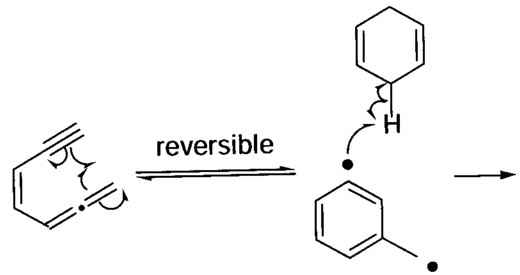
Myers–Saito cyclization

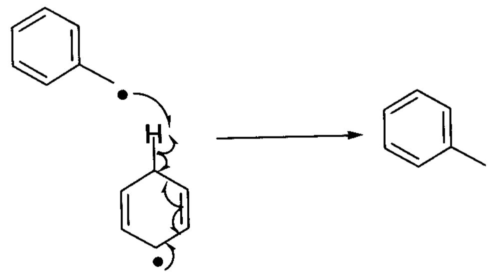
Sometimes known as "Schmittel" cyclization, *Cf.* Bergman cyclization.





allenyl enyne

diradical



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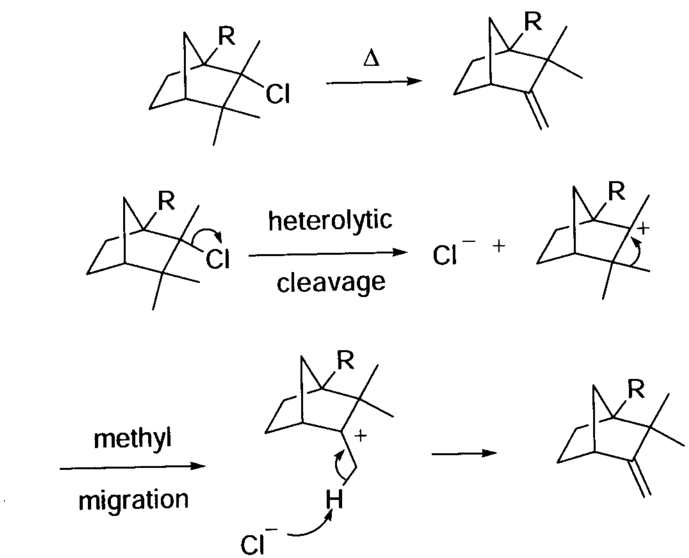
Nametkin rearrangement (Retropinacol rearrangement)



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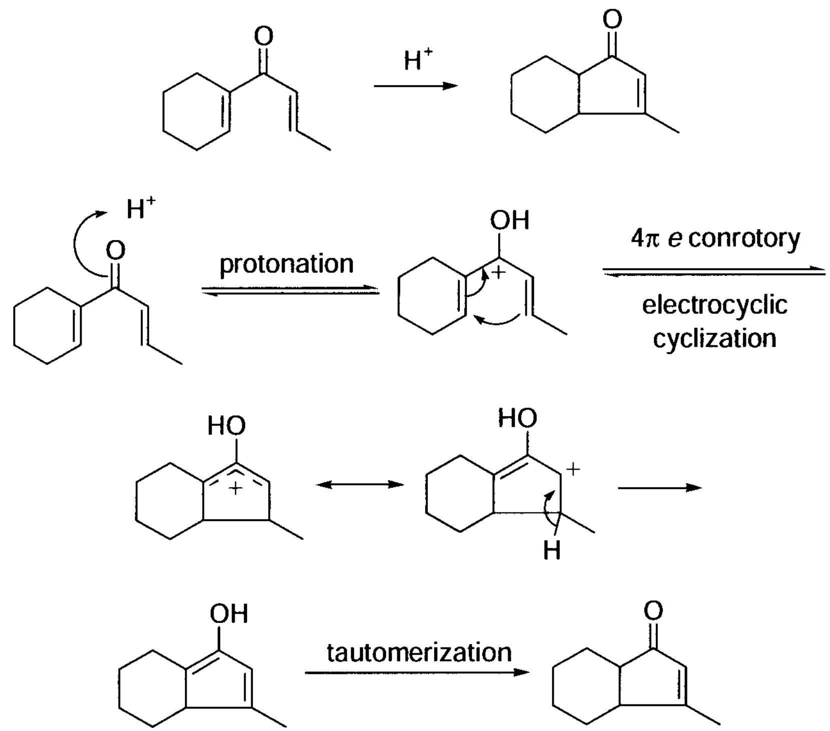
Nazarov cyclization



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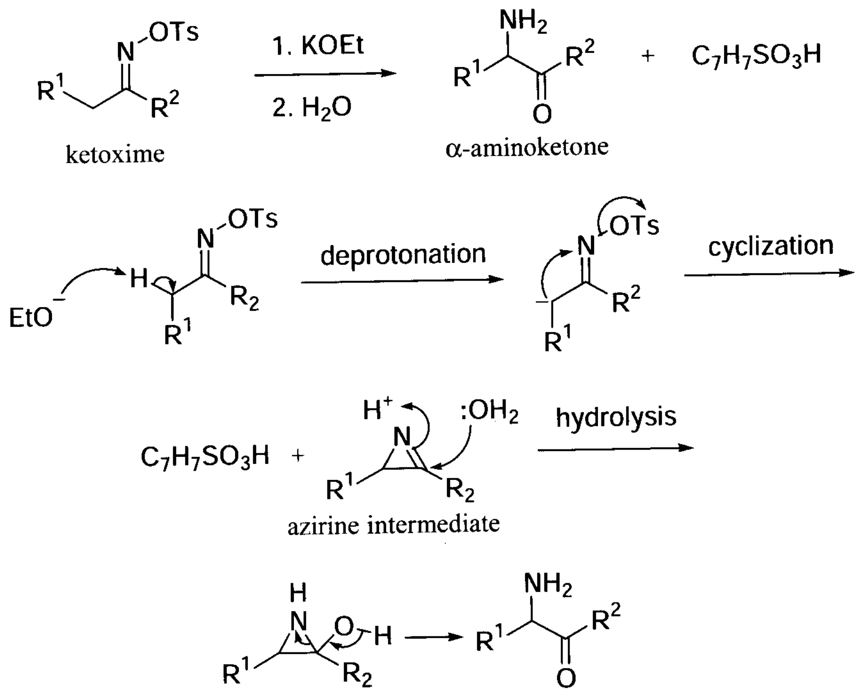
Neber rearrangement



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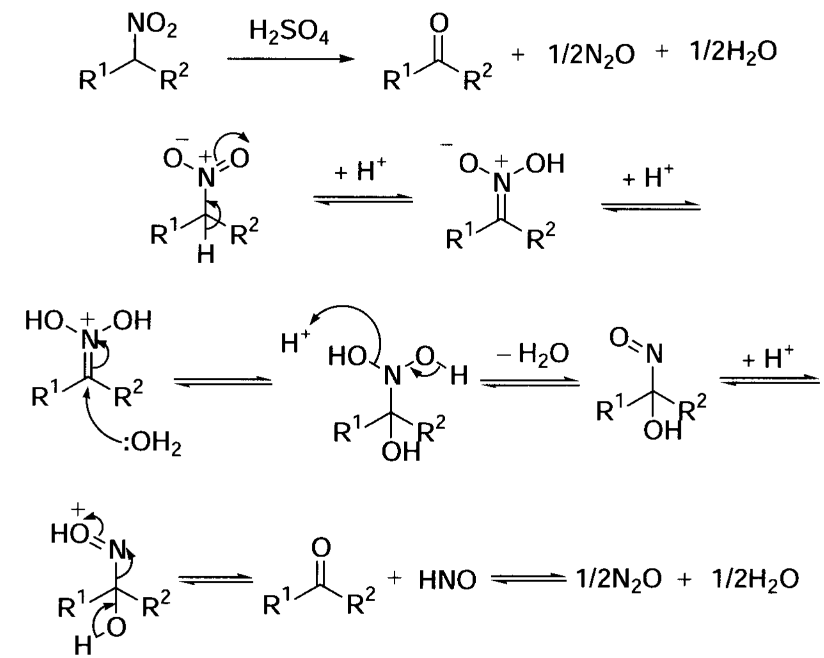
Nef reaction

Treatment of a primary or secondary nitroalkane with an acid, yielding the corresponding carbonyl compound.



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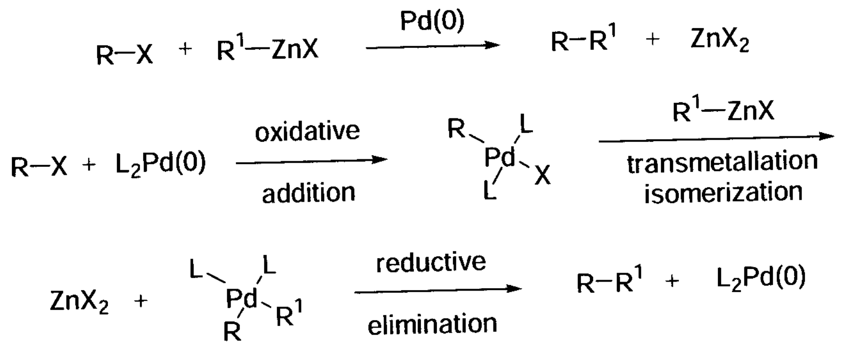
Negishi cross-coupling reaction

Palladium-catalyzed cross-coupling reaction of organozinc reagents with organic halides, triflates, *etc.* For the catalytic cycle, see the Kumada coupling on page 208



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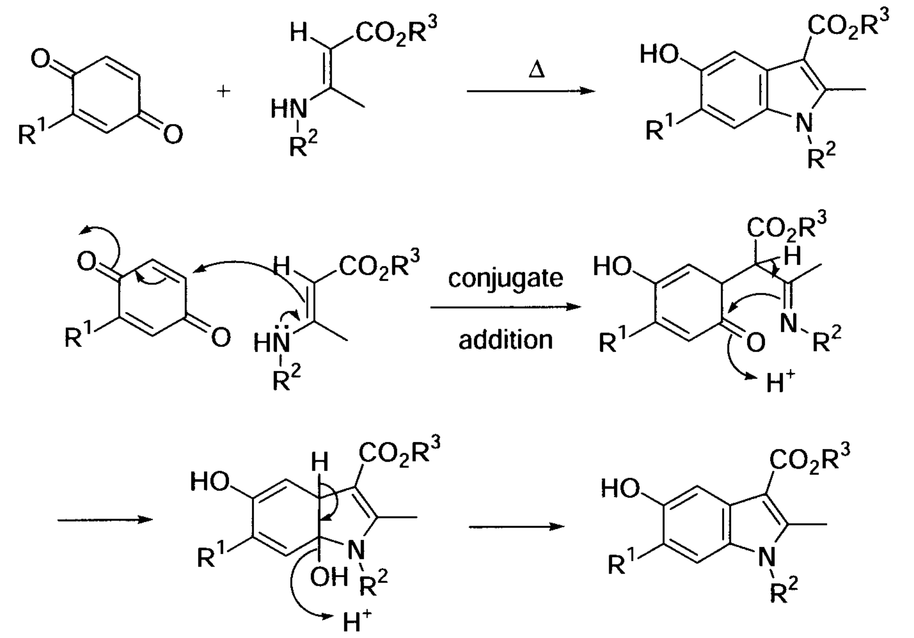
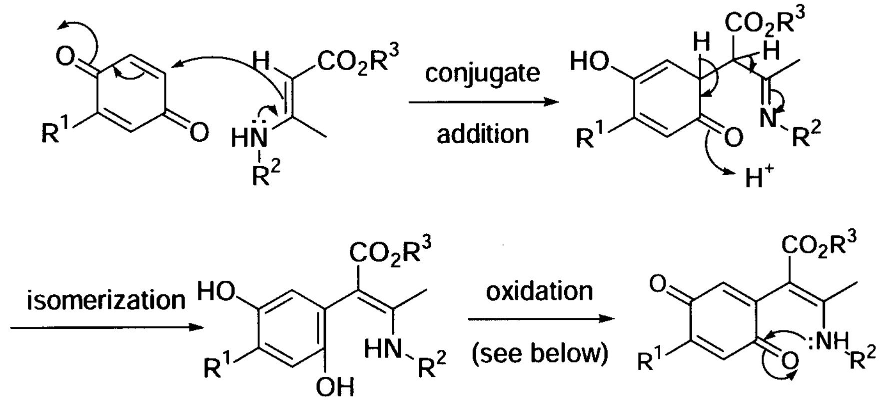
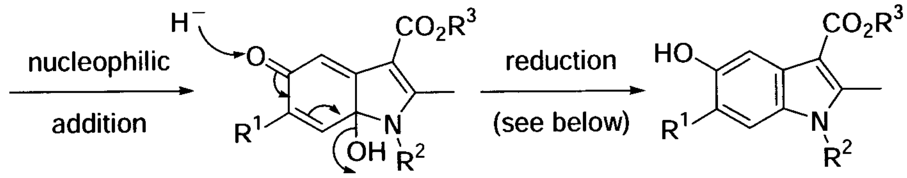
Nenitzescu indole synthesis

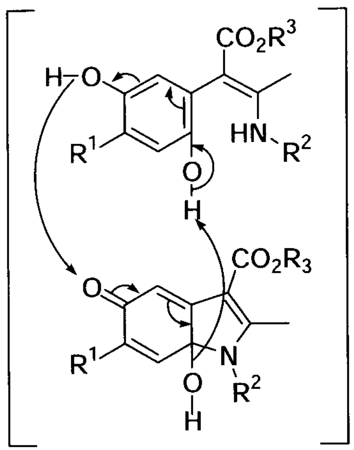


Alternatively:





The internal oxidation-reduction process might involve a bimolecular face-to-face electronic transfer complex (in nitromethane) [3]:



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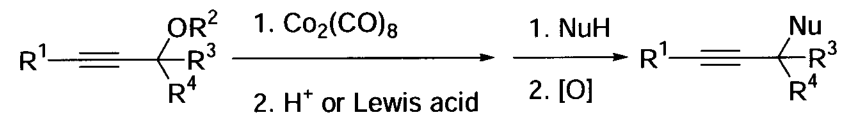
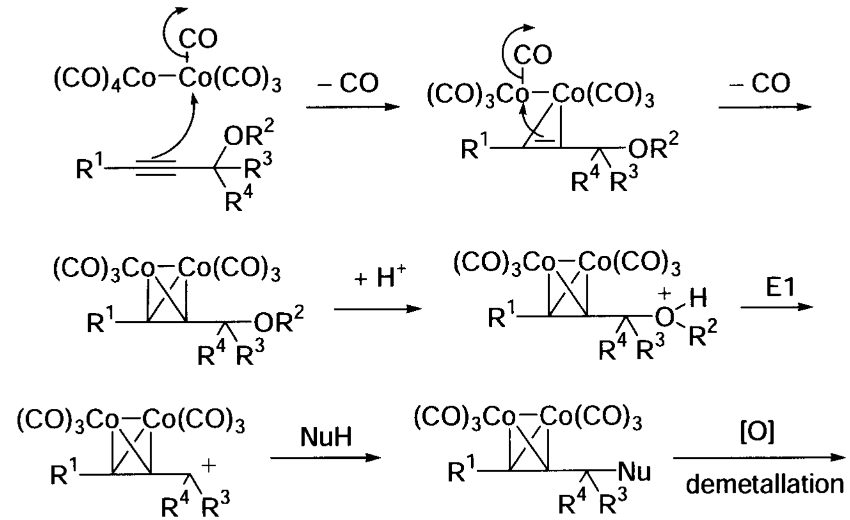
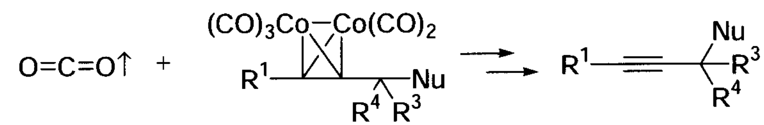
Nicholas reaction





propargyl cation intermediate (stabilized by the hexacarbonyldicobalt complex).



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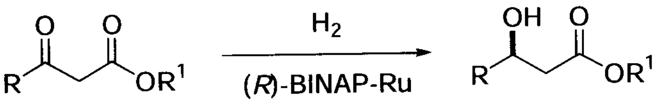
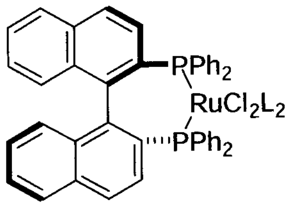
Noyori asymmetric hydrogenation

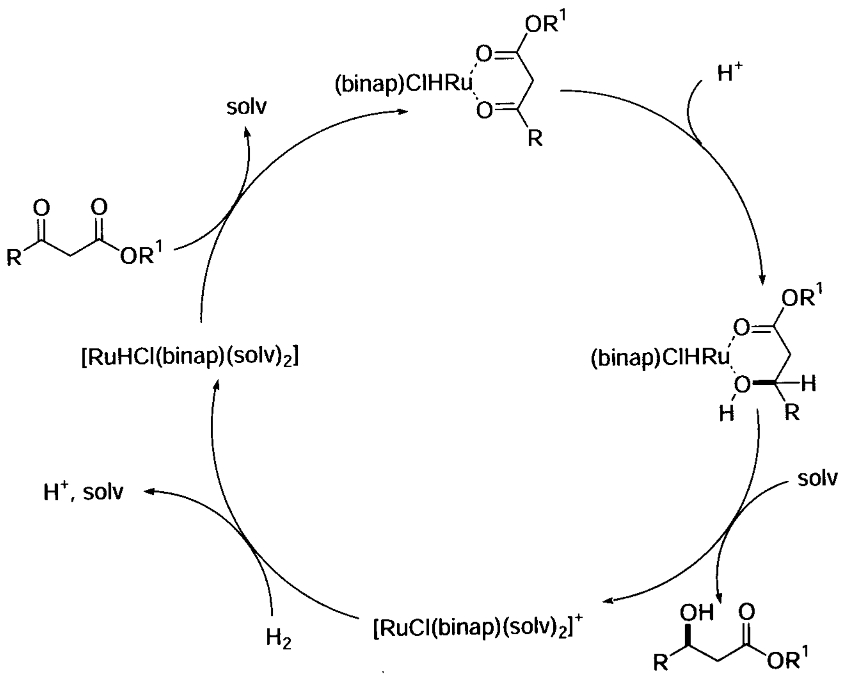


(*R*)-BINAP-Ru =



$$[RuCl_2(binap)(solv)_2] \xrightarrow[-\,HCl]{H_2} [RuHCl(binap)(solv)_2]$$

The catalytic cycle:



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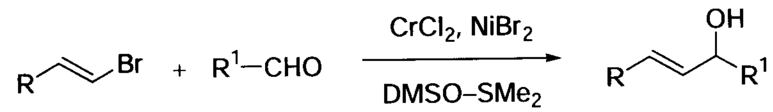
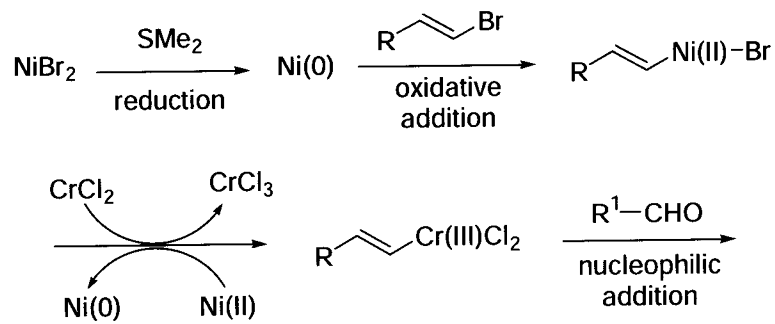
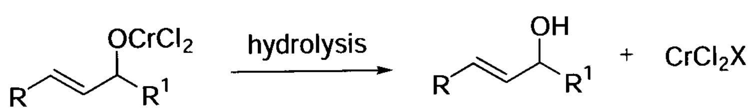
Nozaki–Hiyama–Kishi reaction





Transmetallation and then reduction by Me_2S



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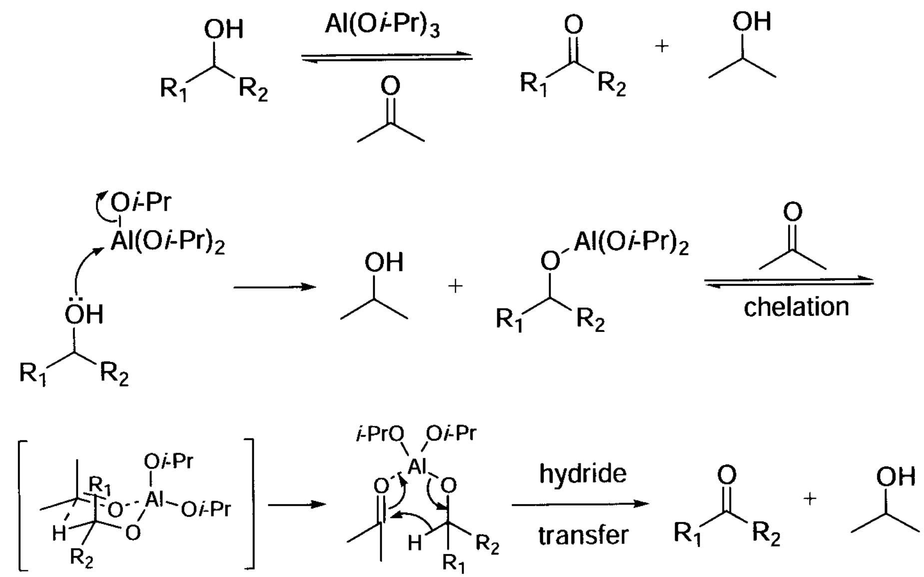
Oppenauer oxidation



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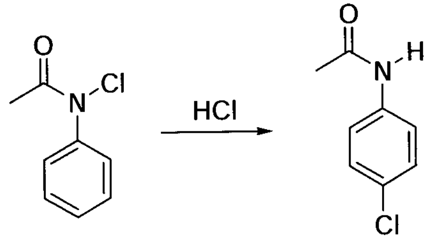
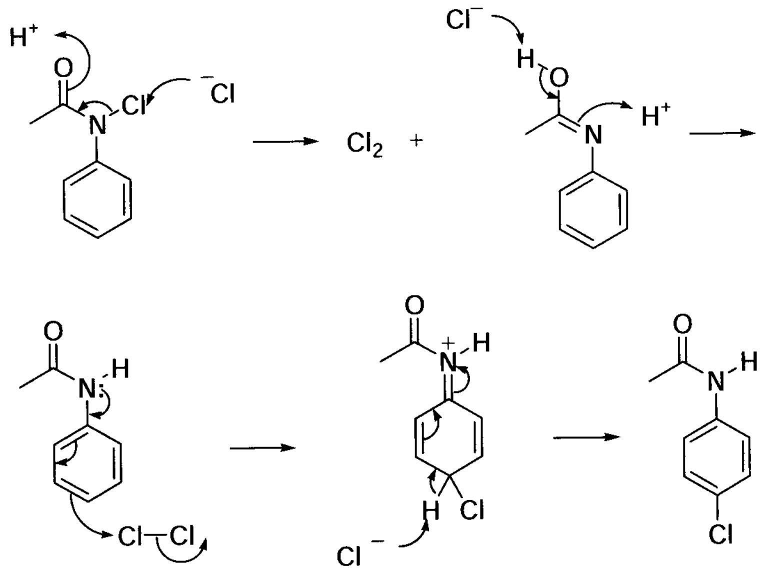
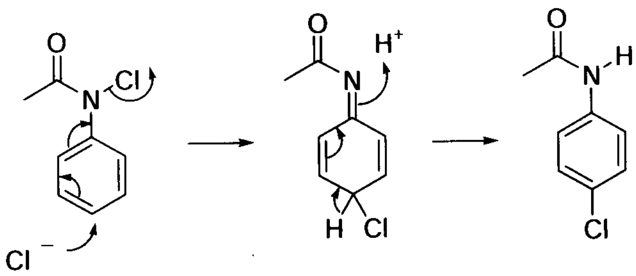
Orton rearrangement

Transformation of *N*-chloroanilides to the corresponding *para*-chloroanilides. *Cf.* Fischer–Hepp rearrangement.





Alternatively:



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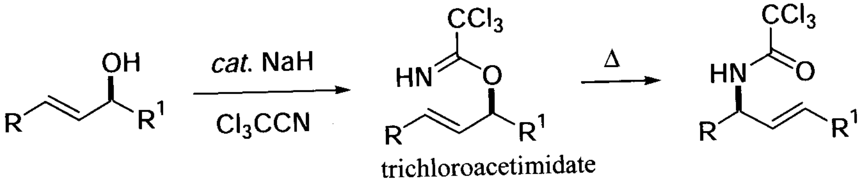
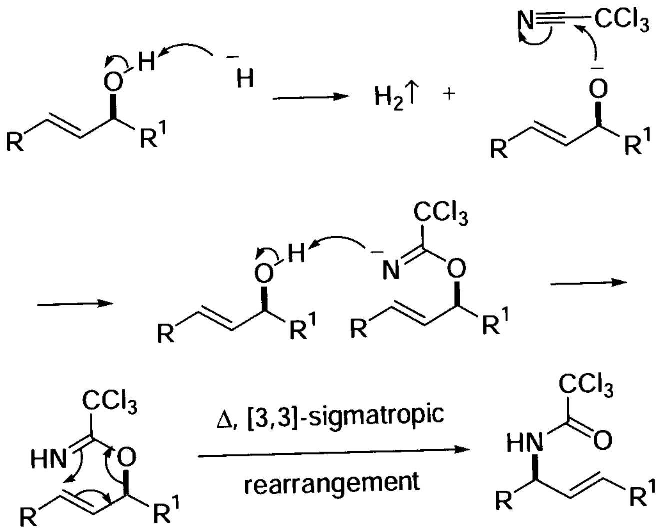
Overman rearrangement

Stereoselective transformation of allylic alcohol to allylic trichloroacetimide *via* trichloroacetimidate intermediate.





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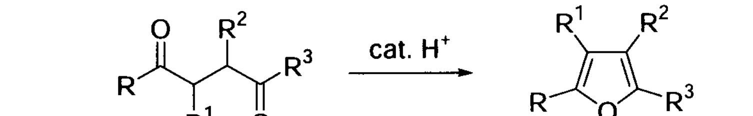
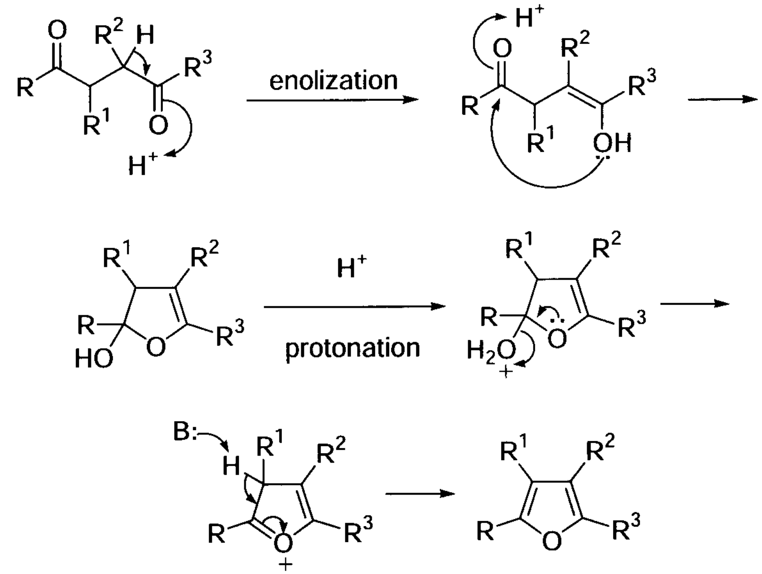
Paal–Knorr furan synthesis





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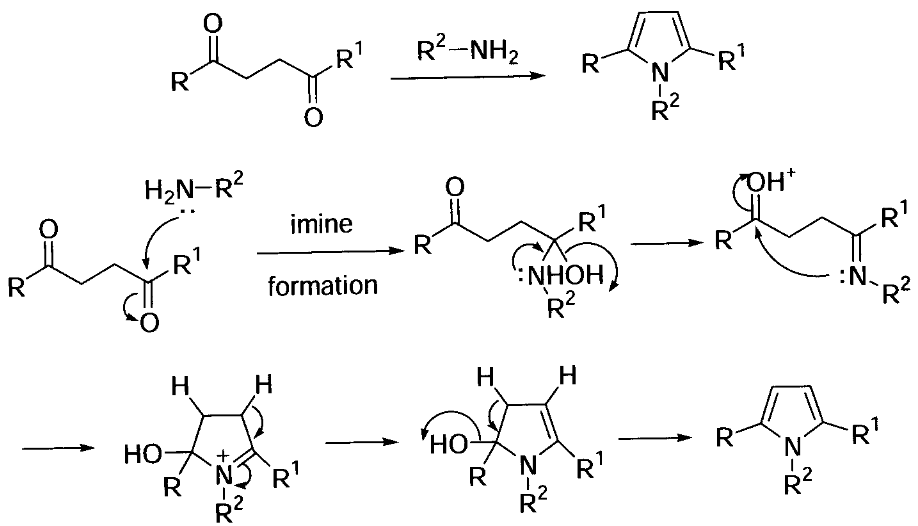
Paal–Knorr pyrrole synthesis



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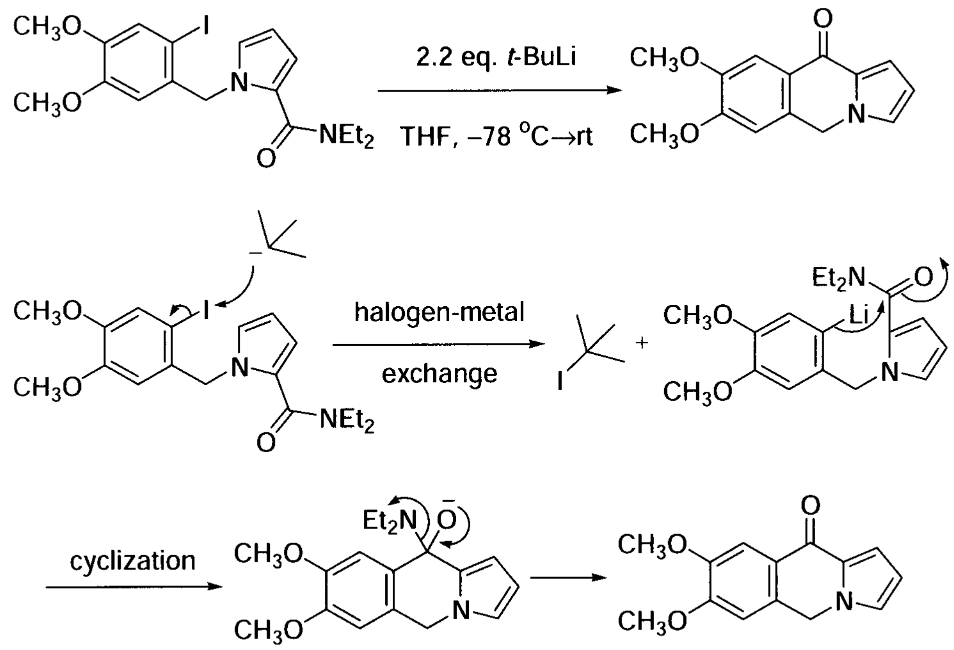
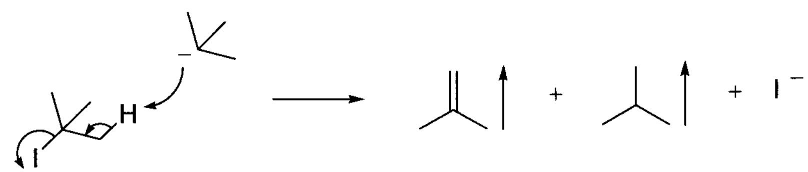
Parham cyclization



The fate of the second equivalent of *t*-BuLi:



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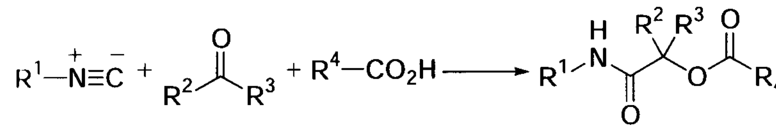
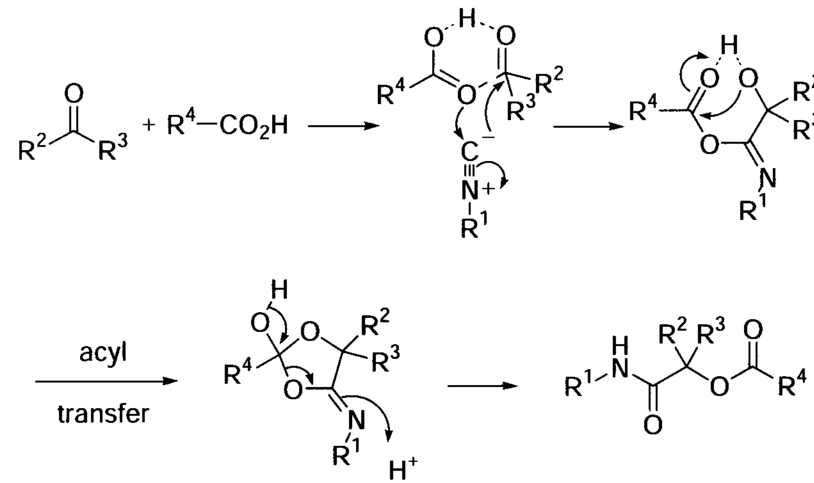
Passerini reaction

Three-component condensation (3CC) of carboxylic acids, *C*-isocyanides, and oxo compounds to afford α-acyloxycarboxamides. *Cf.* Ugi reaction.



isocyanide



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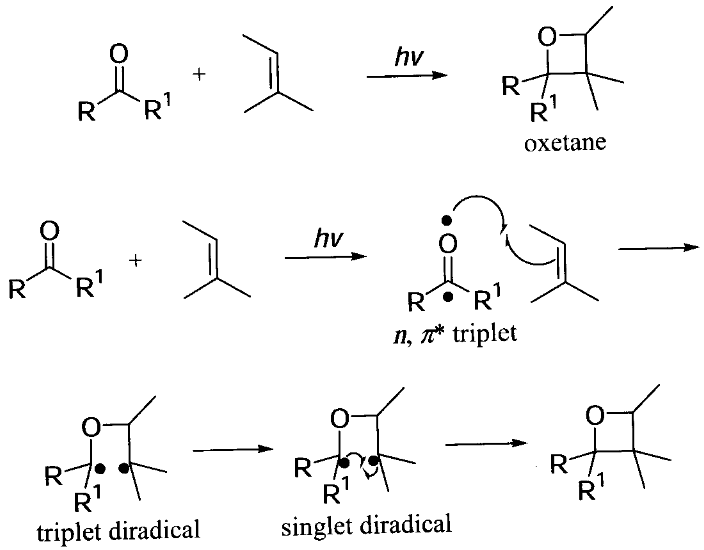
Paterno–Büchi reaction

Photo-induced oxetane formation from a ketone and an olefin.



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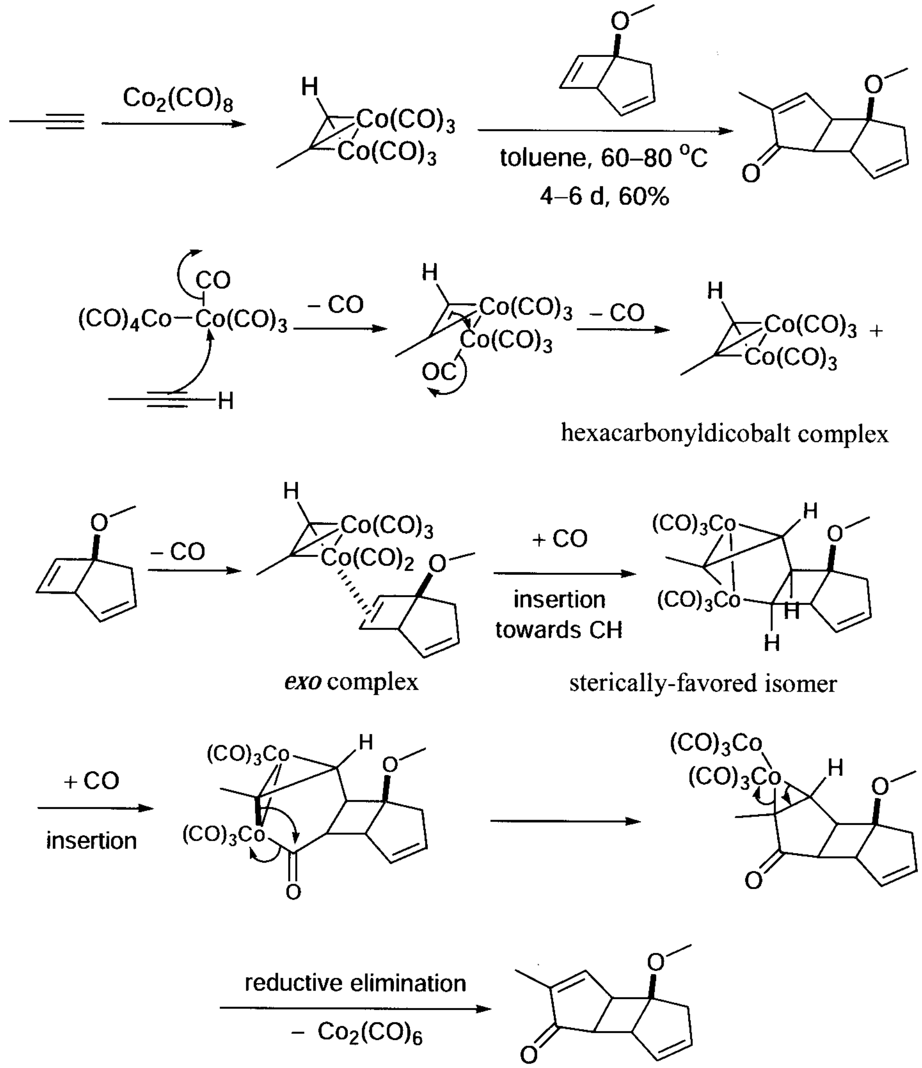
Pauson–Khand cyclopentenone synthesis



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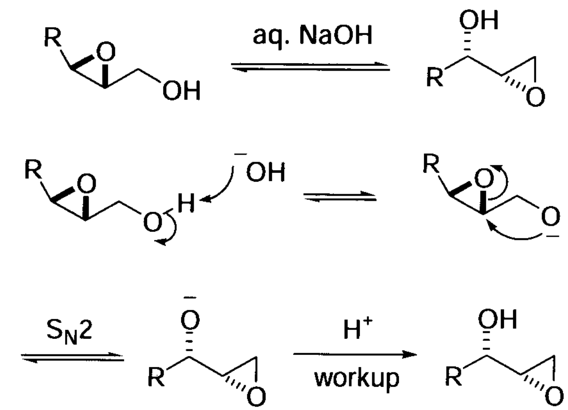
Payne rearrangement



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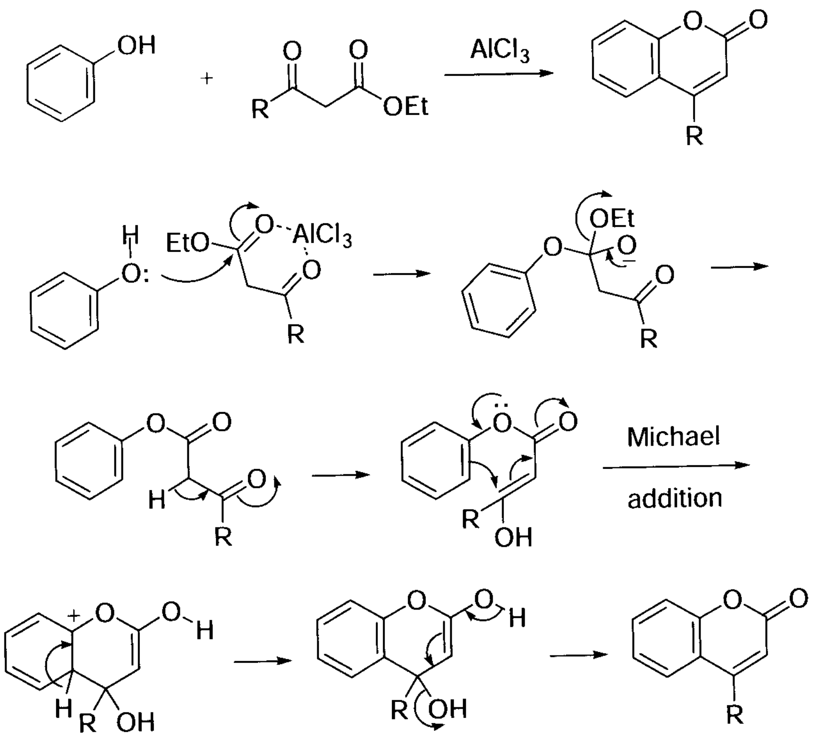
Pechmann condensation (coumarin synthesis)



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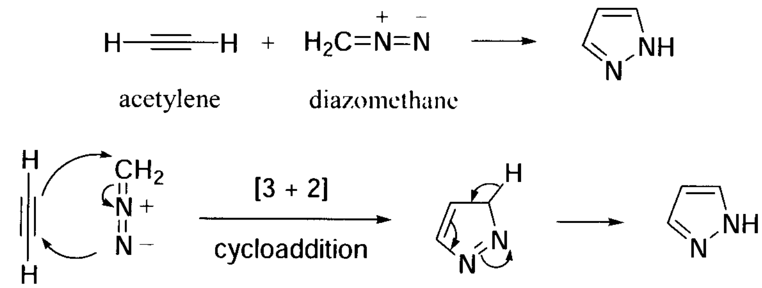
Pechmann pyrazole synthesis



Reference

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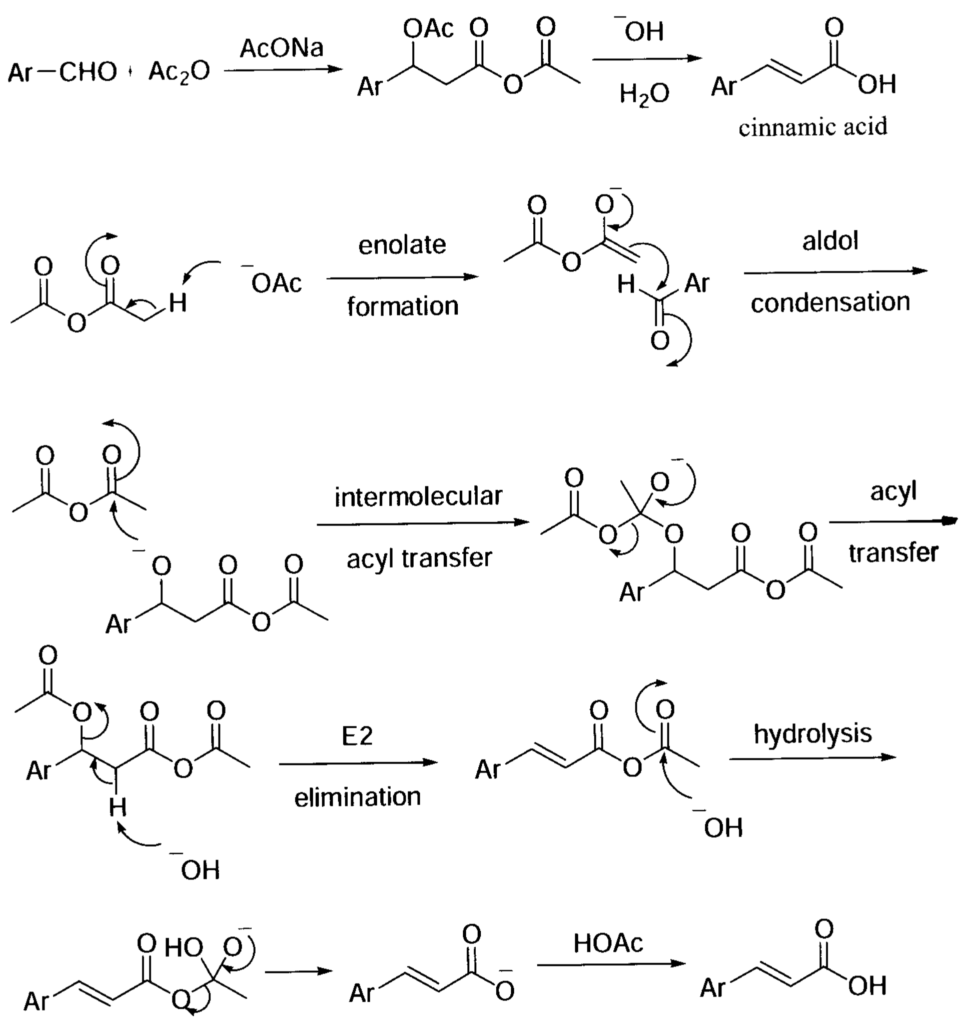
Perkin reaction (cinnamic acid synthesis)



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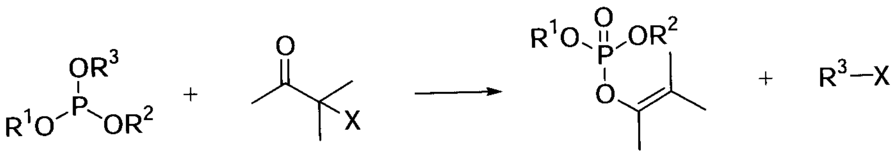
Perkow reaction

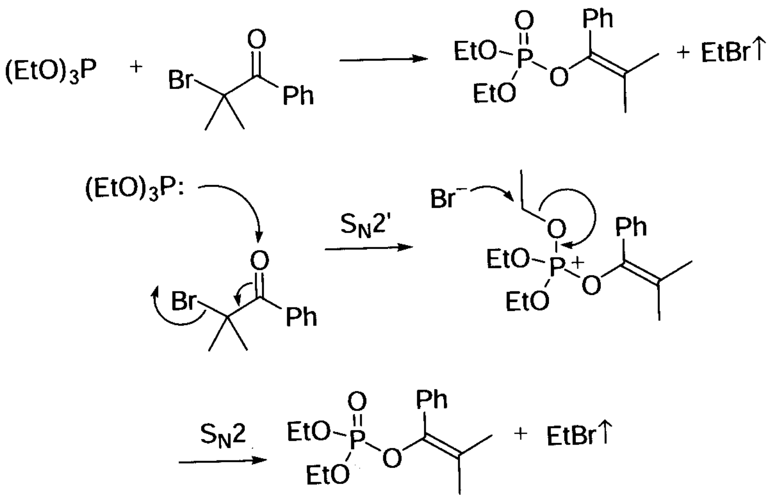
Enol phosphate synthesis from α-halocarbonyls and trialkylphosphites.

General scheme:



X = Cl, Br, I, secondary or tertiary halides are required to prevent the Michaelis–Arbuzov reaction.

e.g.



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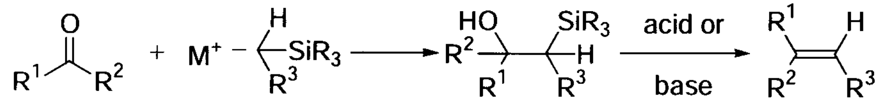
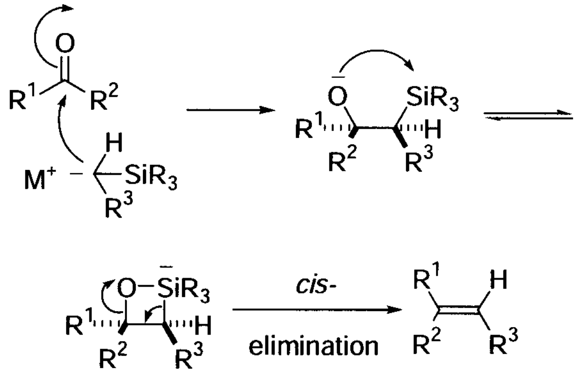
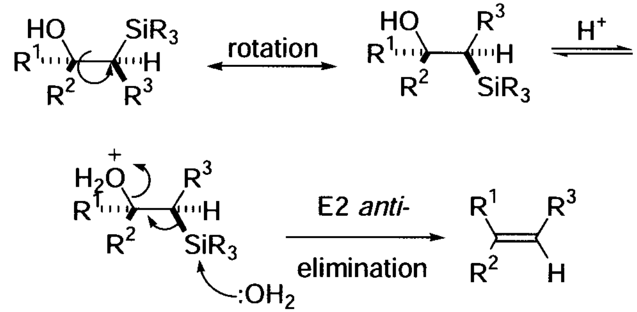
Peterson olefination



Basic conditions:



Acidic conditions:



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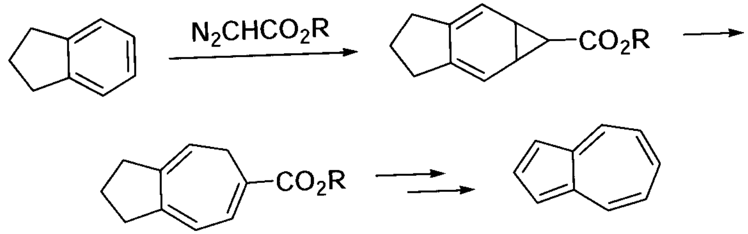
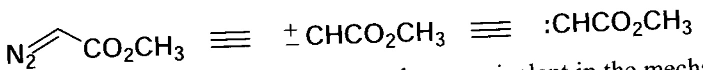
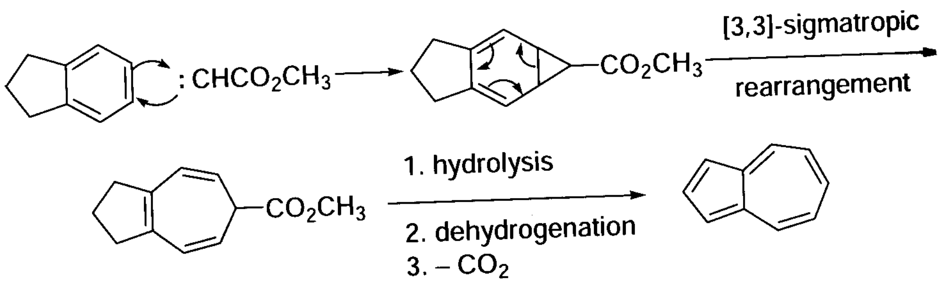
Pfau–Plattner azulene synthesis





The diazo compound is depicted as a carbene equivalent in the mechanism



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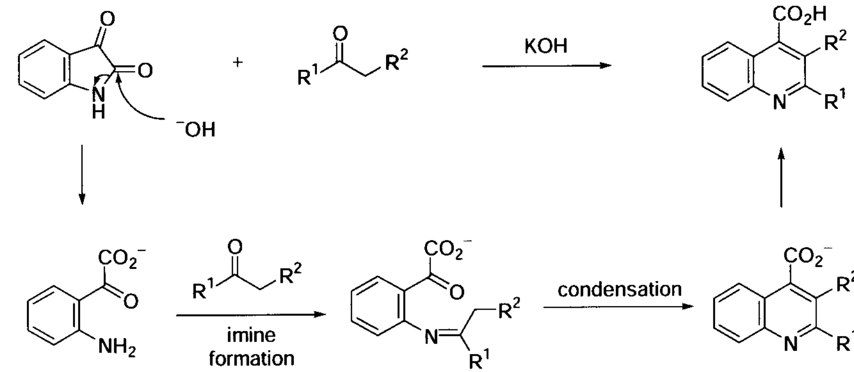
Pfitzinger quinoline synthesis



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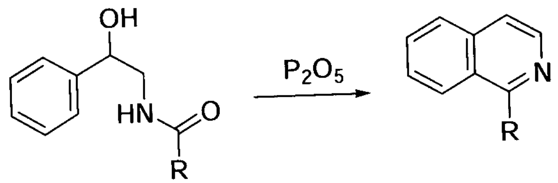
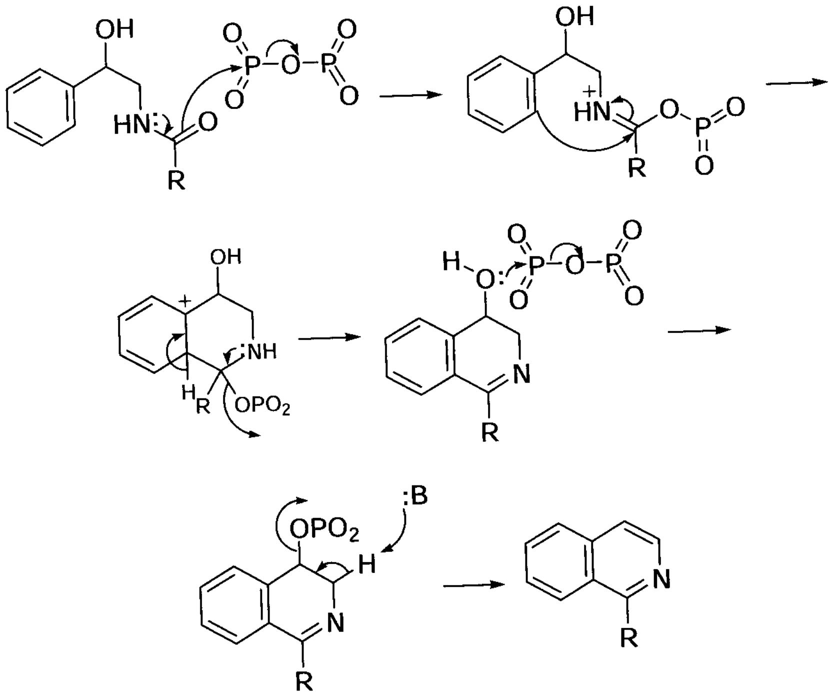
Pictet–Gams isoquinoline synthesis



P_2O_5 actually exists as P_4O_{10}, an adamantane-like structure.



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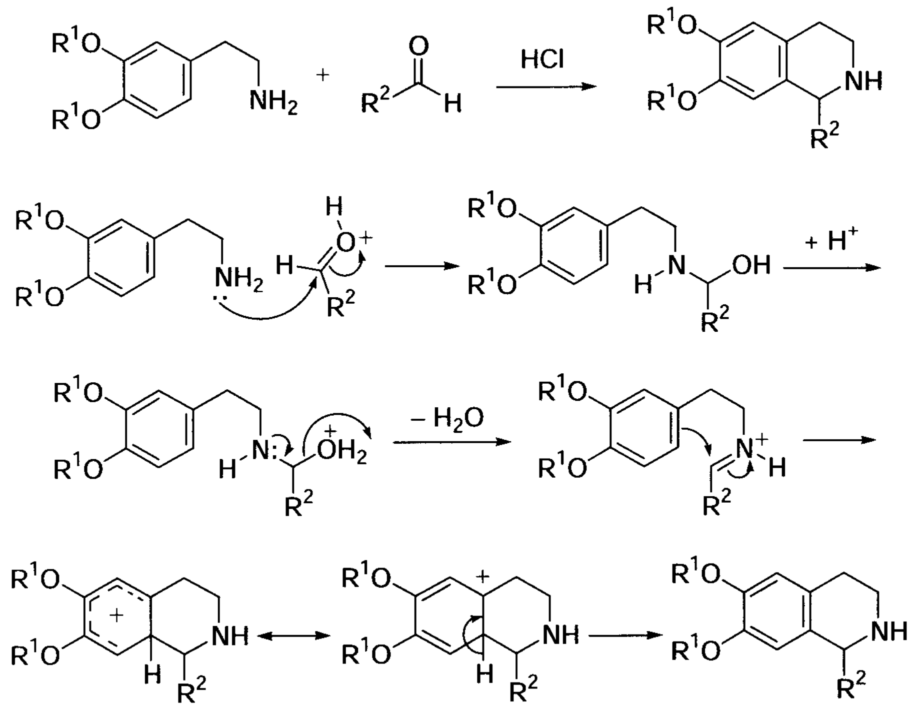
Pictet–Spengler isoquinoline synthesis



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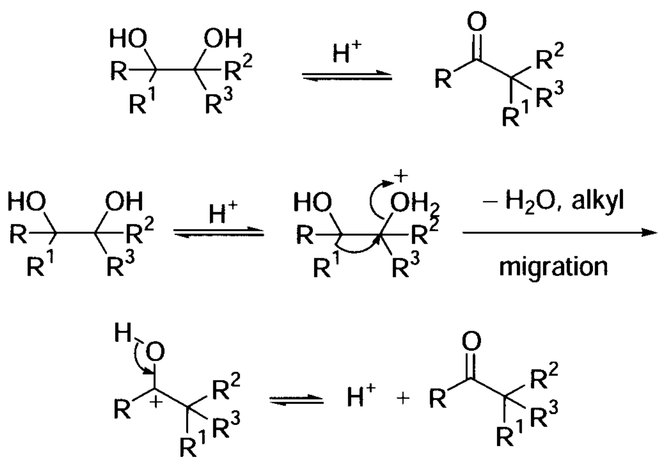
Pinacol rearrangement



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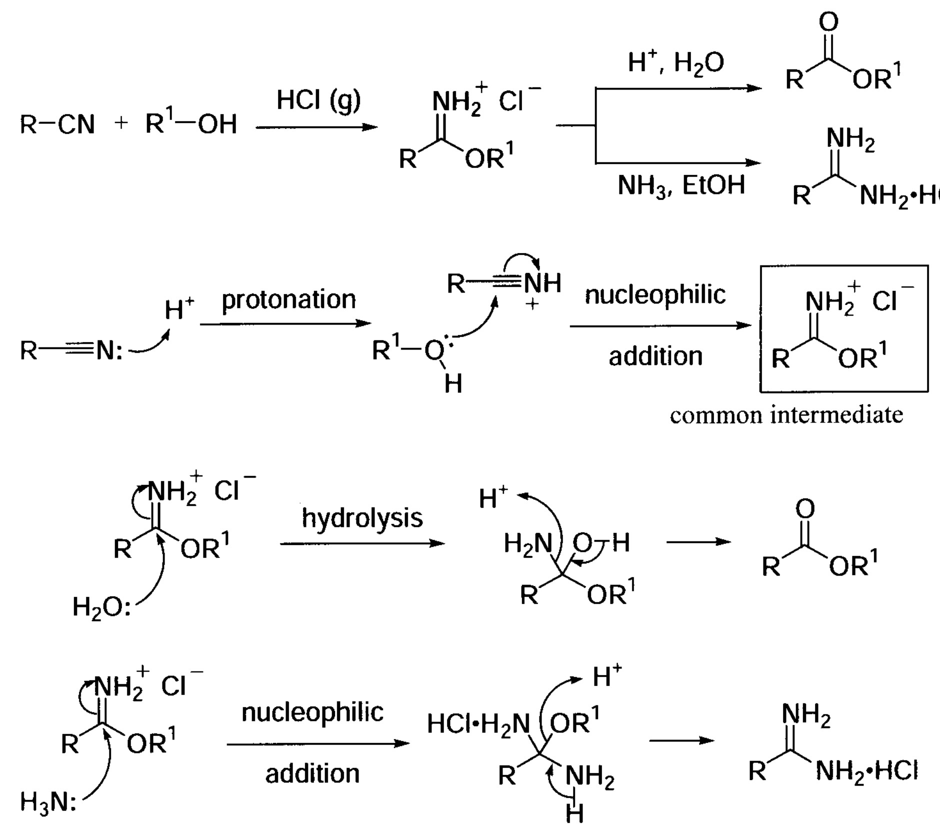
Pinner synthesis

Transformation of a nitrile into an imino ether, which can be converted to either an ester or an amidine.



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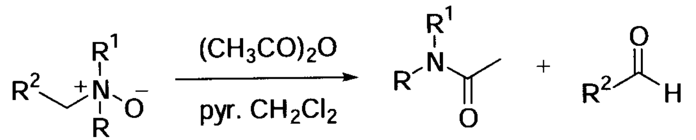
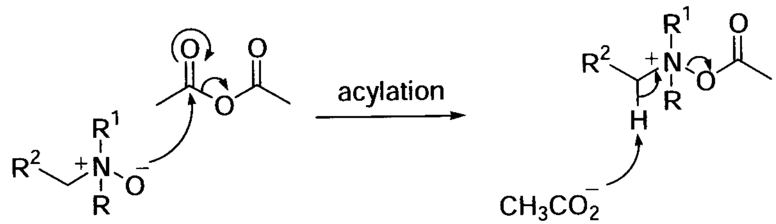
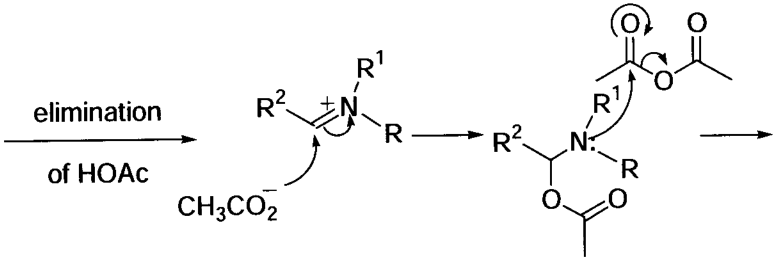
Polonovski reaction

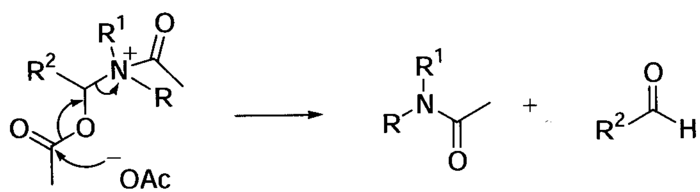
Treatment of a tertiary *N*-oxide with an activating agent such as acetic anhydride, resulting in rearrangement where an *N,N*-disubstituted acetamide and an aldehyde are generated.



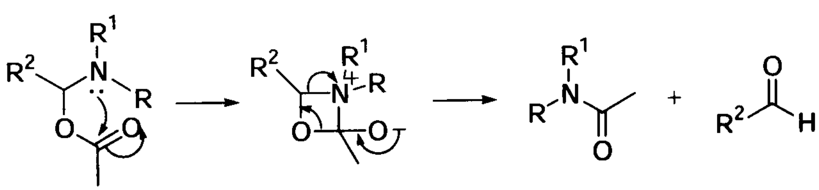




iminium ion



The intramolecular pathway is also possible:



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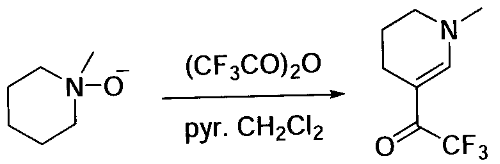
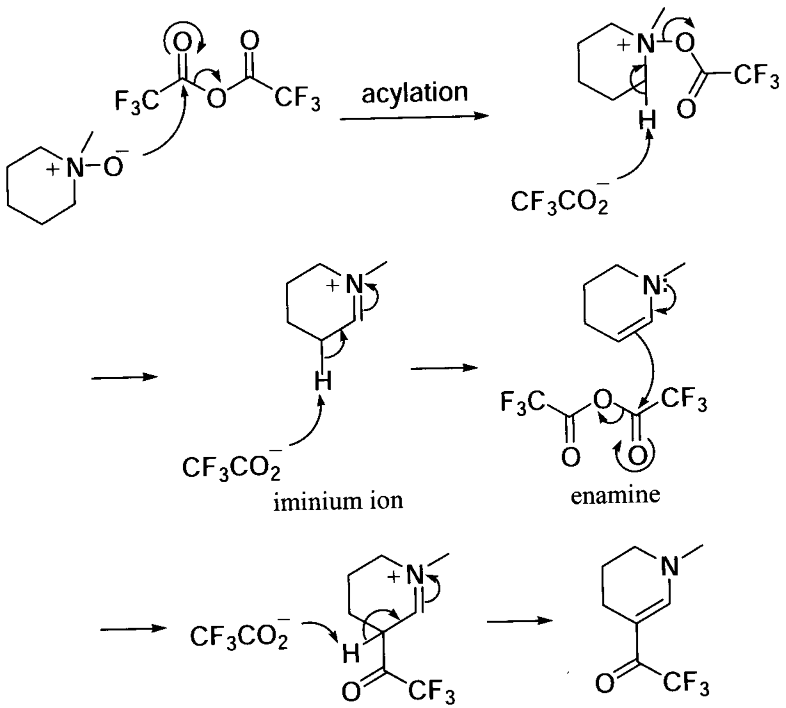
Polonovski–Potier reaction

A modification of the Polonovski reaction where trifluoroacetic anhydride is used in place of acetic anhydride.



tertiary *N*-oxide



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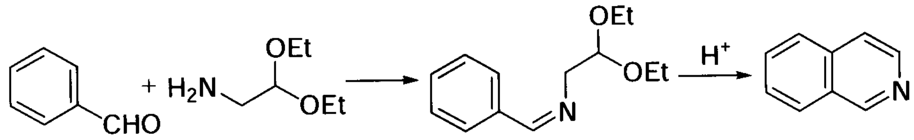
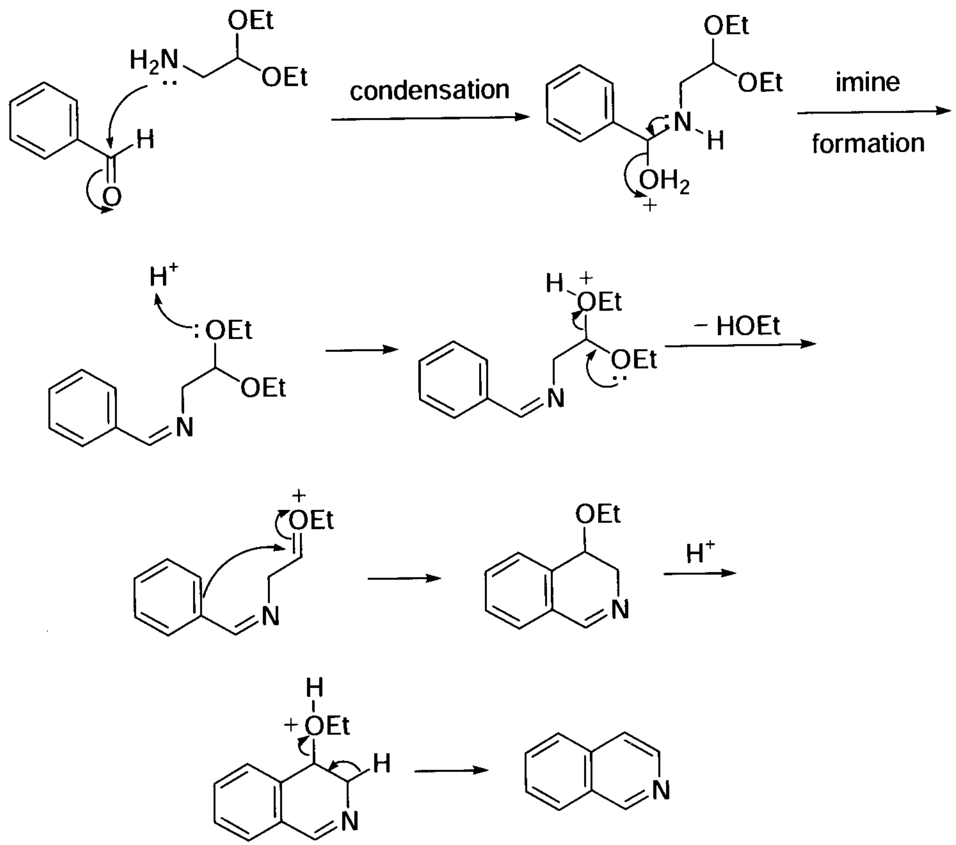
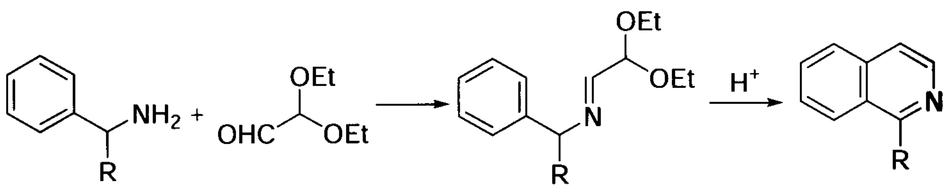
Pomeranz–Fritsch reaction

Isoquinoline synthesis from benzaldehyde and aminoacetal.





Schilittle–Müller modification



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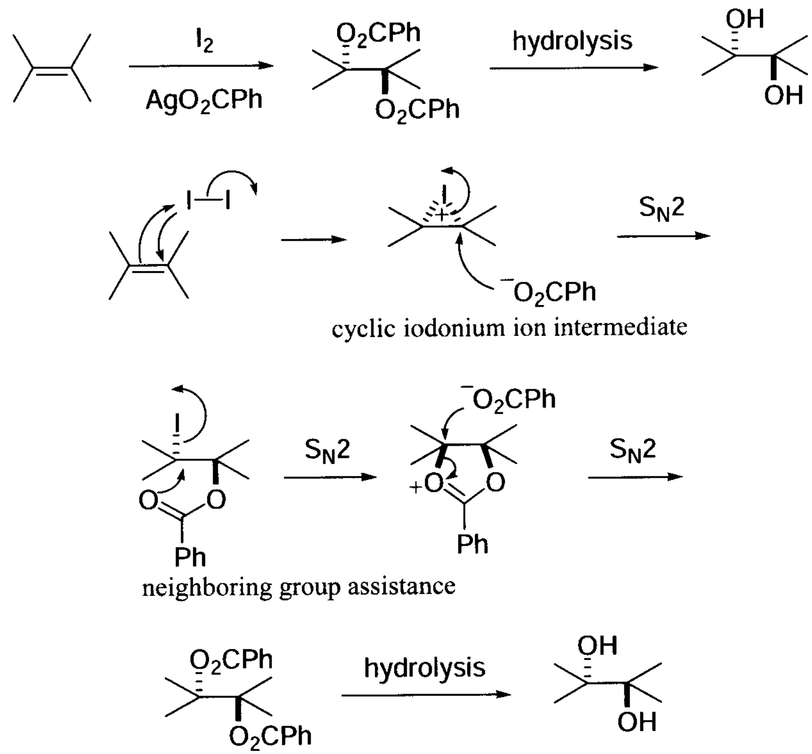
Prévost *trans*-dihydroxylation

Cf. Woodward *cis*-dihydroxylation



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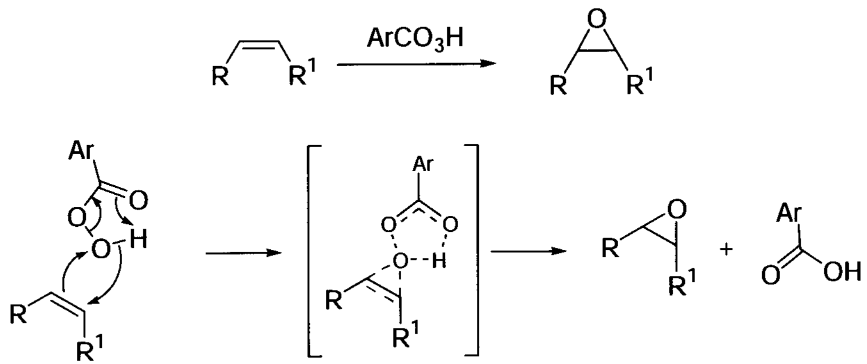
Prilezhaev reaction

Epoxidation of olefins using peracids.



The "butterfly" transition state

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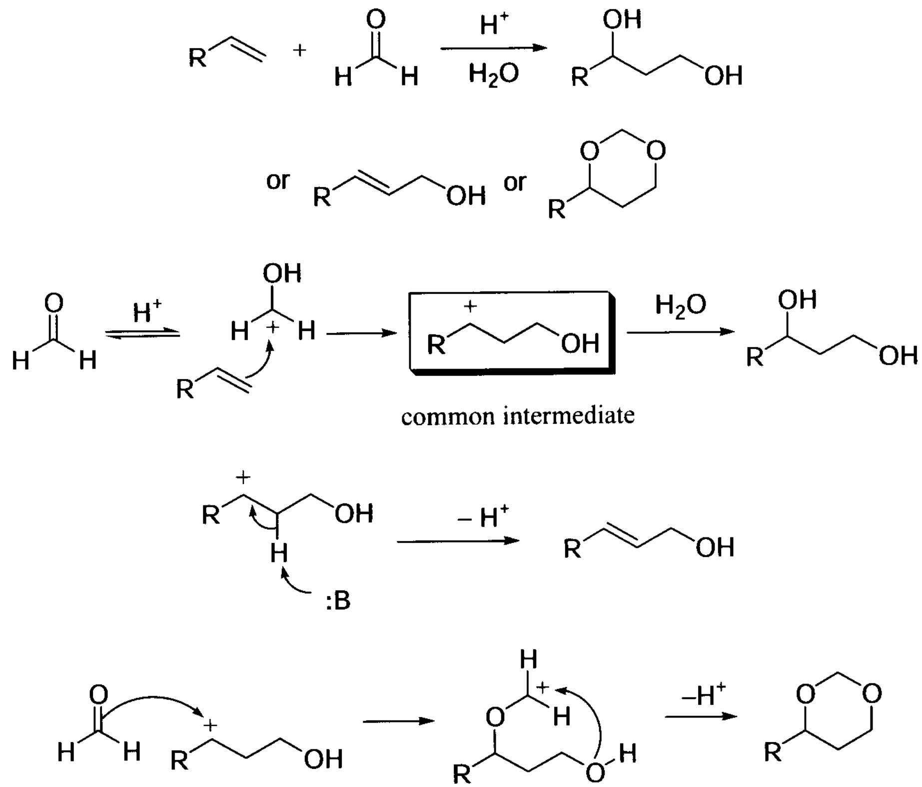
Prins reaction



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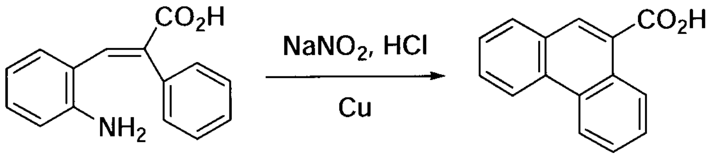
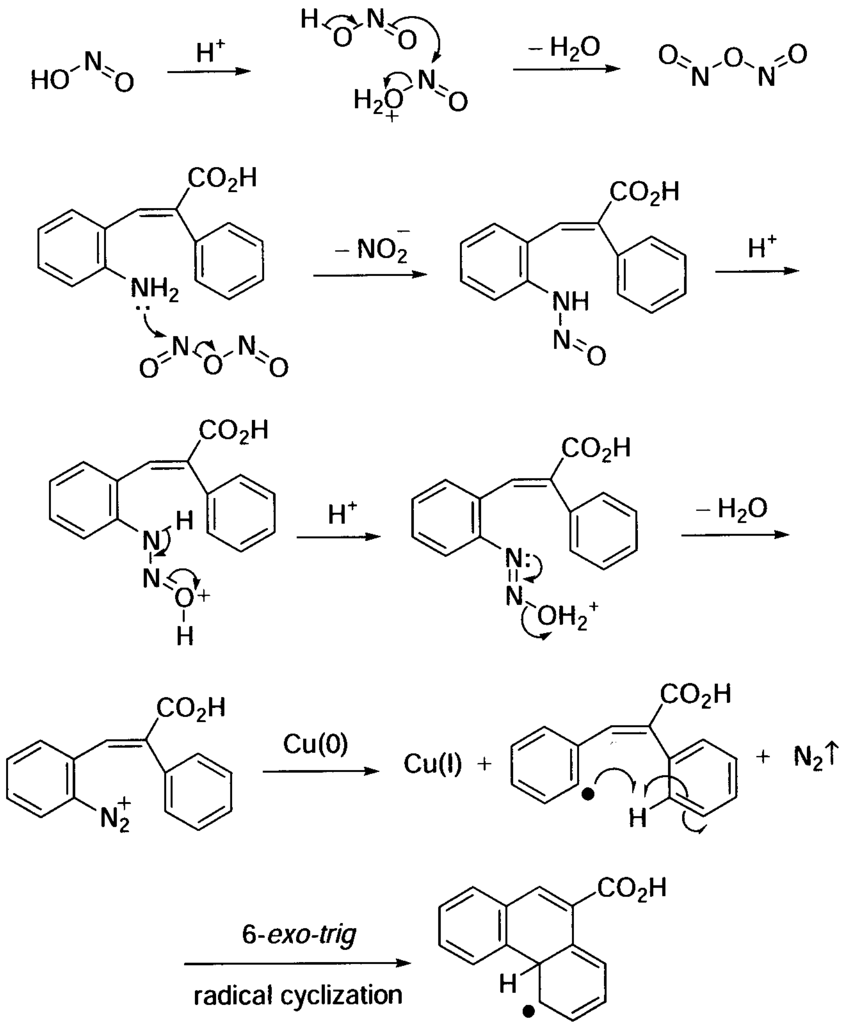
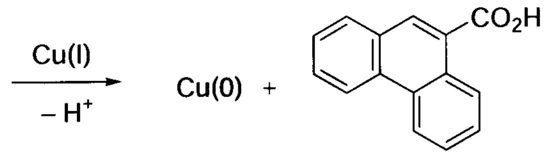
Pschorr ring closure

The intramolecular version of the Gomberg–Bachmann reaction.







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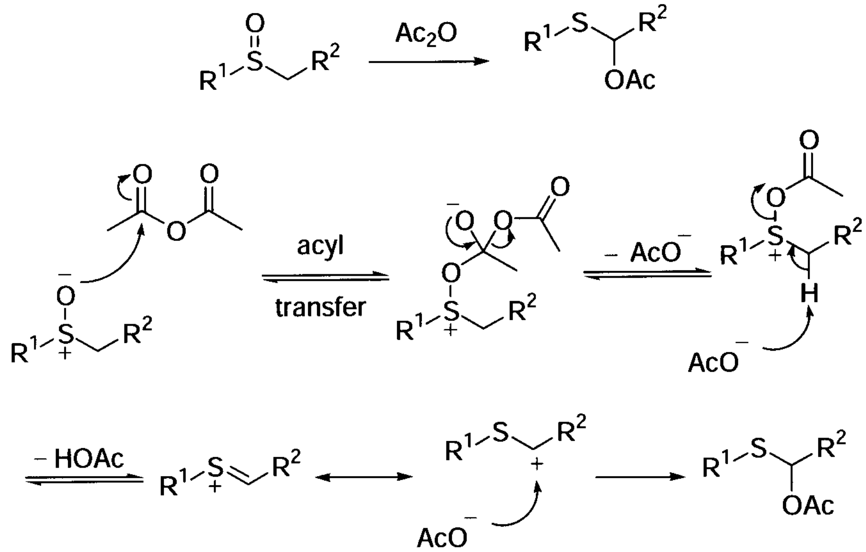
Pummerer rearrangement

The transformation of sulfoxides into α-acyloxythioethers using acetic anhydride.



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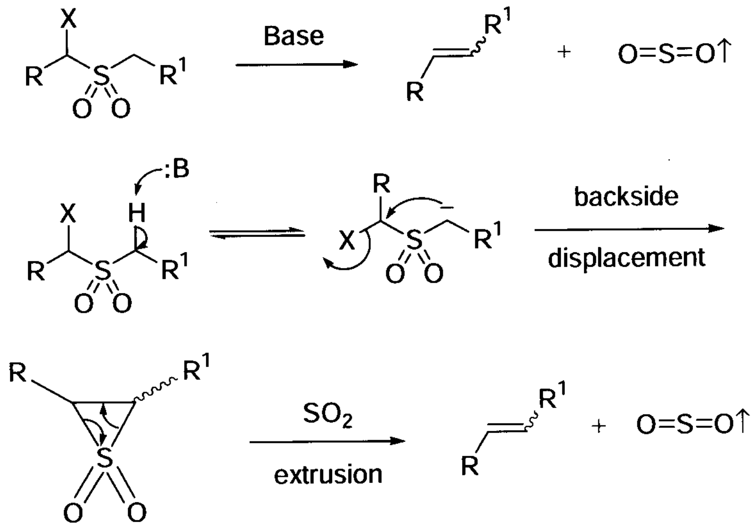
Ramberg–Bäcklund olefin synthesis

Olefin synthesis by treatment of an α-halosulfone with base.



episulfone intermediate

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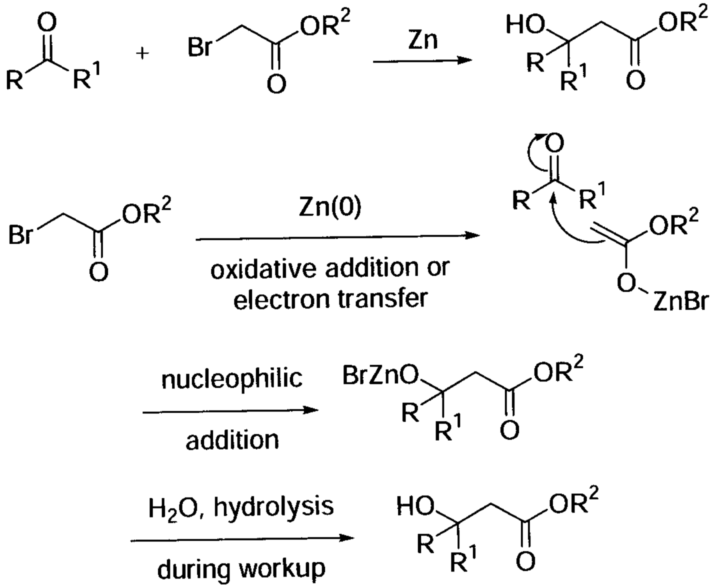
Reformatsky reaction

Nucleophilic addition of organozinc reagents (generated from α-haloesters) to carbonyls.



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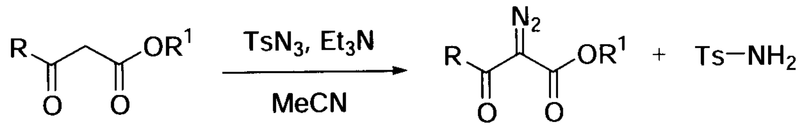
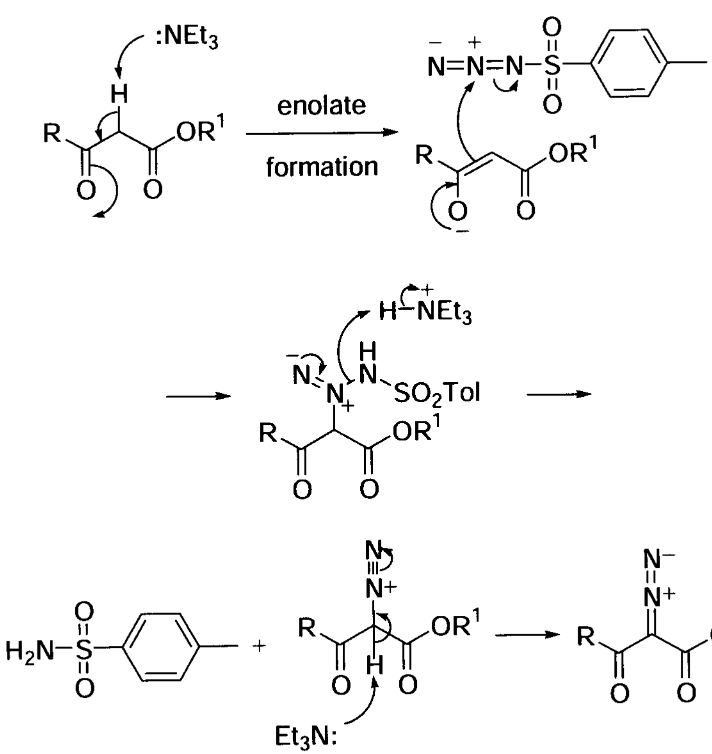
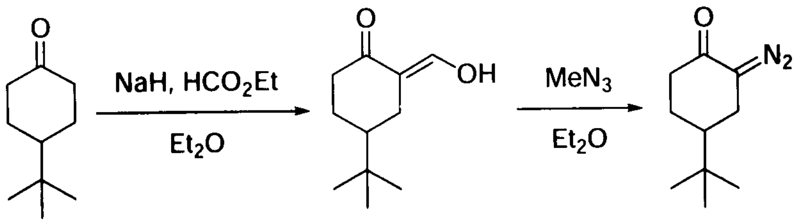
Regitz diazo synthesis

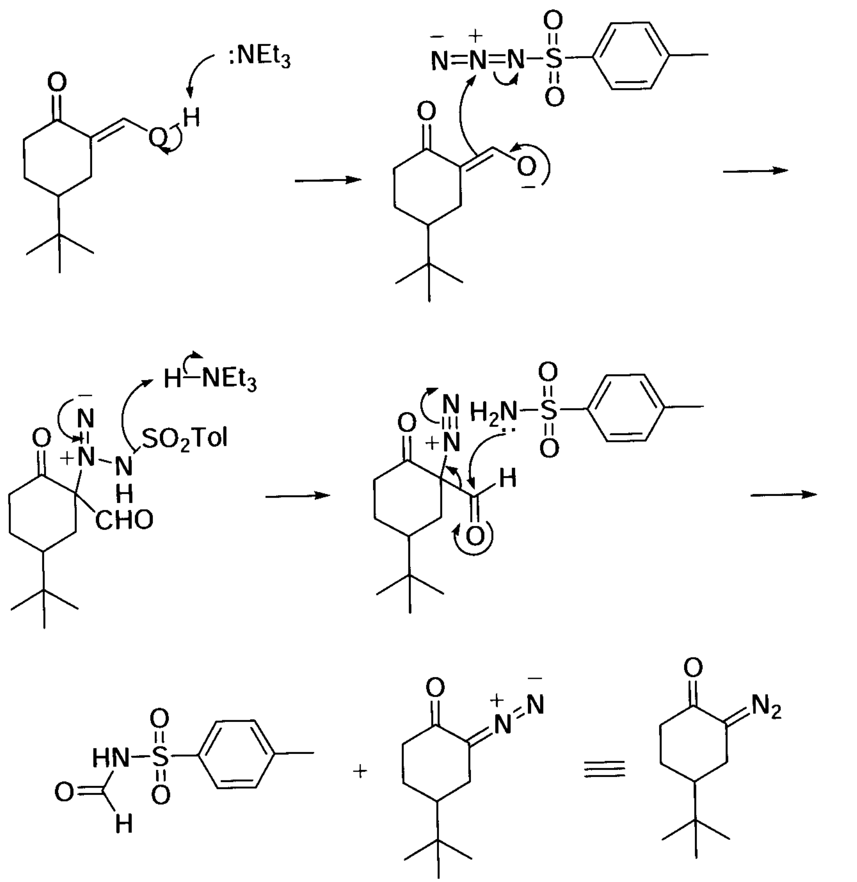
The synthesis of 2-diazo-1,3-dicarbonyl or 2-diazo-3-ketoesters using tosyl azide or mesyl azide.





When only one carbonyl is present, ethylformate can be used as an activating auxiliary [6–9]:





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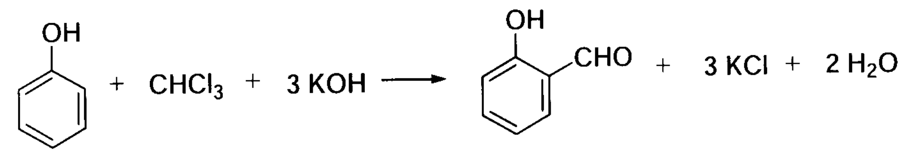
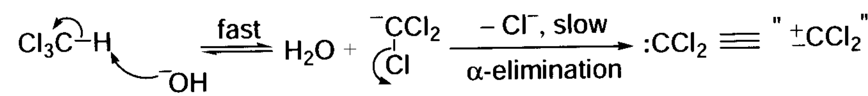
Reimer–Tiemann reaction

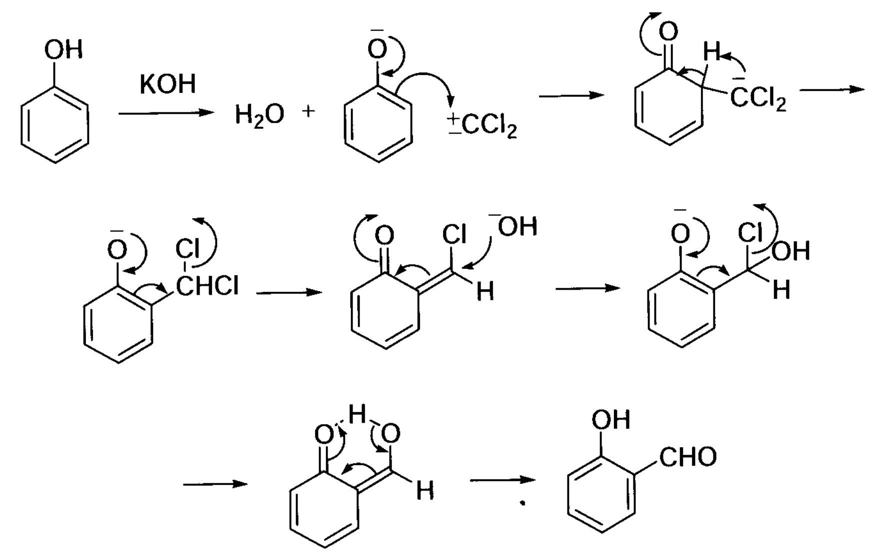
Synthesis of *o*-formylphenol from phenols and chloroform in alkaline medium.



1. Carbene generation:



2. Addition of dichlorocarbene and hydrolysis:



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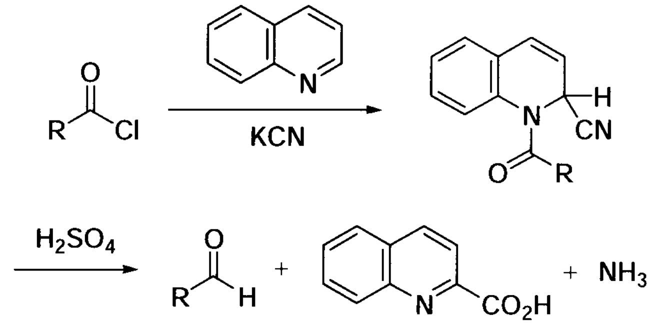
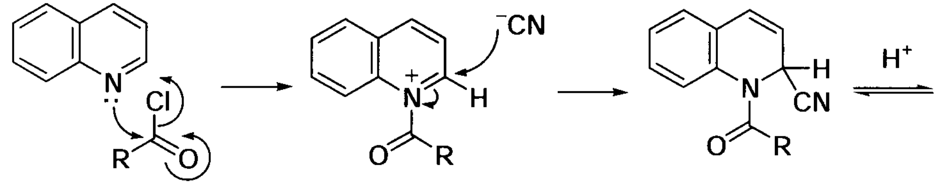
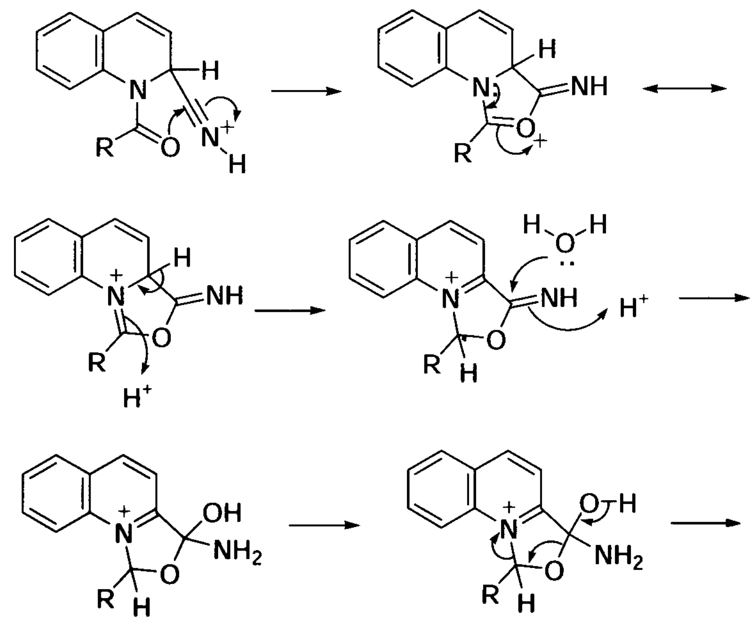
Reissert reaction (aldehyde synthesis)

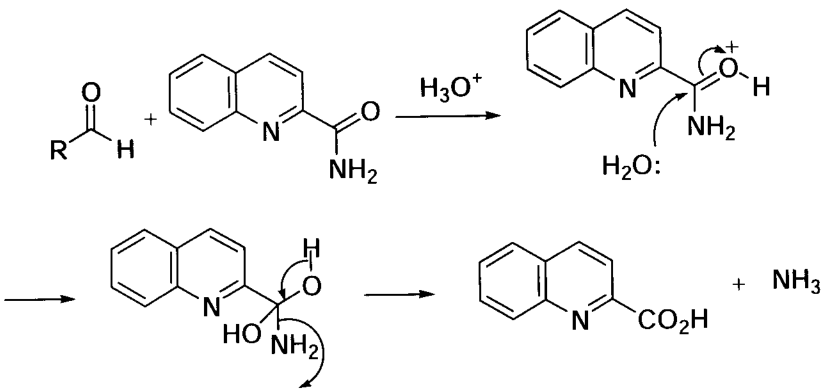
Aldehyde synthesis from the corresponding acid chloride, isoquinoline, and KCN.





Reissert compound





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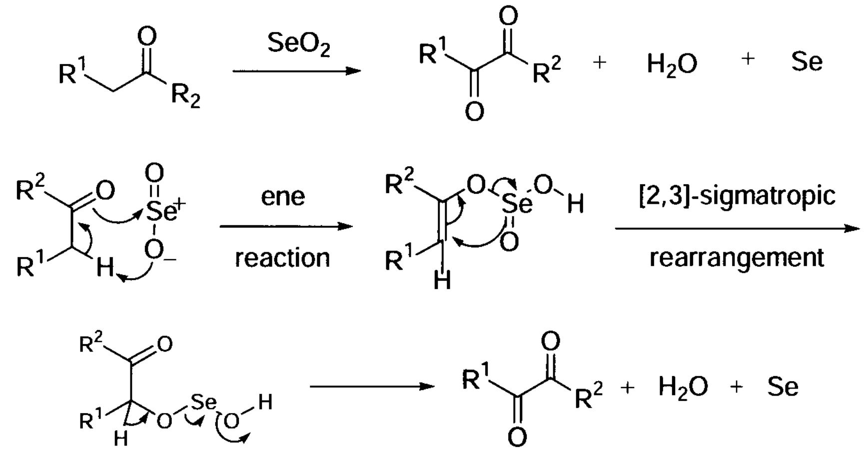
Riley oxidation (Selenium dioxide oxidation)

A selenium dioxide oxidation of activated methylenes into ketones.



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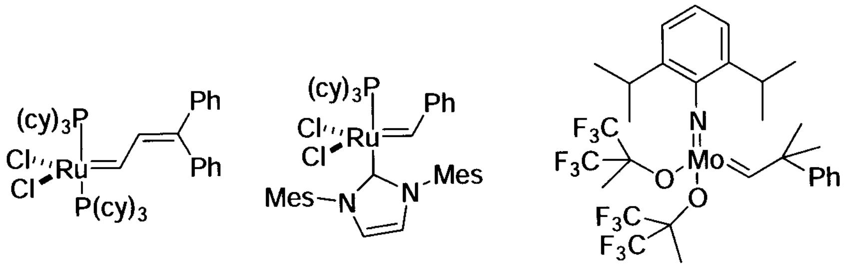
Ring-closing metathesis (RCM) using Grubbs and Schrock catalysts



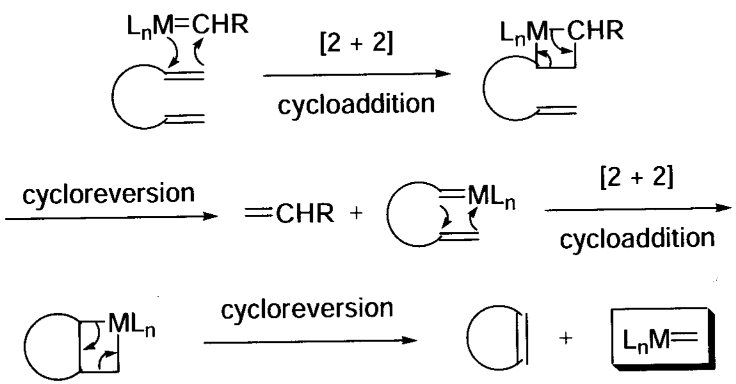
Grubbs' reagents
Mes = mesityl

Schrock's reagent

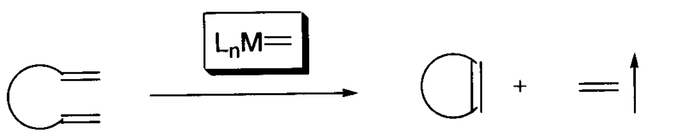
All three catalysts are illustrated as "L_nM=CHR" in the mechanism below.

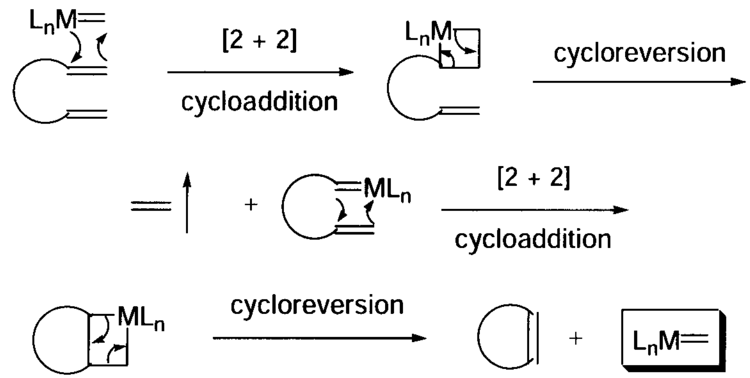
Generation of the catalyst from the precatalysts:

the real catalyst



Catalytic cycle:





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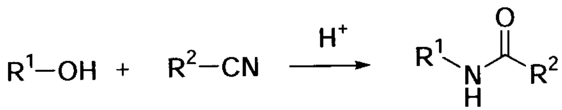
Ritter reaction

General scheme:



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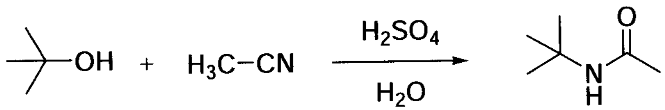

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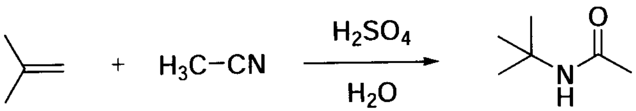

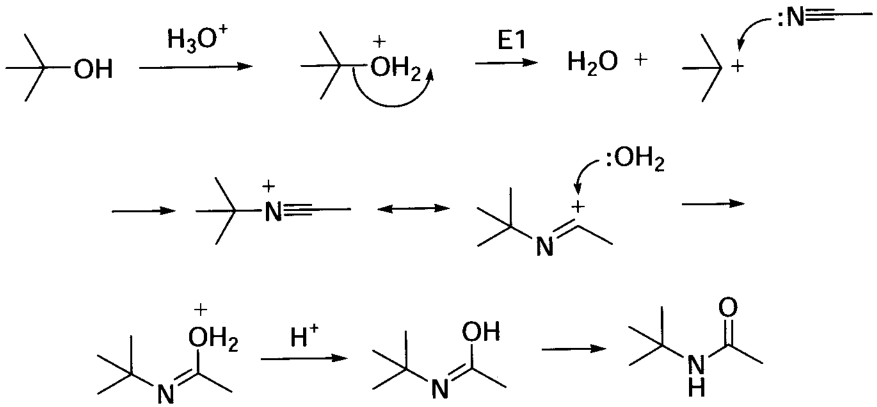

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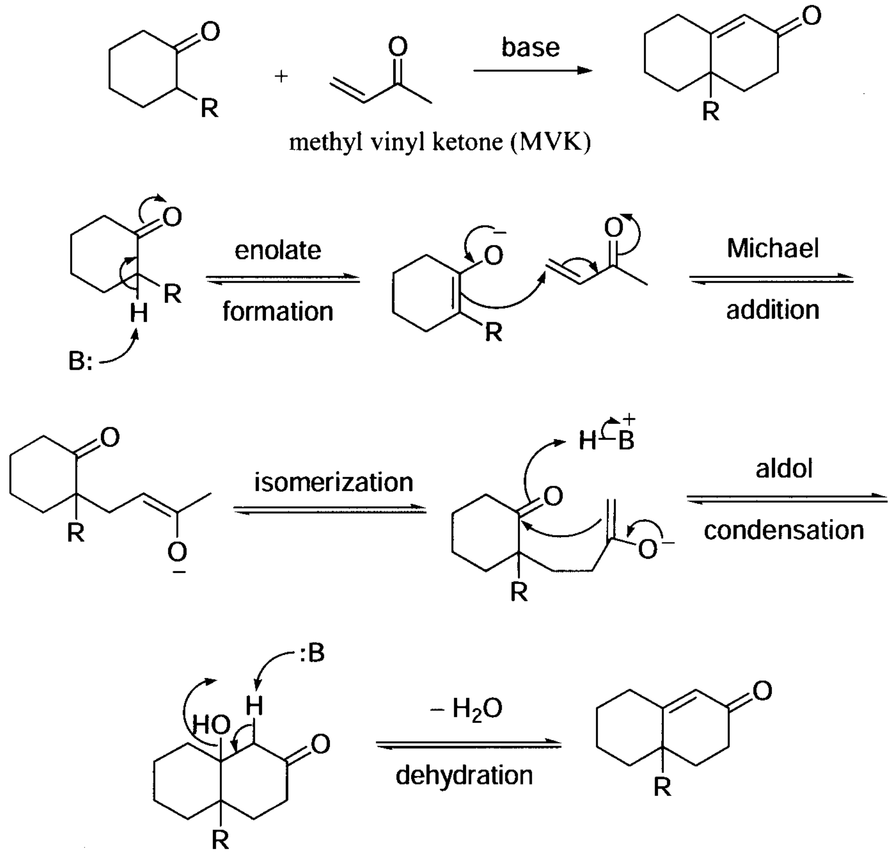
Robinson annulation



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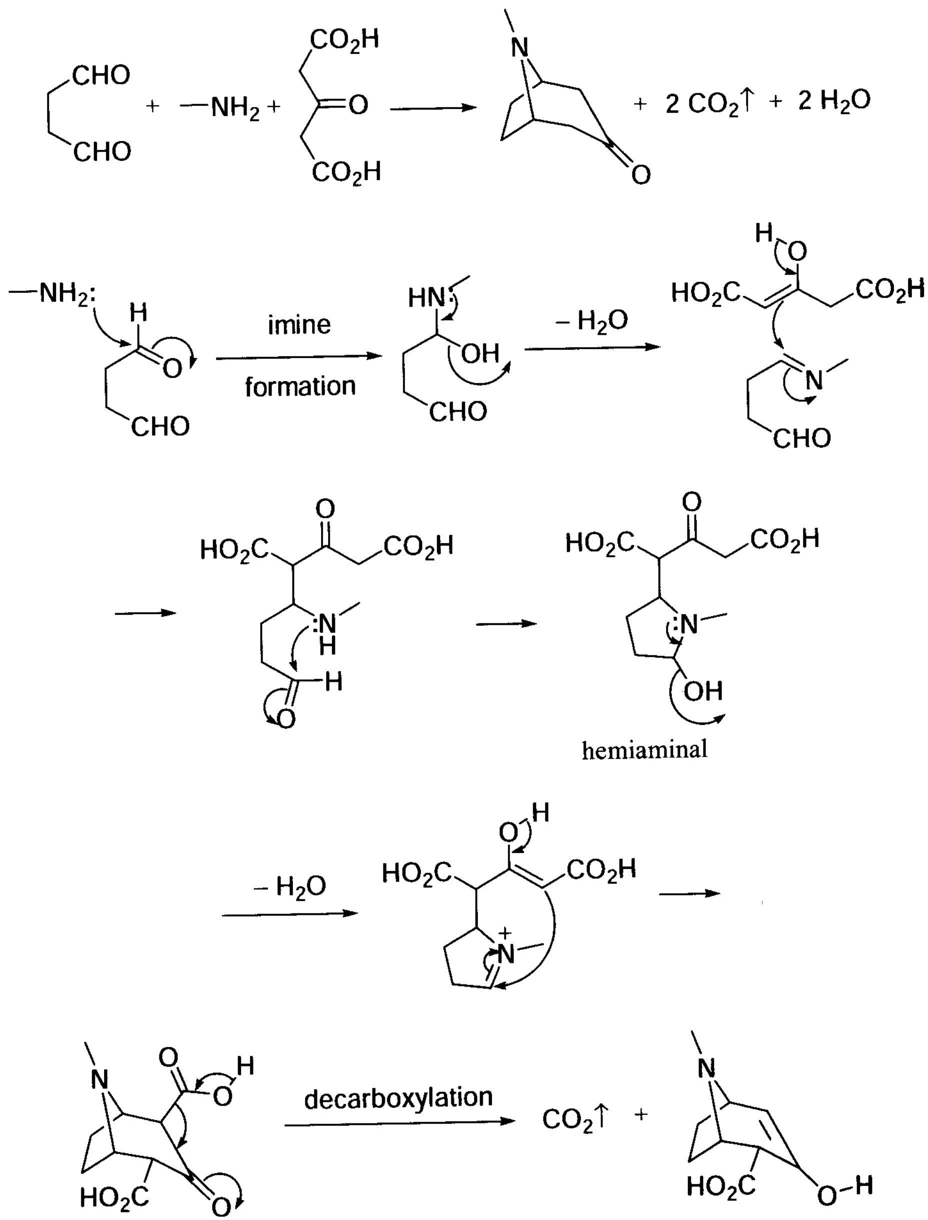
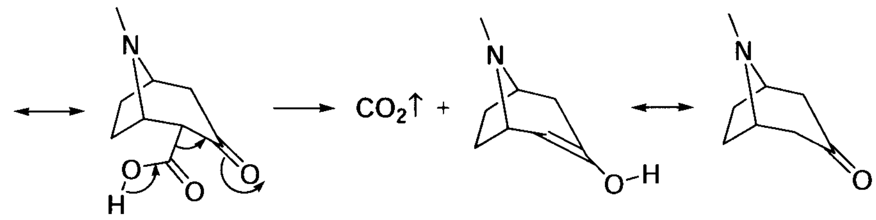
Robinson–Schöpf reaction

Tropinone synthesis.





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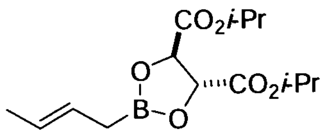
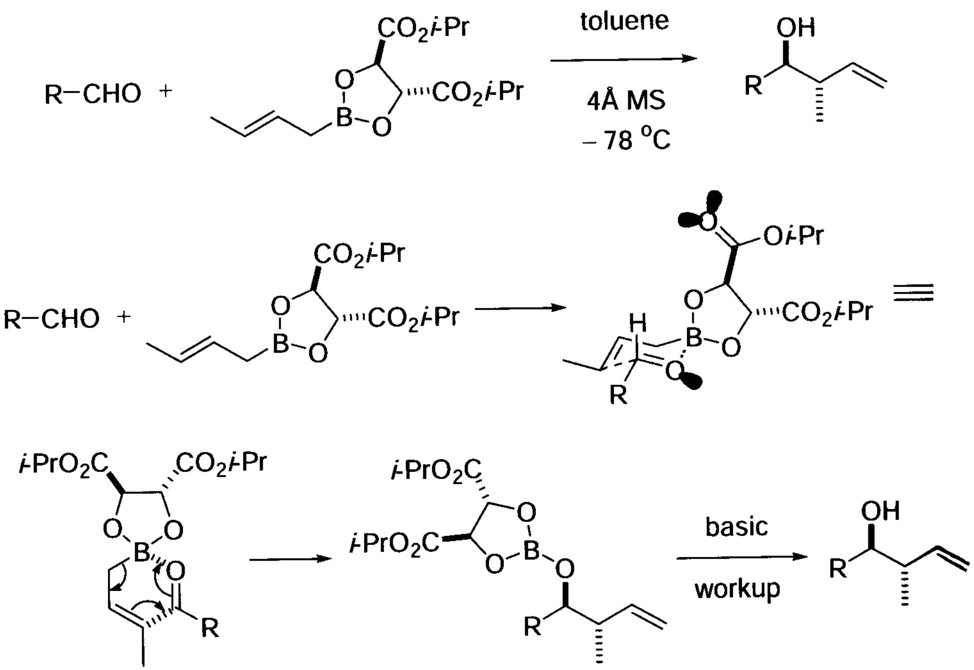
Roush allylboronate reagent



Tartrate allyl boronate, asymmetric allylation agent



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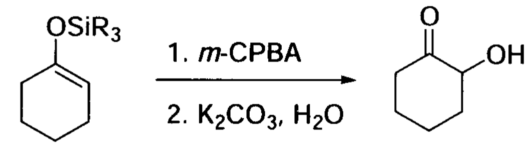
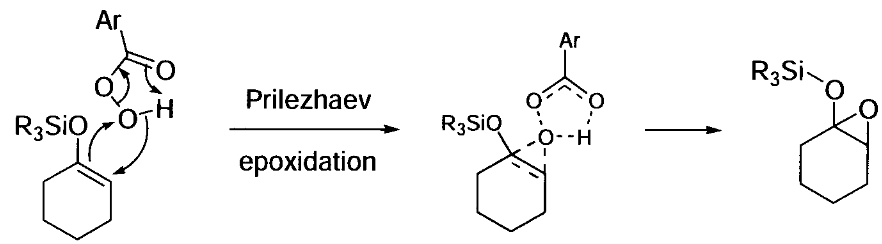
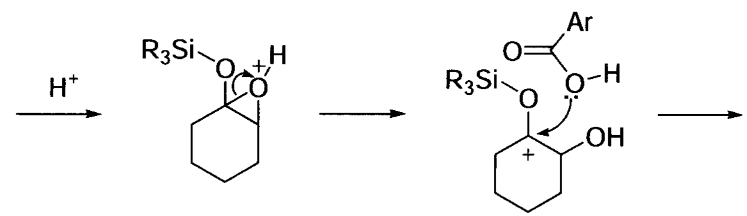
Rubottom oxidation

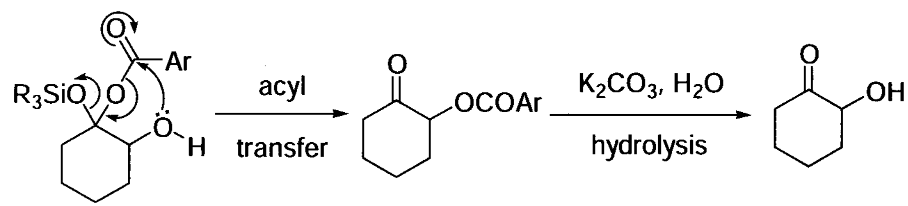
α-Hydroxylation of enolsilanes.





The "butterfly" transition state





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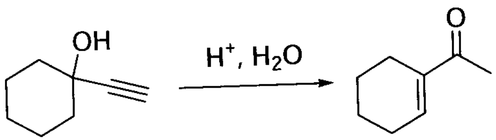
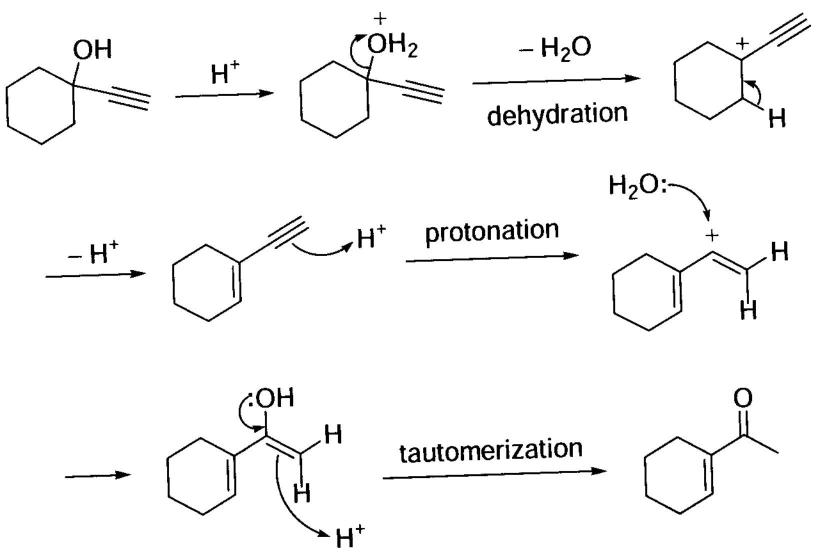
Rupe rearrangement

The acid-catalyzed rearrangement of tertiary α-acetylenic (terminal) alcohols, leading to the formation of α,β-unsaturated ketones rather than the corresponding α,β-unsaturated aldehydes. *Cf.* Meyer–Schuster rearrangement.





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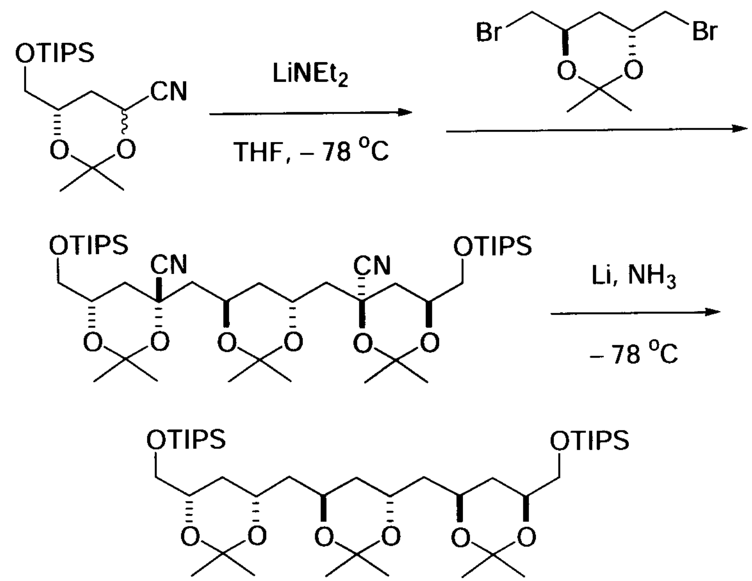
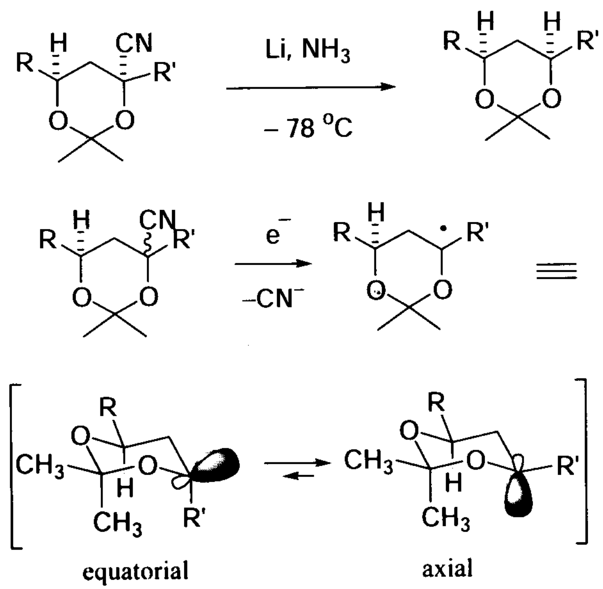
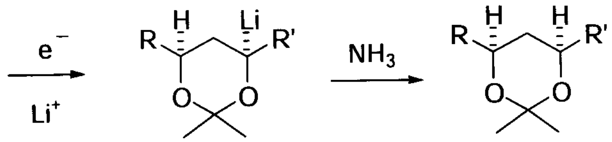
Rychnovsky polyol synthesis



The stereochemical outcome of the reductive decyanation:





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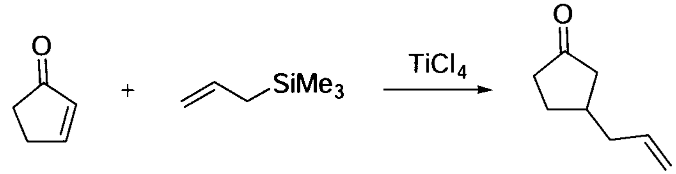
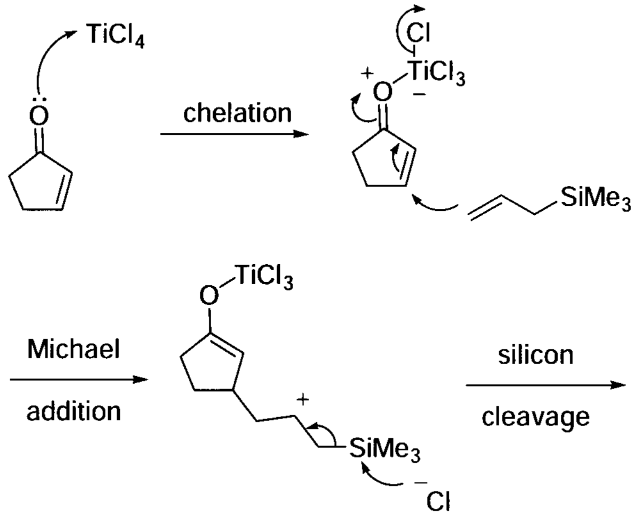
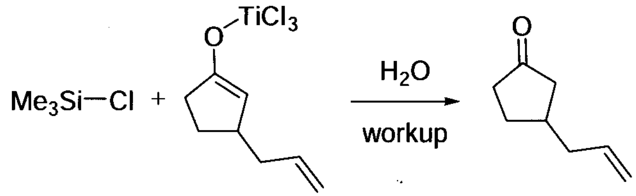
Sakurai allylation reaction (Hosomi–Sakurai reaction)





The β-carbocation is stabilized by the silicon group



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Sandmeyer reaction

Haloarenes from the reaction of diazonium salt and CuX.

$$ArN_2^+\ Y^- \xrightarrow{CuX} Ar{-}X \qquad X = Cl, Br, CN$$

e.g.:

$$ArN_2^+\ Cl^- \xrightarrow{CuCl} Ar{-}Cl$$

$$ArN_2^+\ Cl^- \xrightarrow{CuCl} N_2\uparrow + Ar\bullet + CuCl_2 \longrightarrow Ar{-}Cl + CuCl$$

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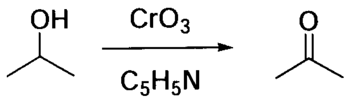
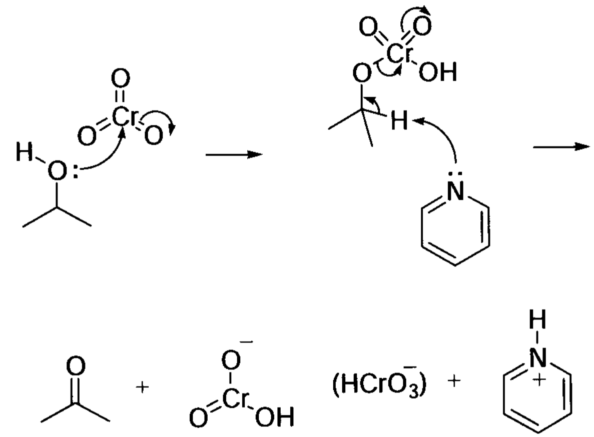
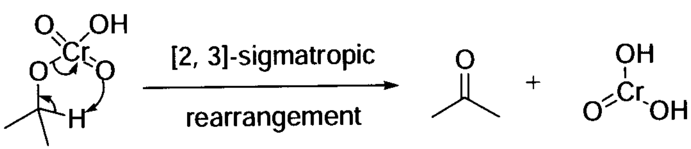
Sarett oxidation





The intramolecular mechanism is also operative:



The Collins oxidation, Jones oxidation, and Corey's PCC (pyridinium chlorochromate) and PDC (pyridinium dichromate) oxidations follow a similar pathway.

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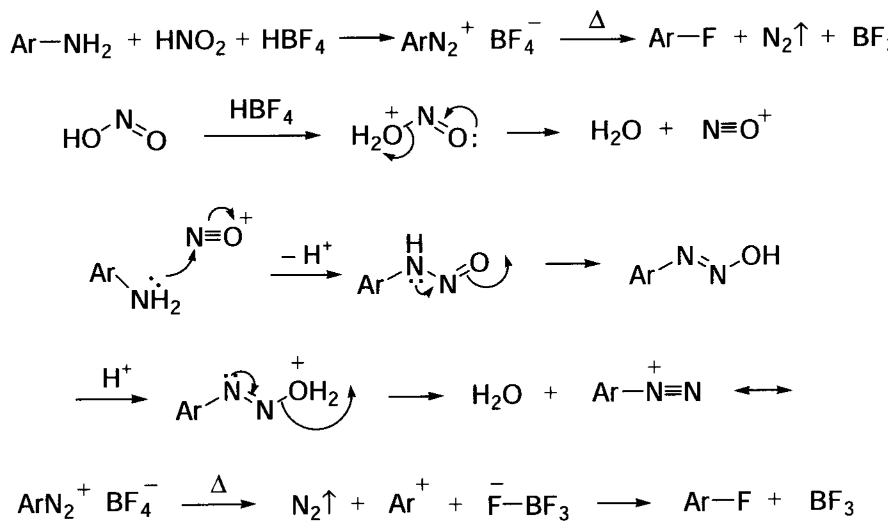
Schiemann reaction (Balz–Schiemann reaction)

Fluoroarene formation from arylamines.



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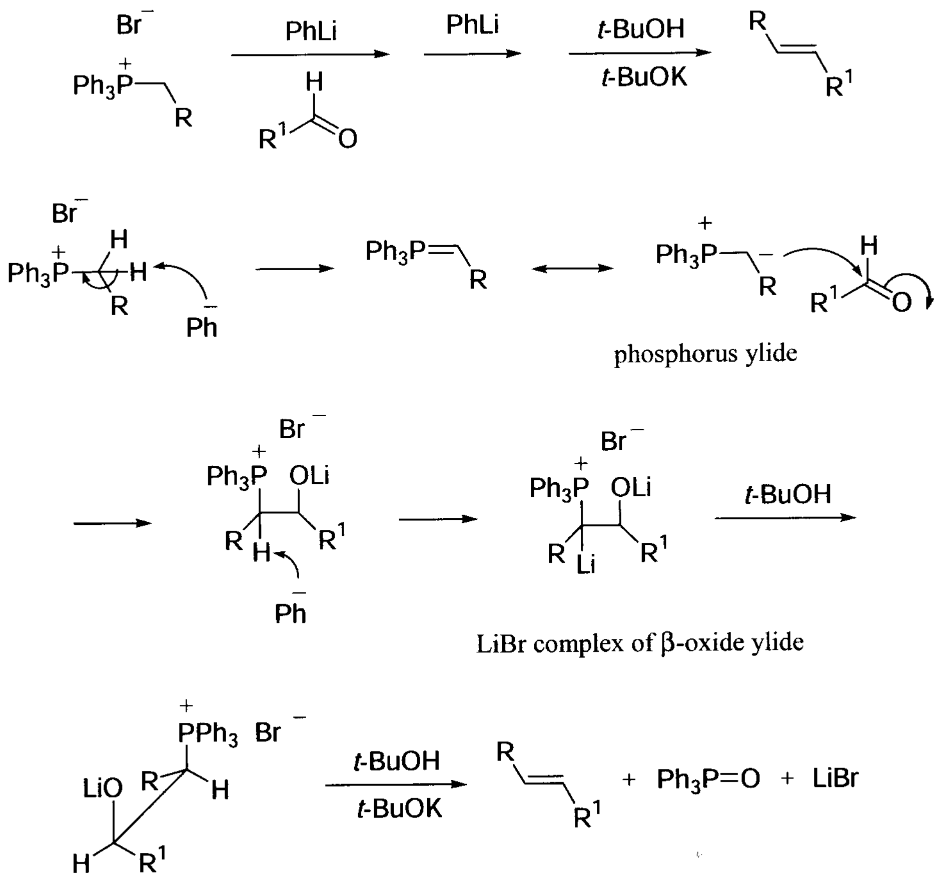
Schlosser modification of the Wittig reaction

The normal Wittig reaction of nonstabilized ylides with aldehydes gives *Z*-olefins. The Schlosser modification of the Wittig reaction of nonstabilized ylides furnishes *E*-olefins instead.



LiBr complex of *threo*-betaine

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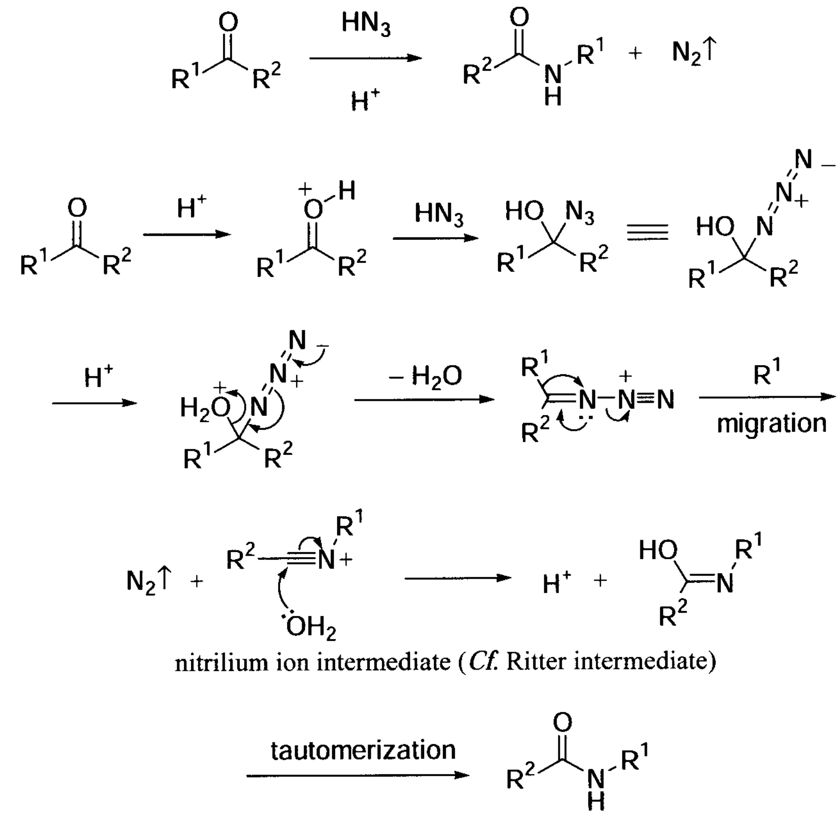
Schmidt reaction



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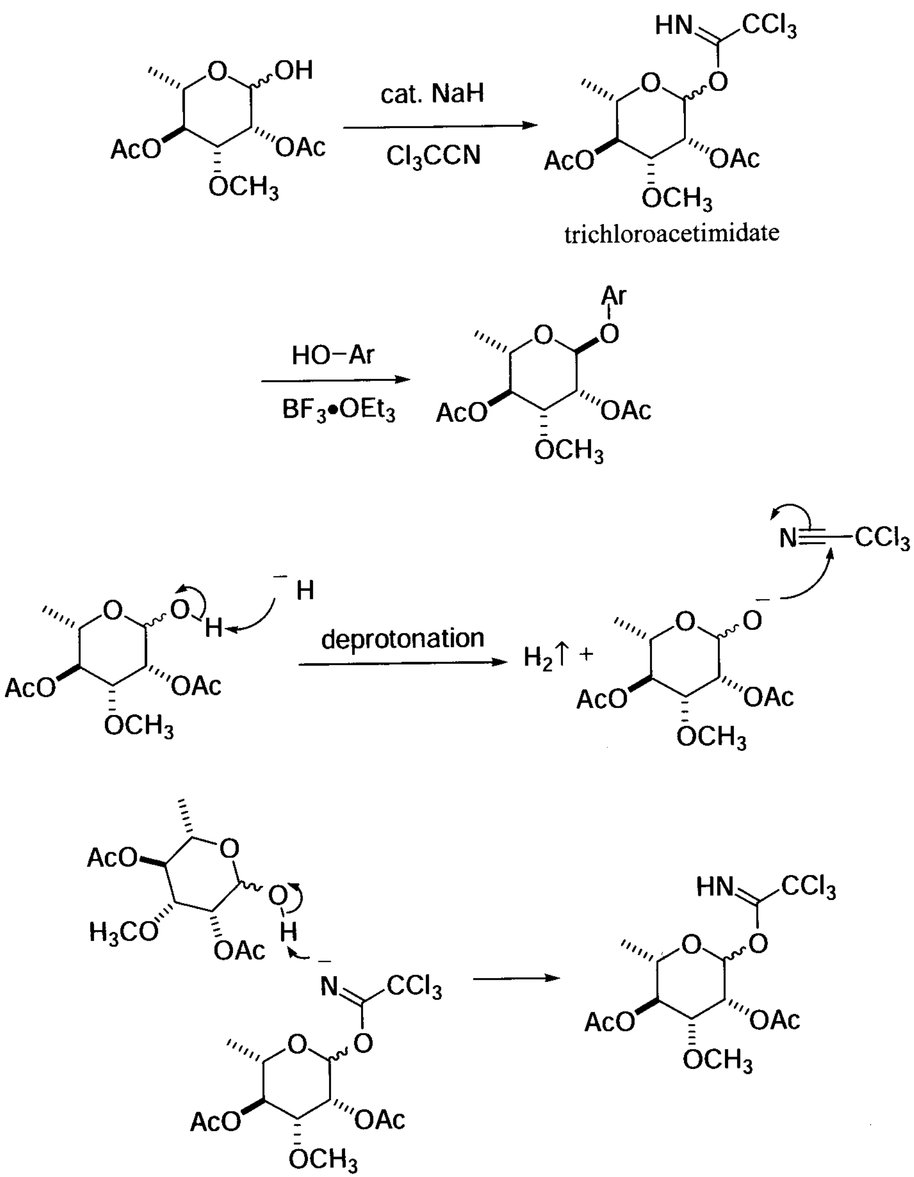
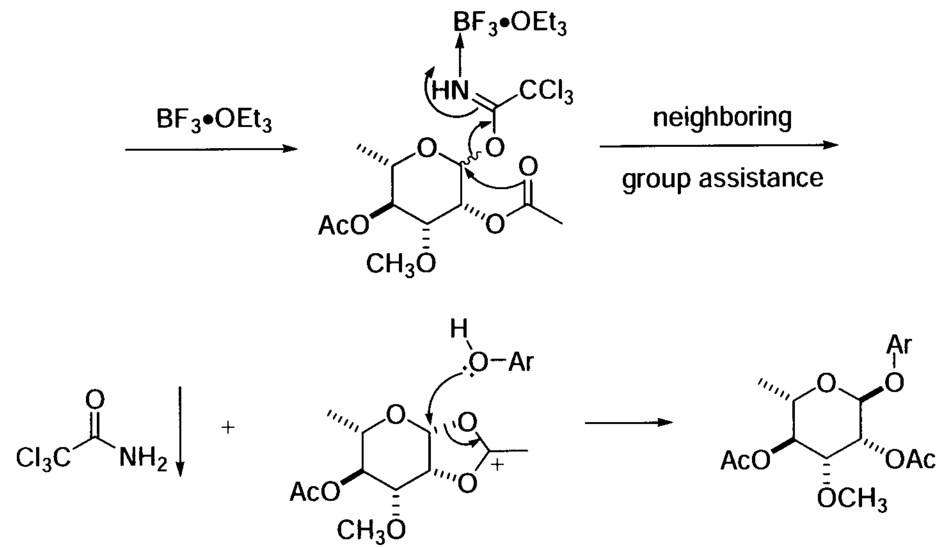
Schmidt's trichloroacetimidate glycosidation reaction





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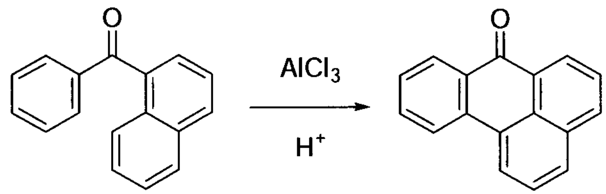
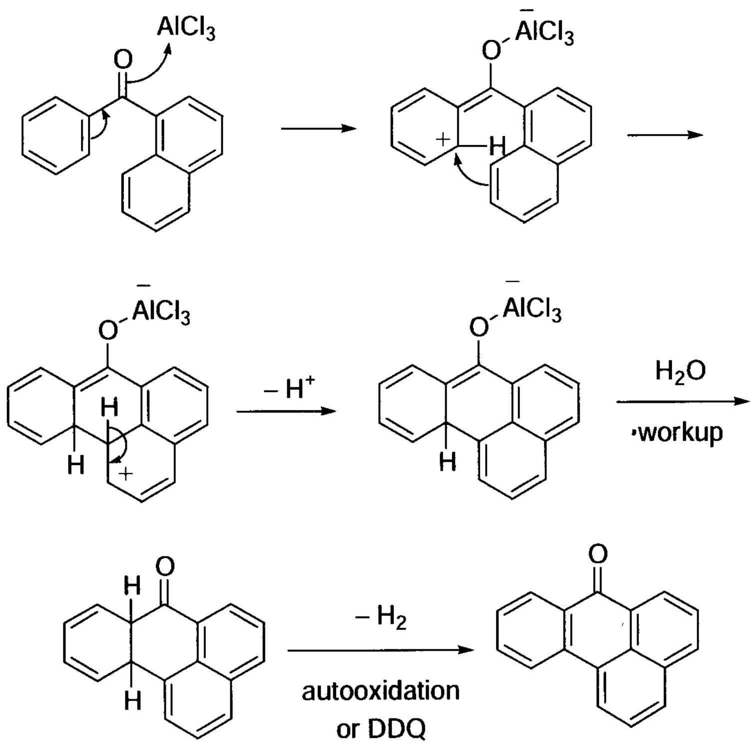
Scholl reaction

The elimination of two aryl-bound hydrogens accompanied by the formation of an aryl-aryl bond under the influence of Friedel–Crafts catalysts. *Cf.* Friedel–Crafts reaction.





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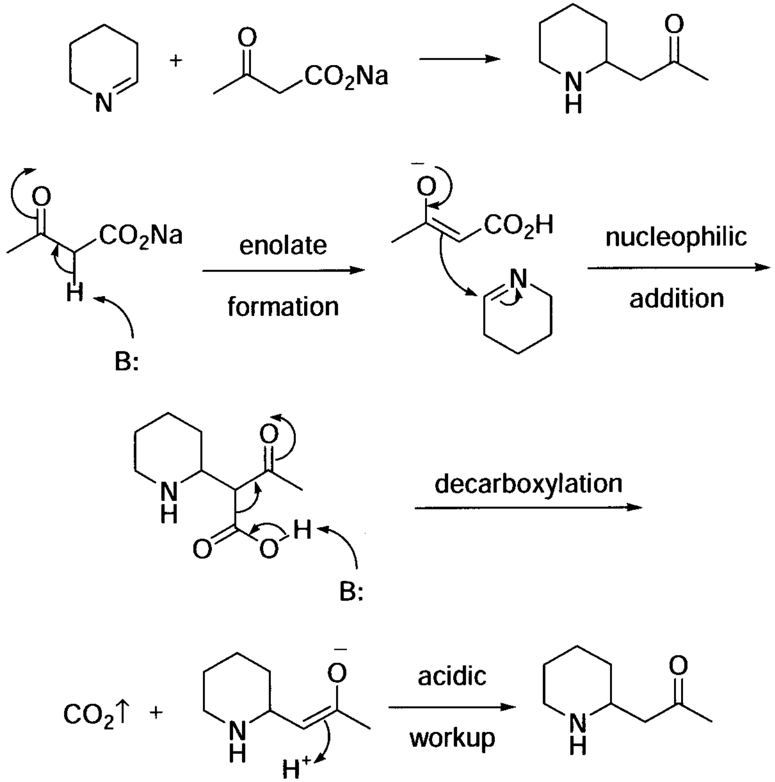
Schöpf reaction



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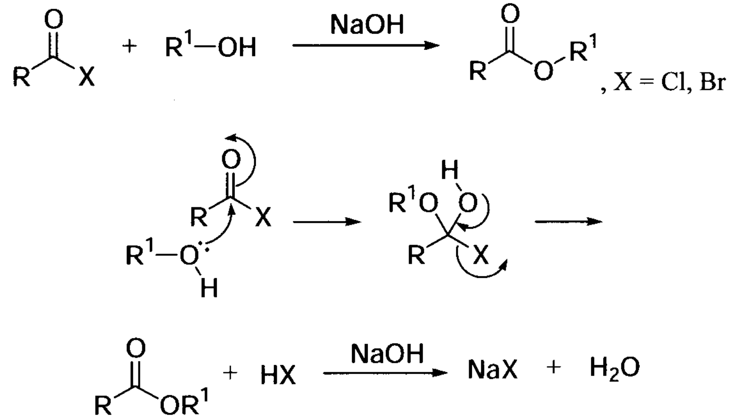
Schotten–Baumann reaction

Esterification or amidation of acid chloride with alcohol or amine under basic conditions.



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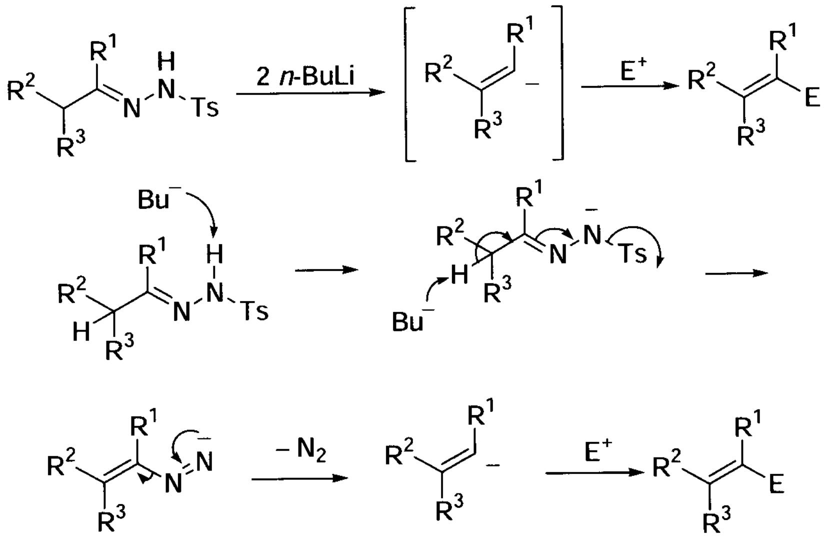
Shapiro reaction

The Shapiro reaction is a variant of the Bamford–Stevens reaction. The former uses bases such as alkyllithiums and Grignard reagents whereas the latter employs bases such as Na, NaOMe, LiH, NaH, $NaNH_2$, *etc.* As a result, the Shapiro reaction generally affords the less-substituted olefins as the kinetic products, while the Bamford–Stevens reaction delivers the more-substituted olefins as the thermodynamic products.



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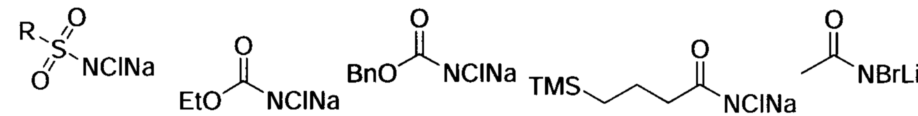
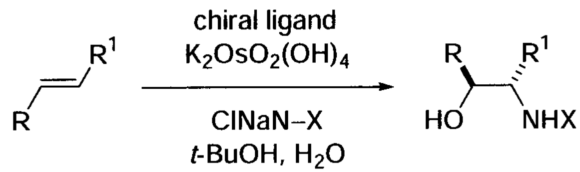
Sharpless asymmetric aminohydroxylation

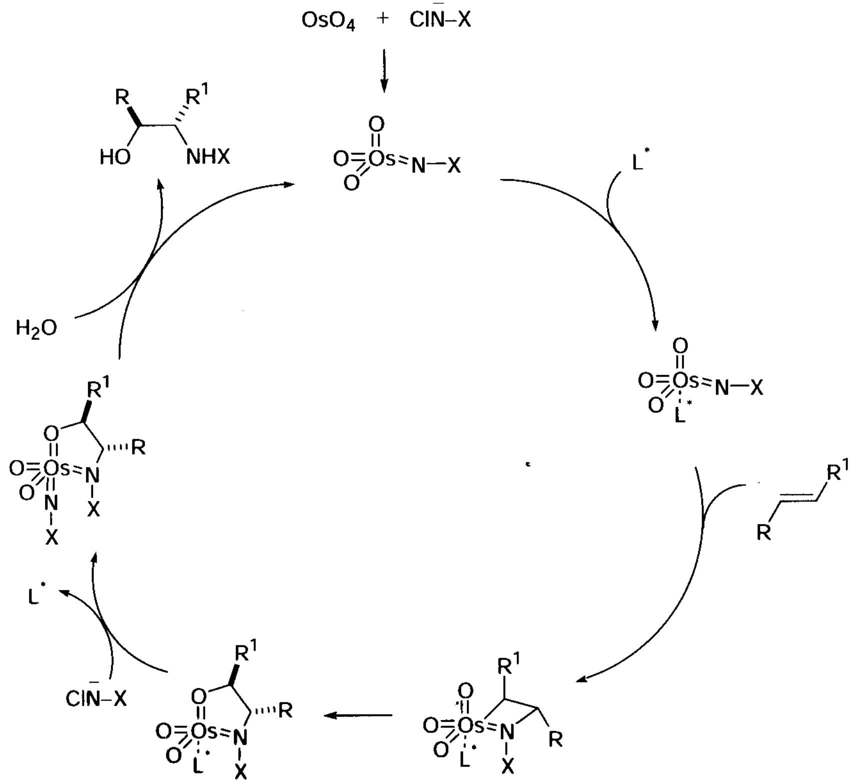
Osmium-mediated *cis*-addition of nitrogen and oxygen to olefins. Nitrogen sources (X–NClNa) include:



R = *p*-Tol; Me



The catalytic cycle:



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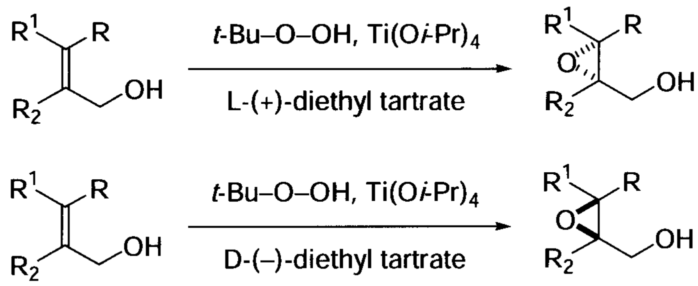
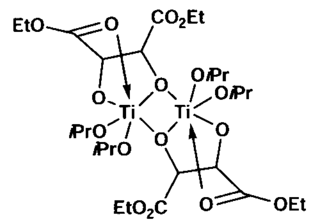
Sharpless asymmetric epoxidation

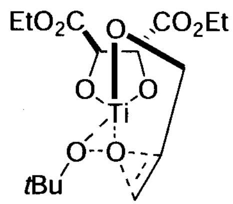
Enantioselective epoxidation of allylic alcohols using *t*-butyl peroxide, titanium tetra-*iso*-propoxide, and optically pure diethyl tartrate.



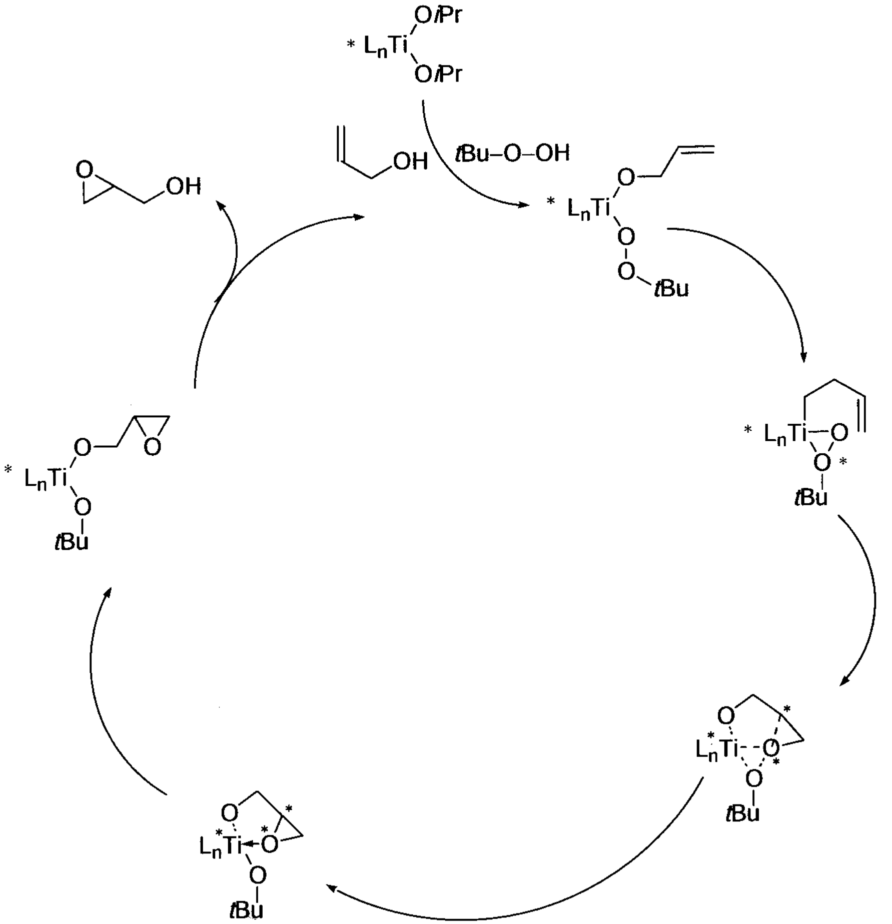
The putative active catalyst [2]:



The transition state:



The catalytic cycle:



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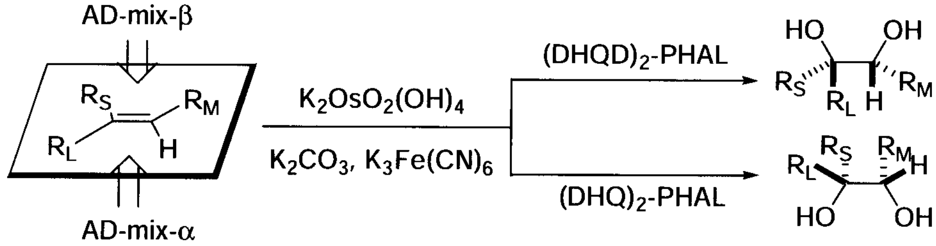
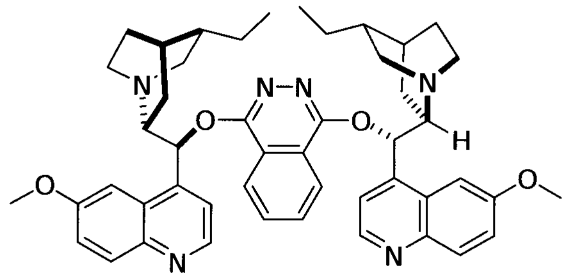
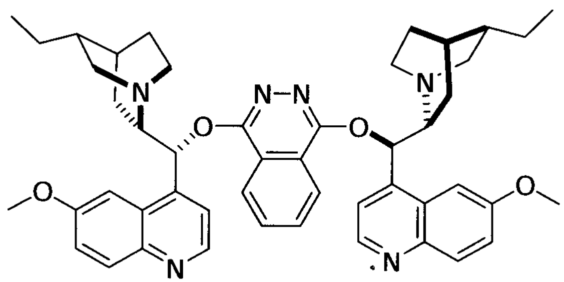
Sharpless dihydroxylation



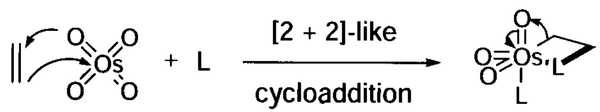
$(DHQD)_2$-PHAL = 1,4-bis(9-*O*-dihydroquinidine)phthalazine:

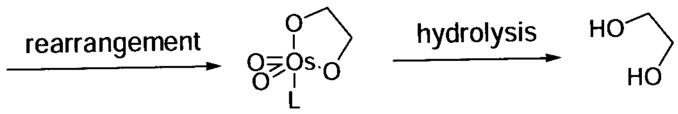


$(DHQ)_2$-PHAL = 1,4-bis(9-*O*-dihydroquinine)phthalazine:



A stepwise mechanism involving osmaoxetane seems to be more consistent with the experimental data than the corresponding concerted [3 + 2] mechanism:





The catalytic cycle is shown on the next page (page 337, the secondary cycle is shut off by maintaining a low concentration of olefin):

References

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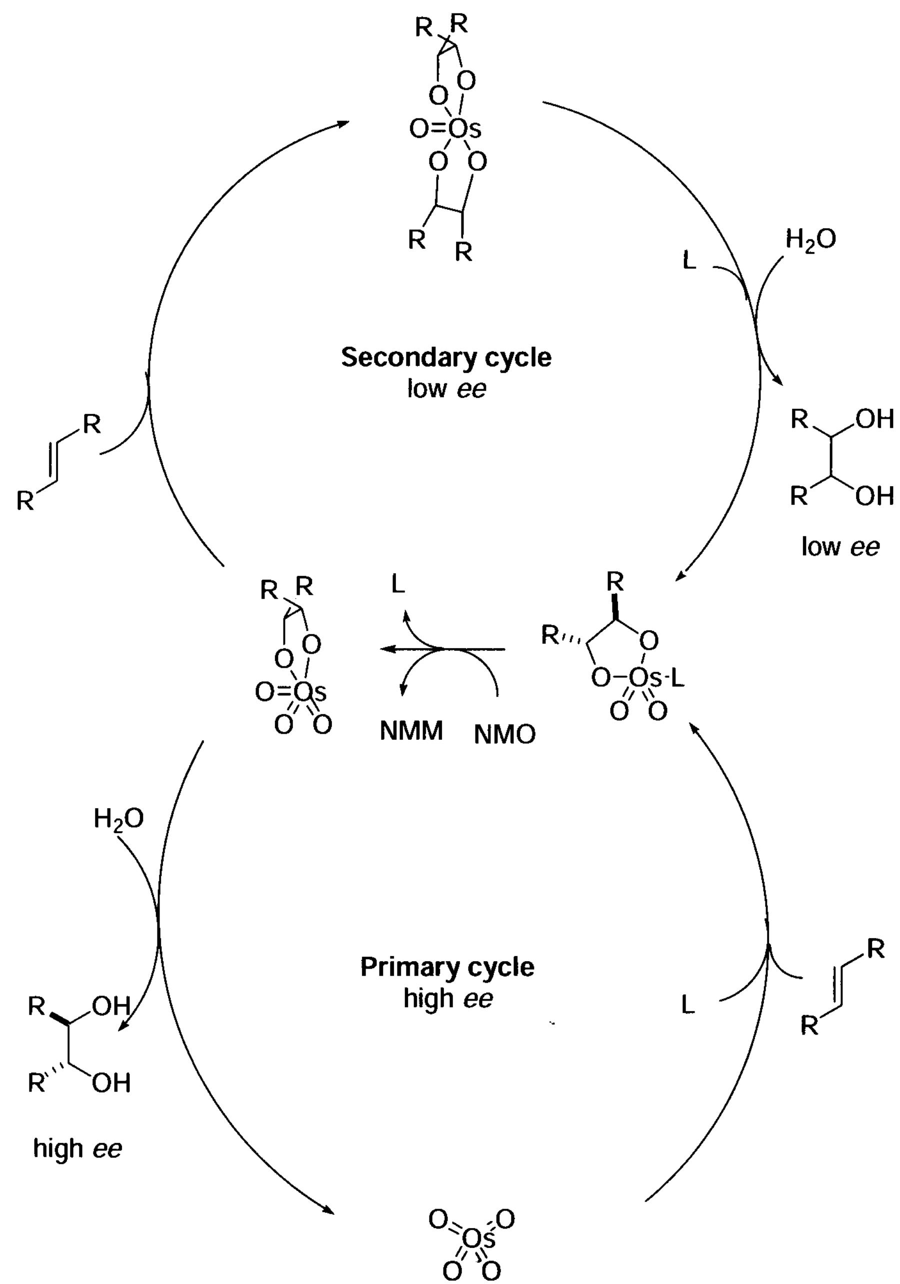
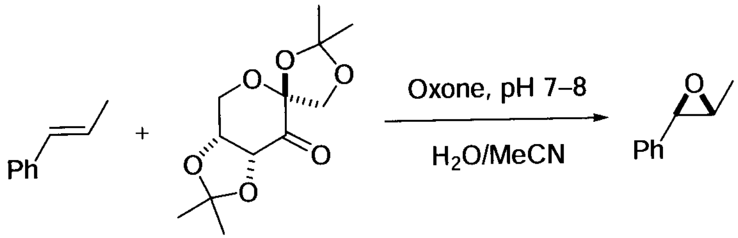
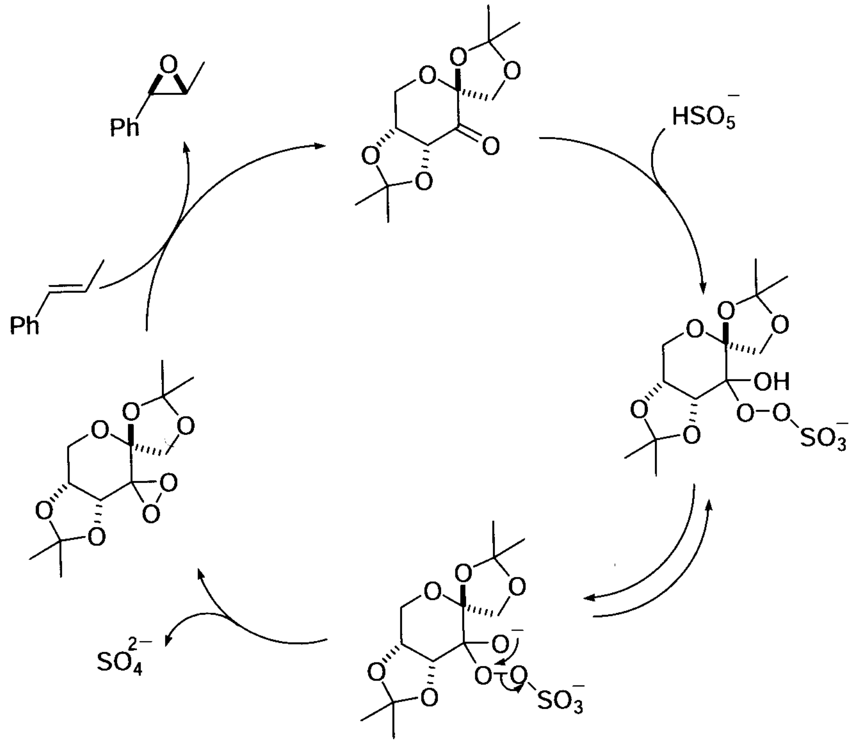


Shi asymmetric epoxidation

An asymmetric epoxidation using fructose-derived chiral ketone.



The catalytic cycle:



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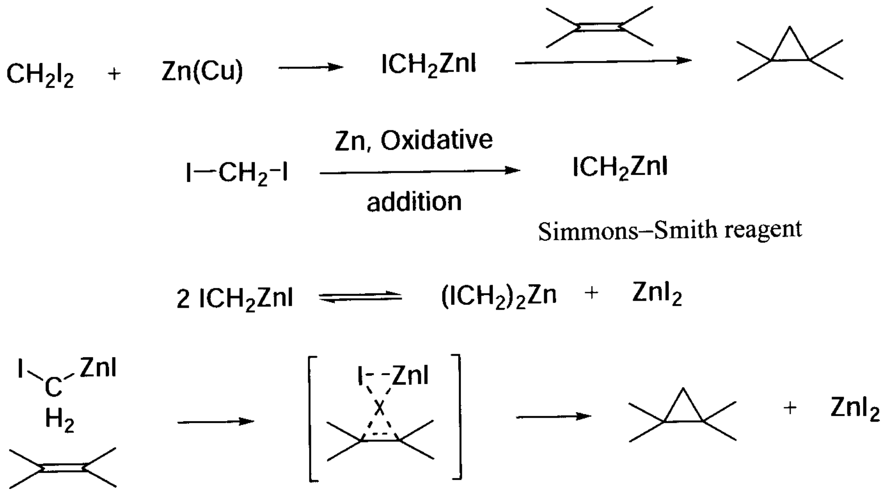
Simmons–Smith reaction

Cyclopropanation of olefins using CH_2I_2 and Zn(Cu).



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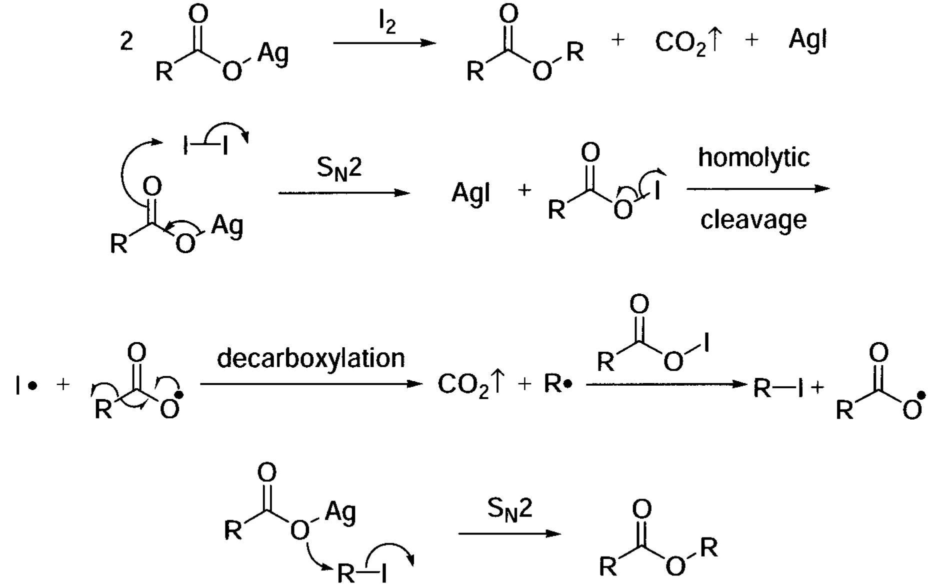
Simonini reaction

Ester formation when silver carboxylate is treated with iodine. On the other hand, when silver carboxylate is treated with bromine, the product is alkyl bromide, R–Br (**Hunsdiecker reaction**, page 178).



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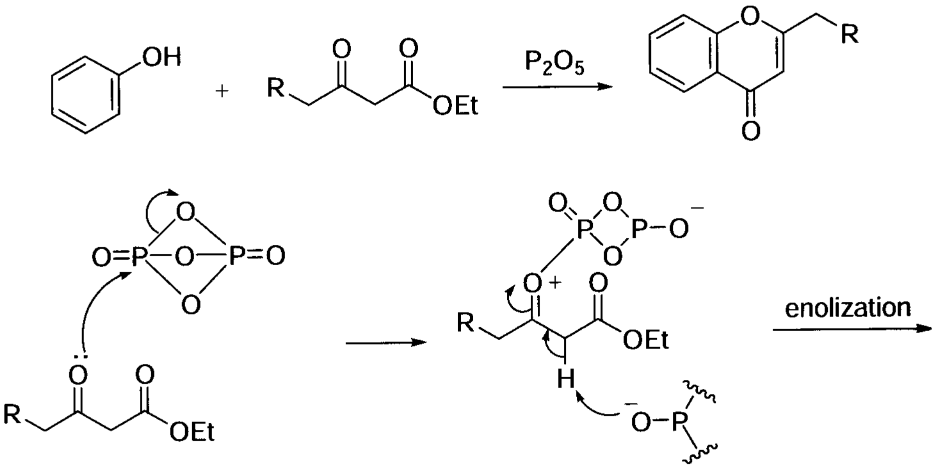
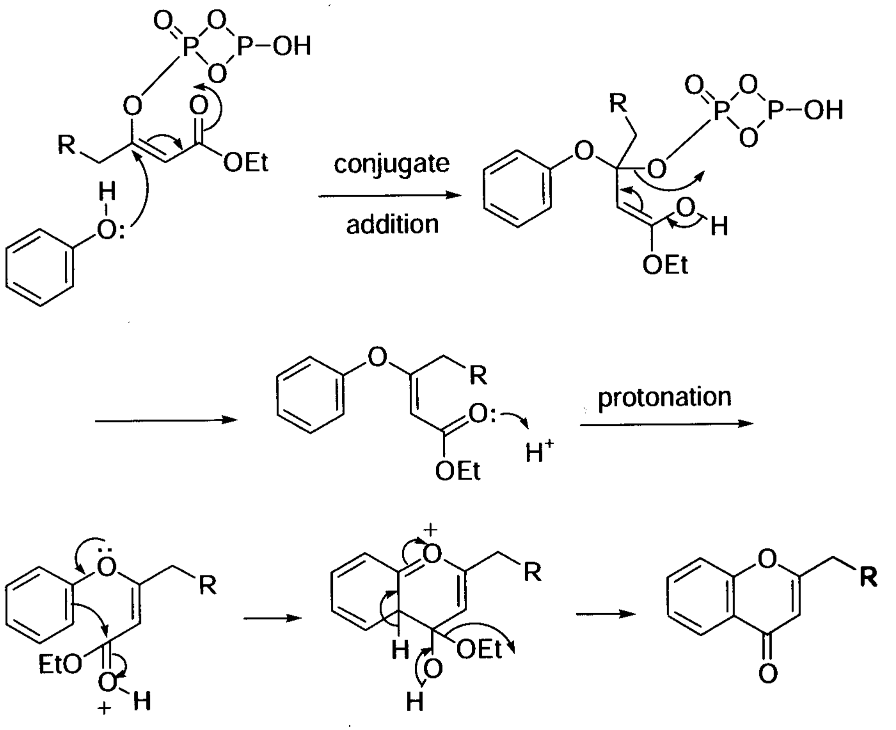
Simonis chromone cyclization



P_2O_5 actually exists as P_4O_{10}, an adamantane-like structure.



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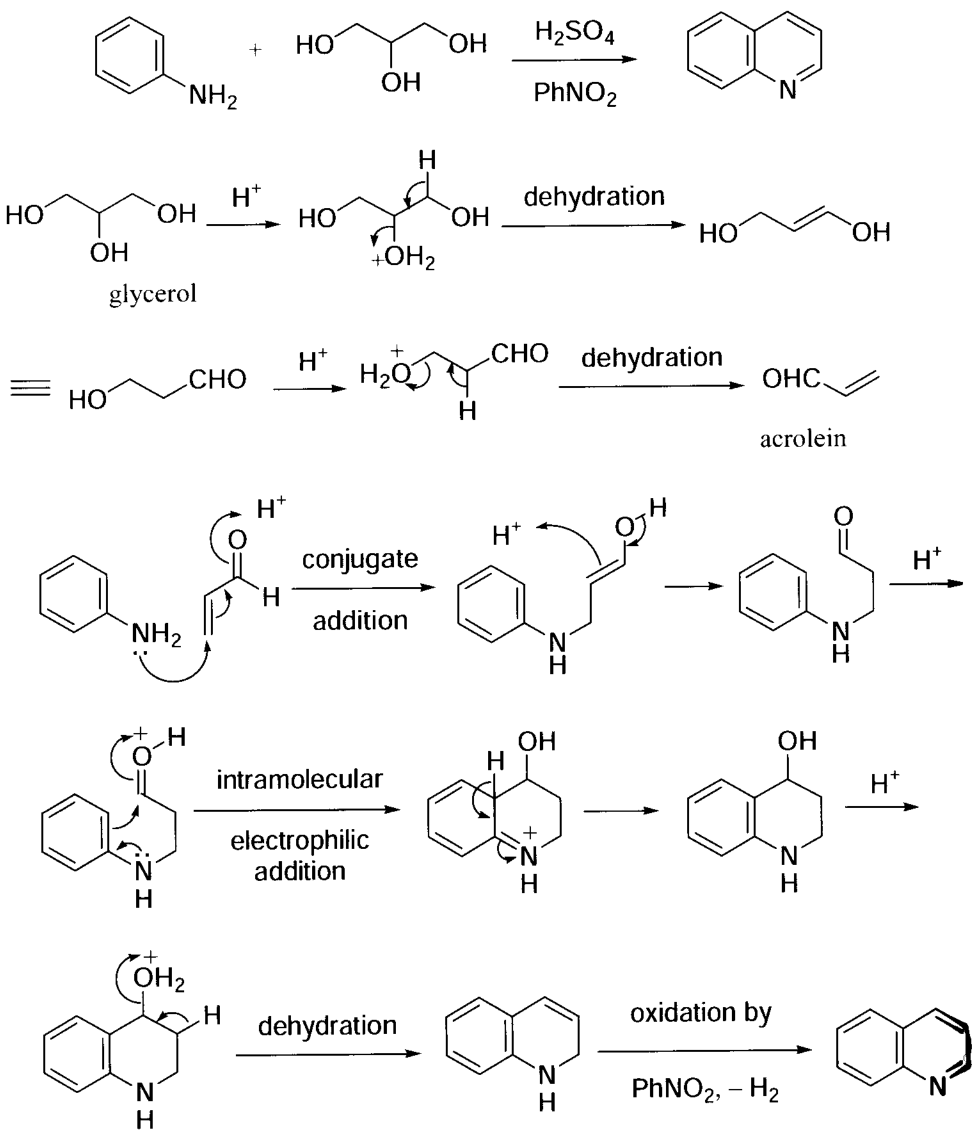
Skraup quinoline synthesis



For an alternative mechanism, see that of the Doebner–von Miller reaction (page 104).

References

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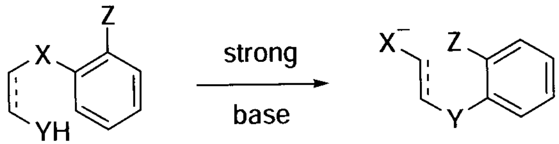
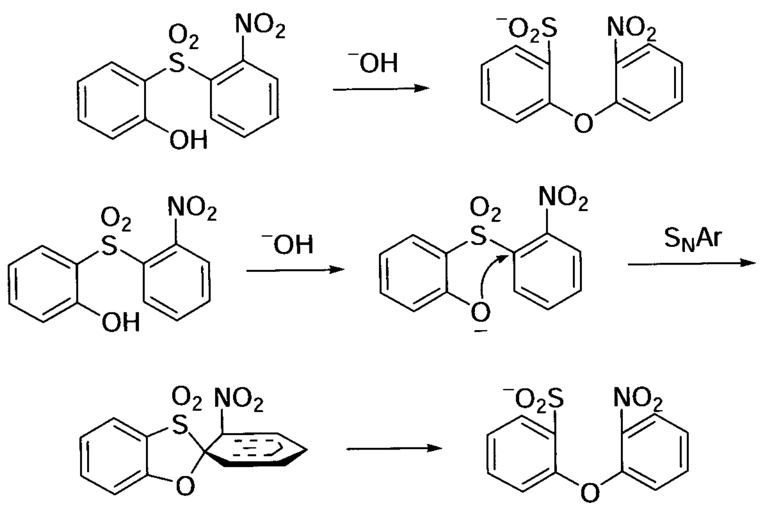
Smiles rearrangement

General scheme:



X = S, SO, SO_2, O, CO_2
YH = OH, NHR, SH, CH_2R, CONHR
Z = NO_2, SO_2R

e.g.



spirocyclic anion intermediate
(Meisenheimer complex)

References

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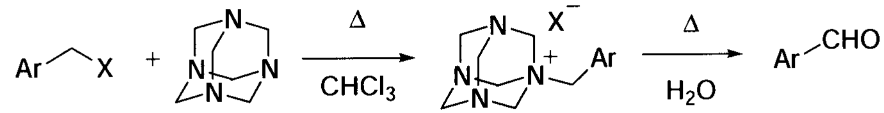
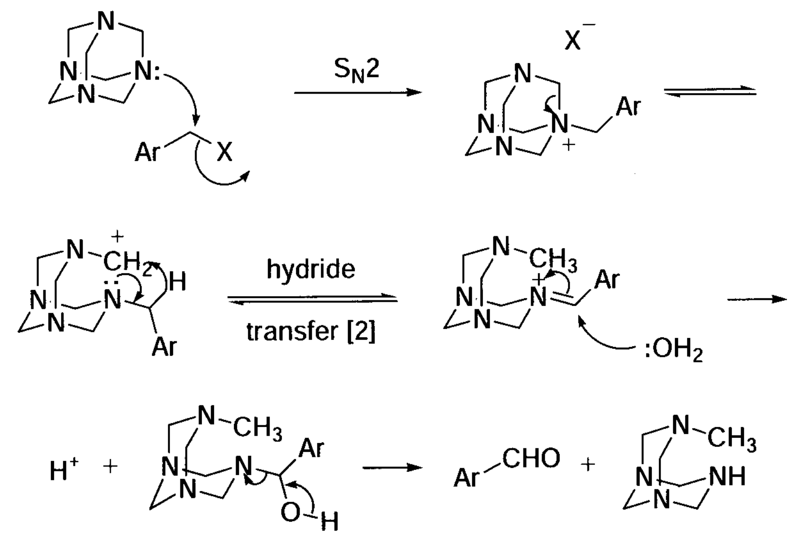
Sommelet reaction

Transformation of benzyl halides to the corresponding benzaldehydes with the aide of hexamethylenetetramine.

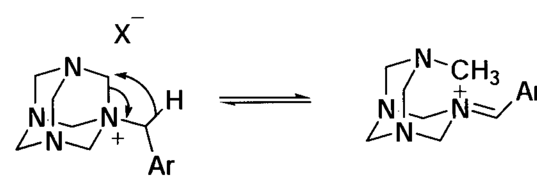


Hexamethylenetetramine



hemiaminal

The hydride transfer and the ring-opening of hexamethylenetetramine may occur in a synchronized fashion:



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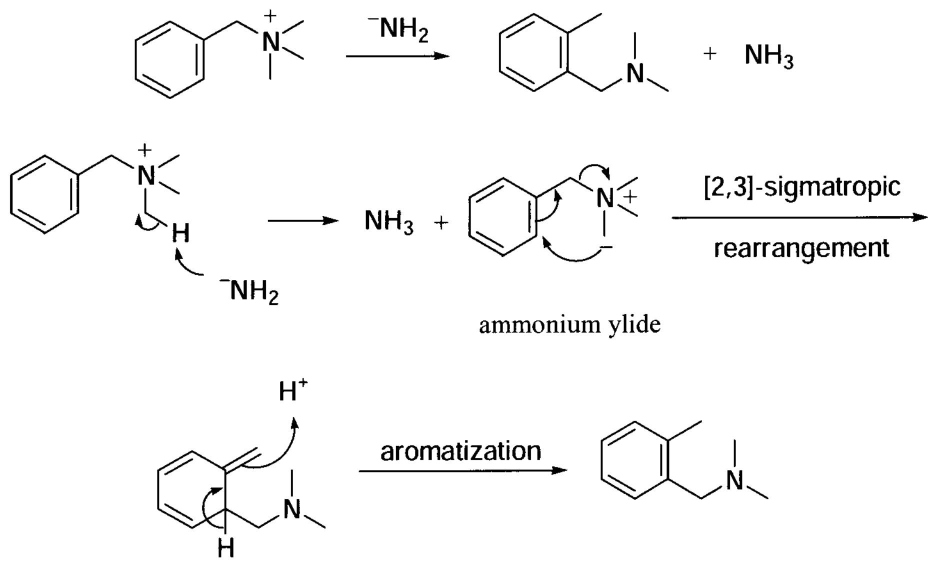
Sommelet–Hauser (ammonium ylide) rearrangement



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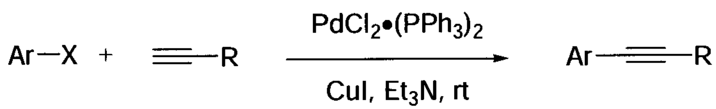
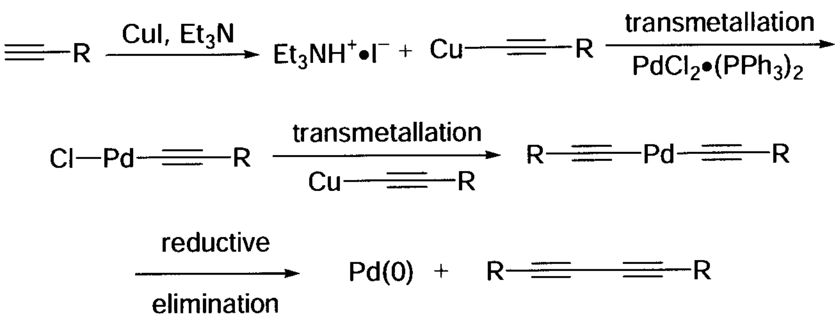
Sonogashira reaction

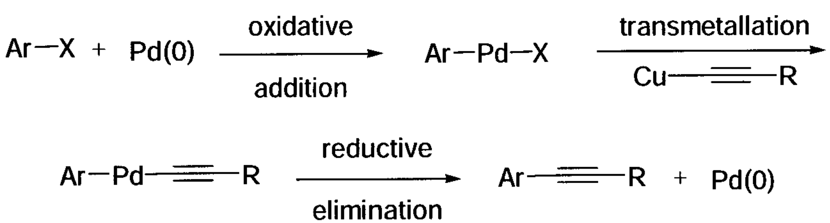
Pd-Cu-catalyzed cross-coupling of organohalides with terminal alkynes. *Cf.* Castro–Stephens reaction.



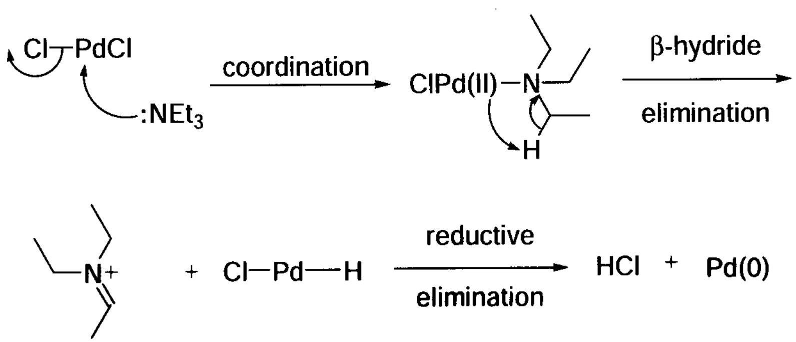
Generation of Pd(0):



Coupling reaction:



Note that Et_3N may reduce Pd(II) to Pd(0) as well, where Et_3N is oxidized to iminium ion at the same time [8]:



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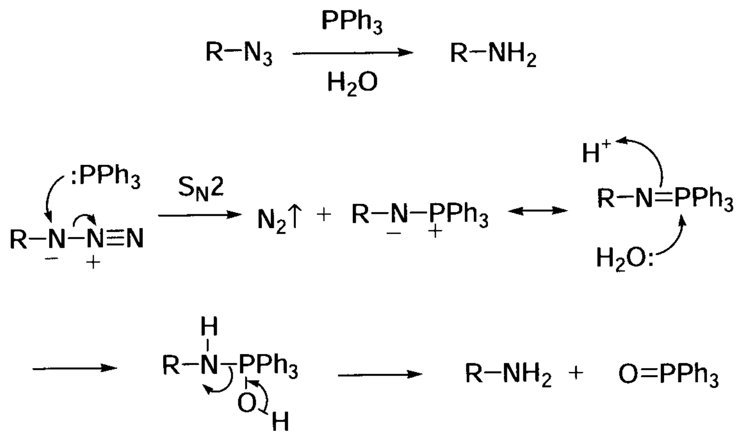
Staudinger reaction

Reduction of azides to amines by Ph_3P/H_2O.



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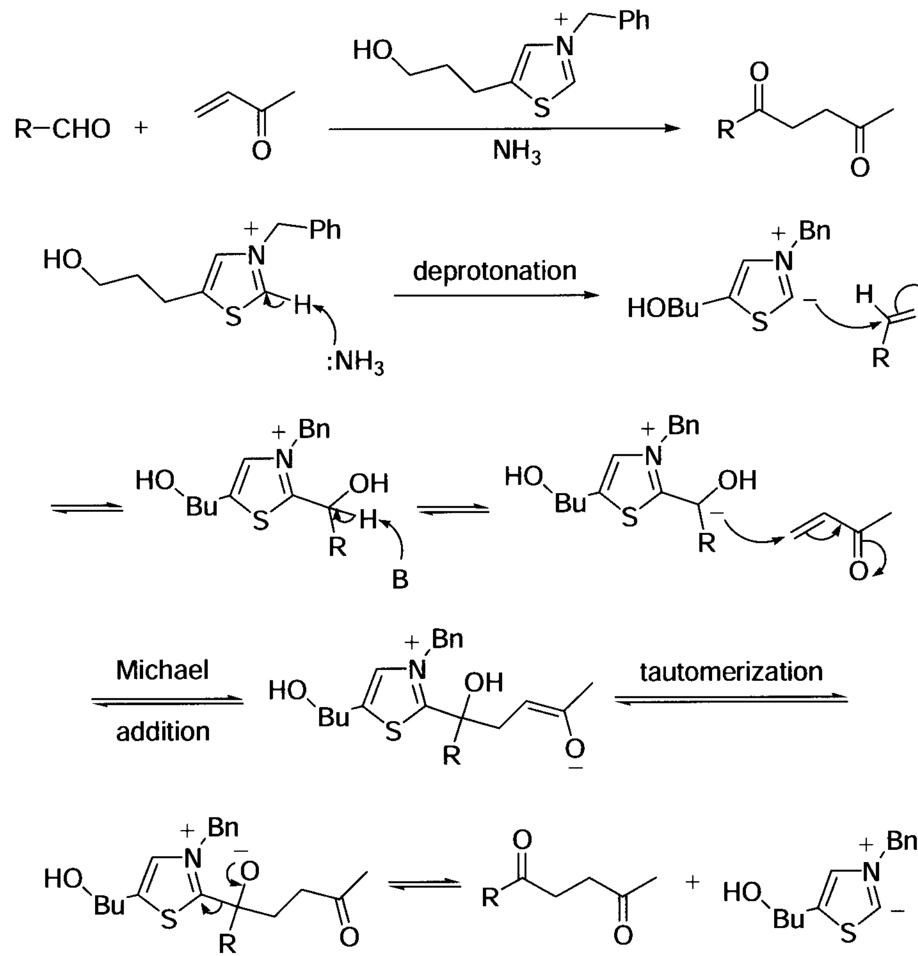
Stetter reaction (Michael–Stetter reaction)

1,4-Dicarbonyl derivatives from aldehydes and α,β-unsaturated ketones. The thiazolium catalyst serves as a safe surrogate for $^{-}$CN. *Cf.* Benzoin condensation.



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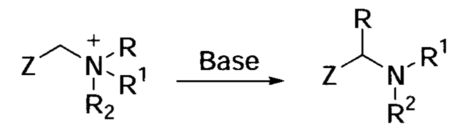
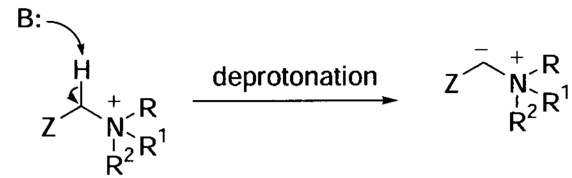
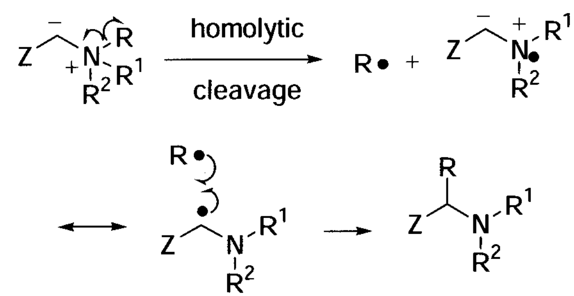
Stevens rearrangement

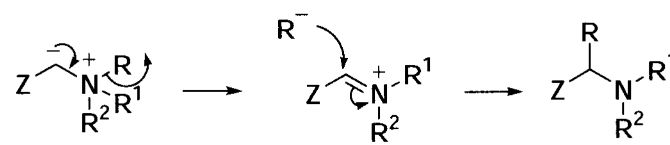




The contemporary radical mechanism:



The original ionic mechanism:



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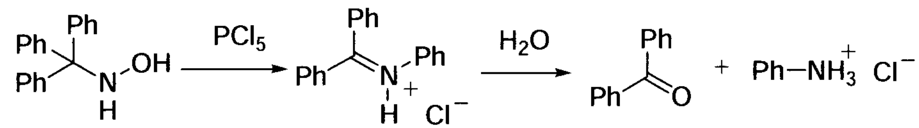
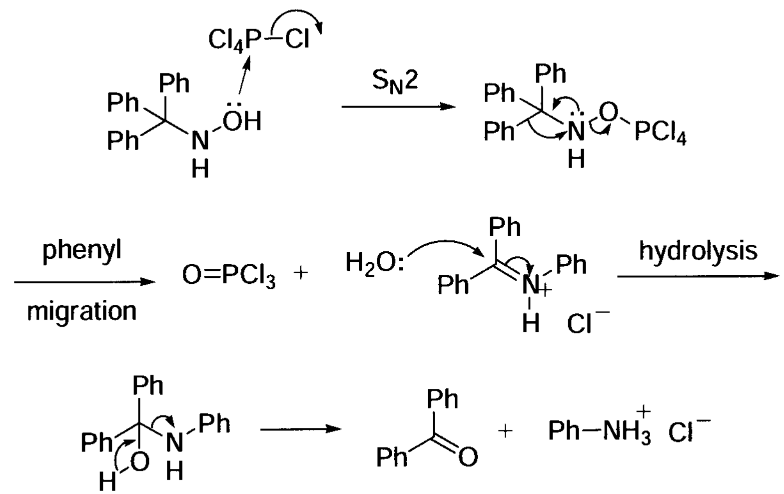
Stieglitz rearrangement





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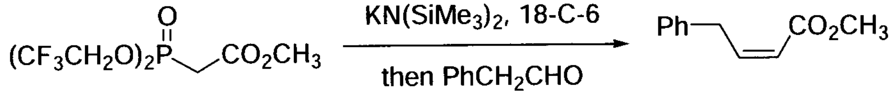
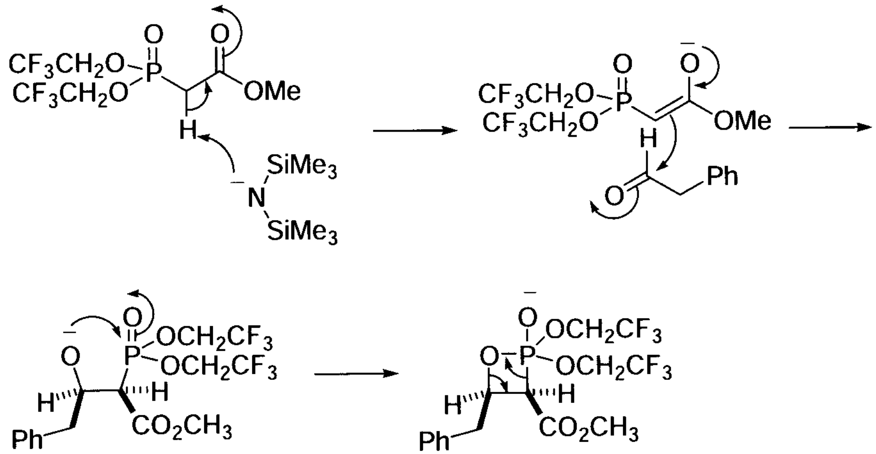
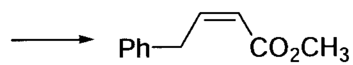
Still–Gennari phosphonate reaction

Horner–Emmons reaction using bis(trifluoroethyl)phosphonate to give *Z*-olefins.





erythro isomer, kinetic adduct



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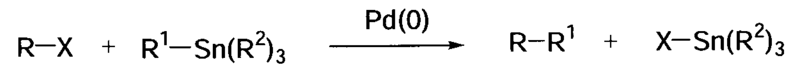
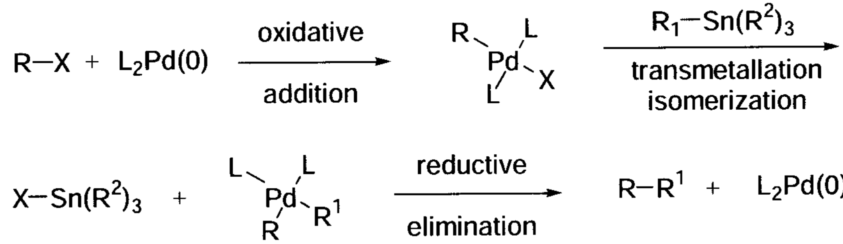
Stille coupling

Palladium-catalyzed cross-coupling reaction of organostannanes with organic halides, triflates, *etc.* For the catalytic cycle, see Kumada coupling on page 208.





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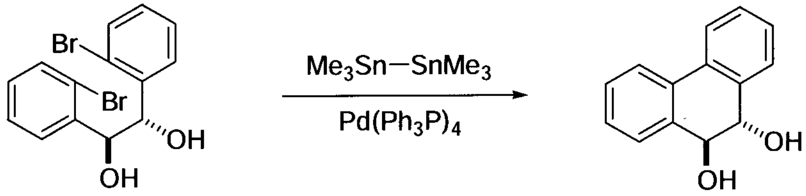
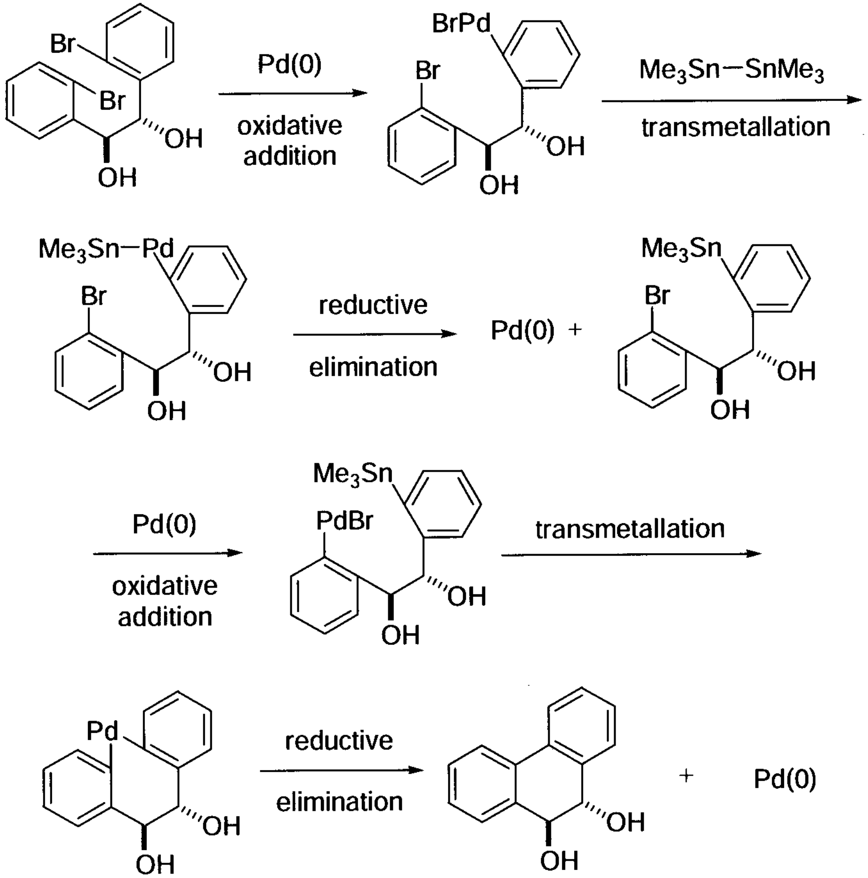
Stille–Kelly reaction

Palladium-catalyzed intramolecular cross-coupling reaction of bis-aryl halides using ditin reagents.





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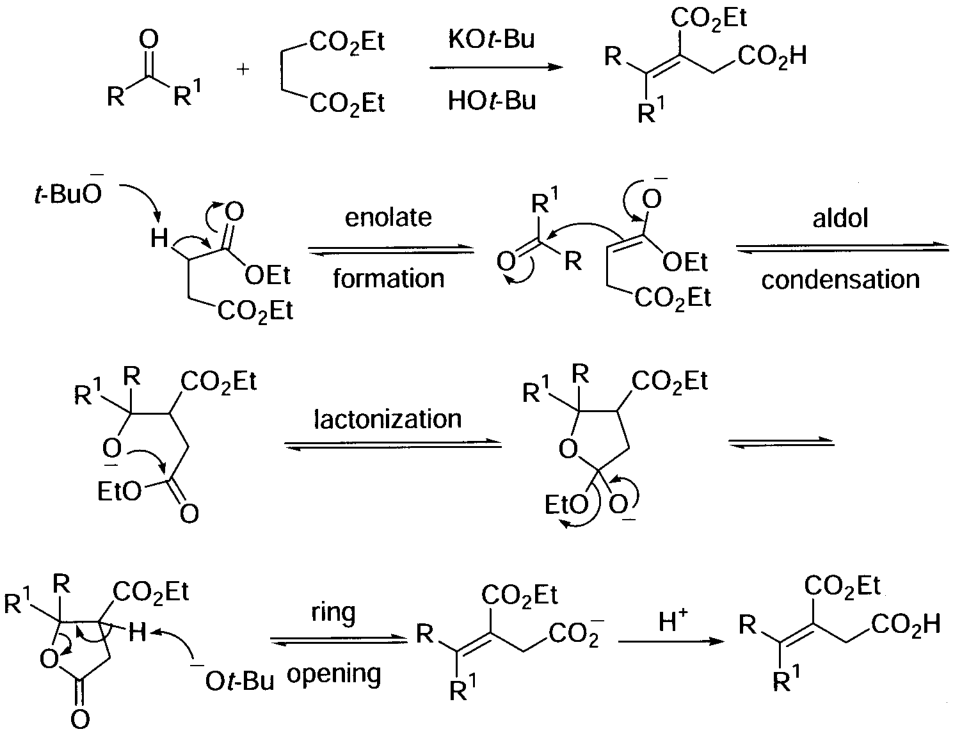
Stobbe condensation



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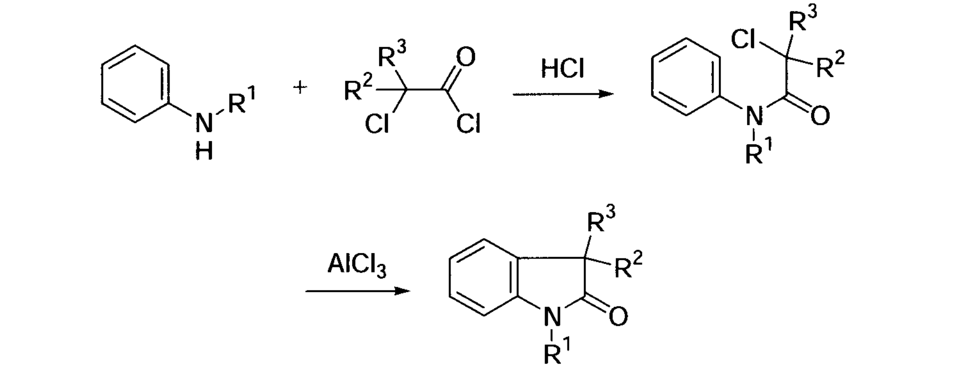
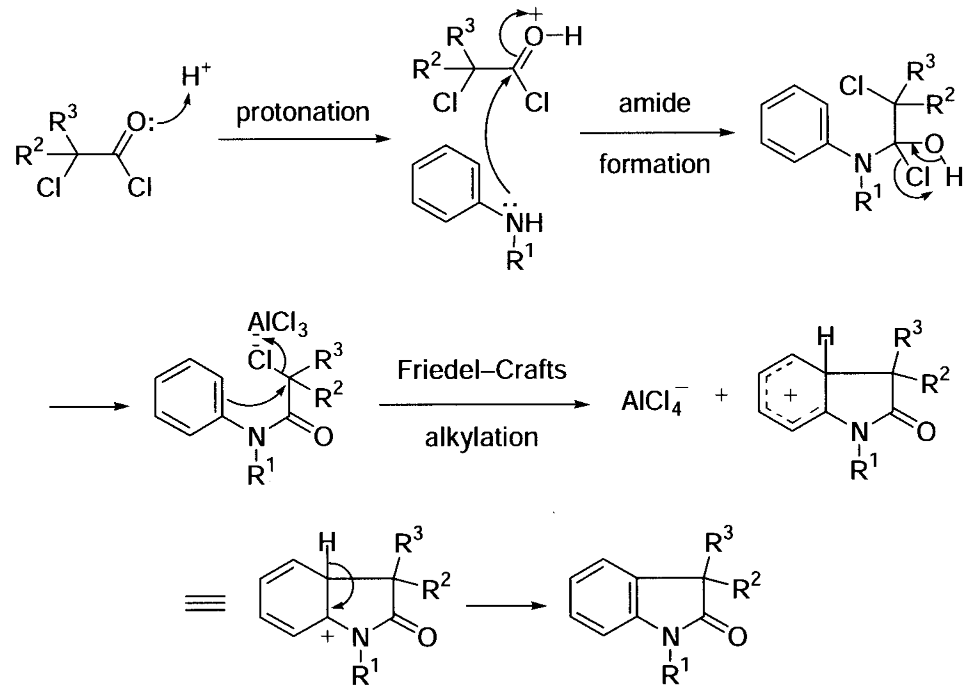
Stollé synthesis

Acid-catalyzed indolinone formation from aniline and α-chlorocarboxylic acid chloride.





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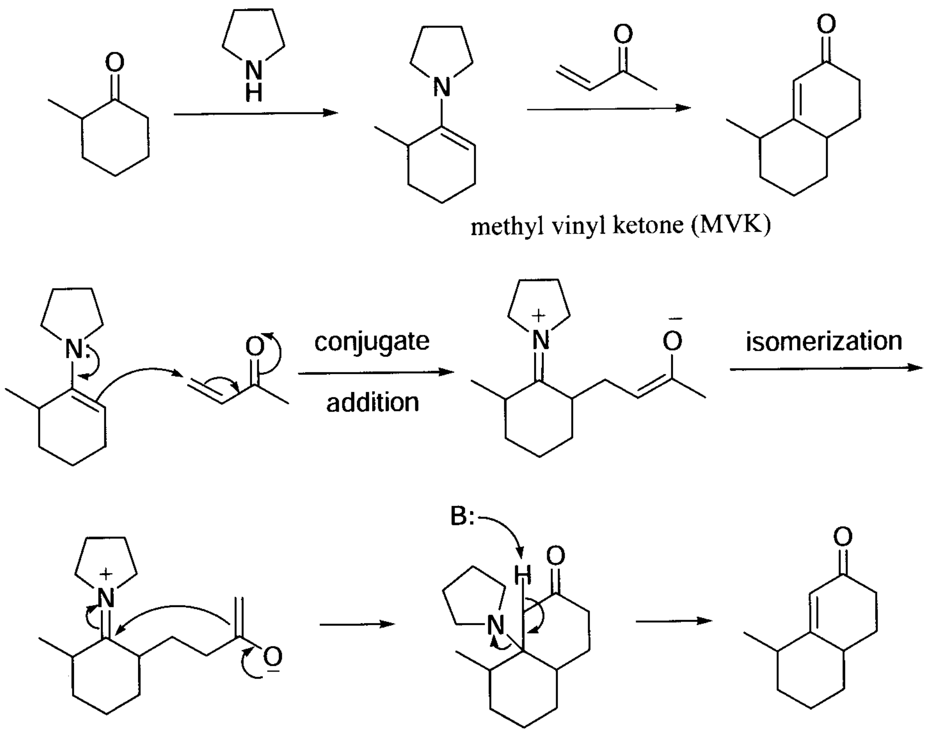
Stork enamine reaction

A variant of the Robinson annulation, where bulky amines such as pyrrolidine are used, making the conjugate addition to MVK take place at the less hindered side of two possible enamines.



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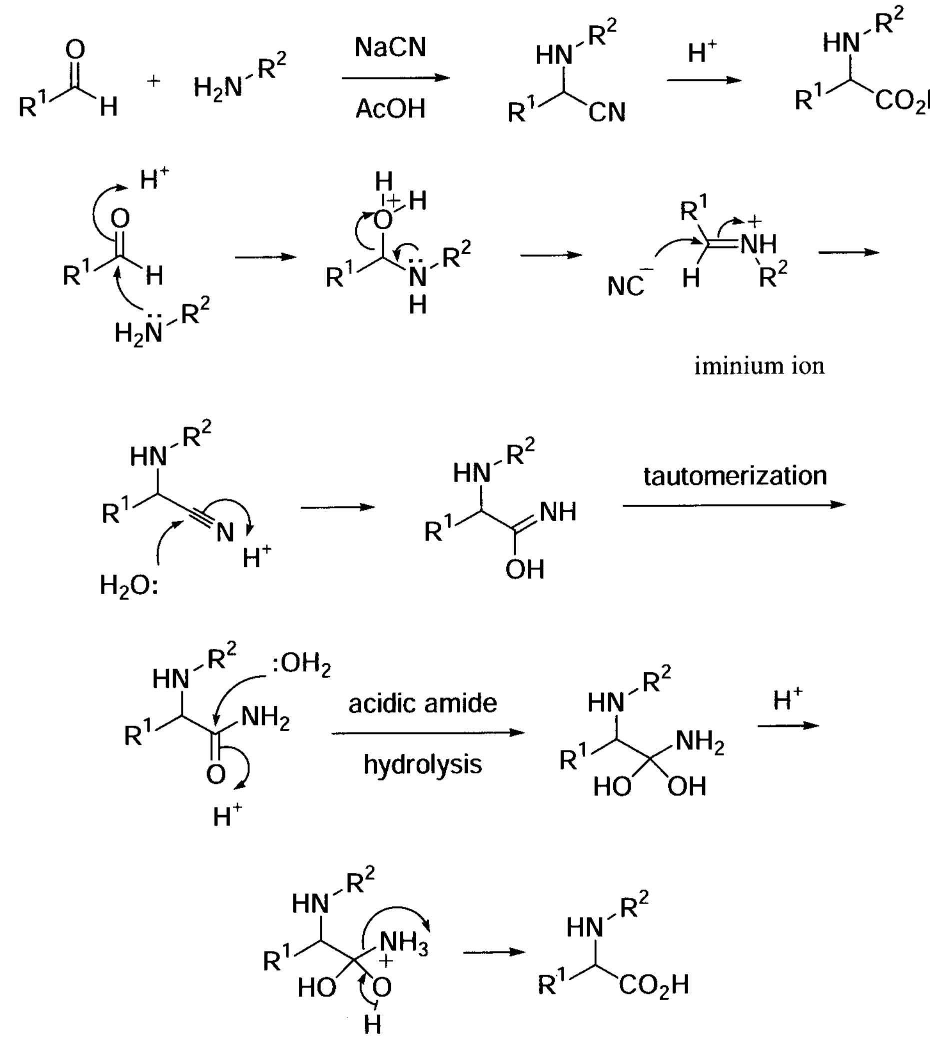
Strecker amino acid synthesis



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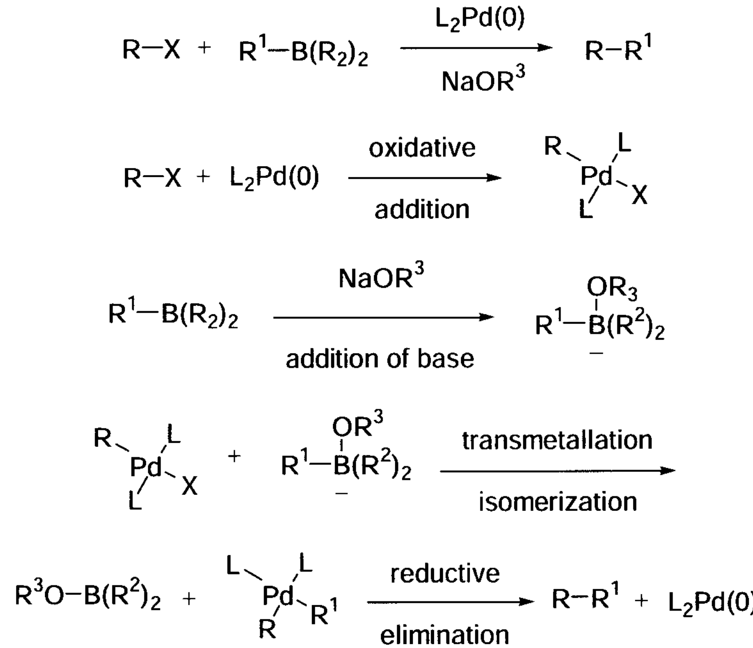
Suzuki coupling

Palladium-catalyzed cross-coupling reaction of organoboranes with organic halides, triflates, *etc.* in the presence of a base (transmetallation is reluctant to occur without the activating effect of a base). For the catalytic cycle, see Kumada coupling on page 208.



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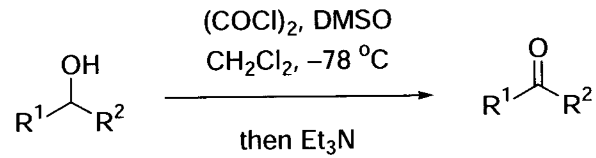
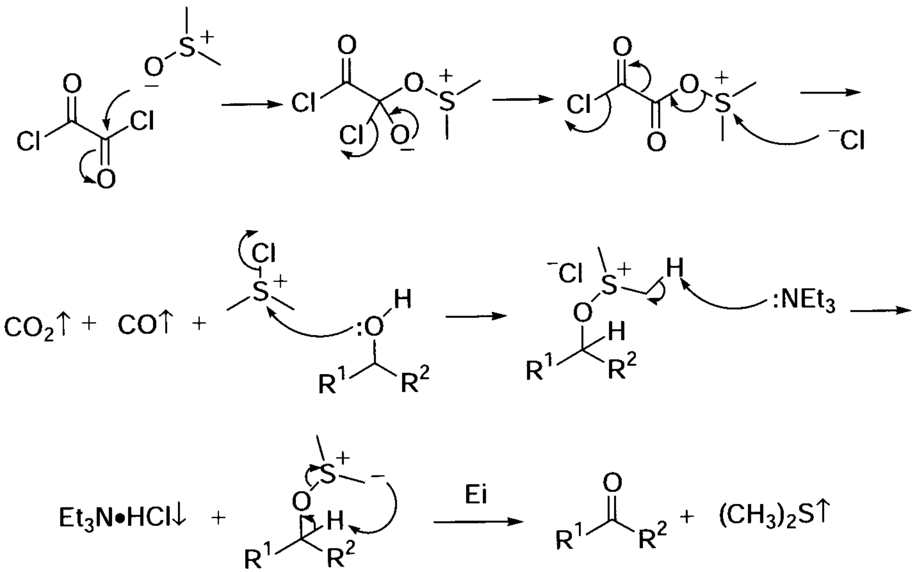
Swern oxidation

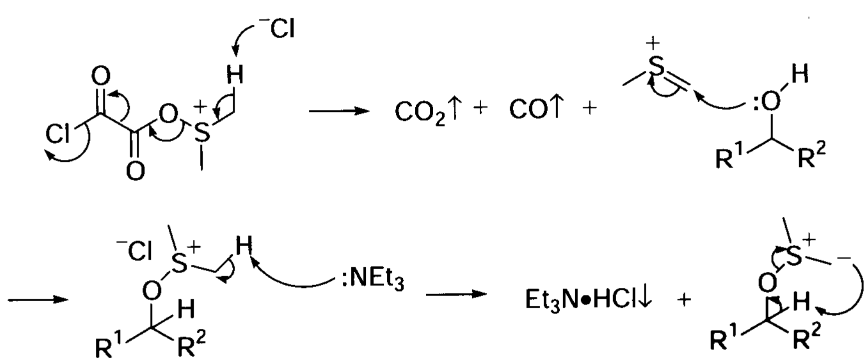
Oxidation of alcohols to the corresponding carbonyl compounds using $(COCl)_2$, DMSO, and quenching with Et_3N. Not applicable to allylic and benzylic alcohols.

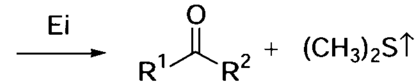




sulfur ylide

Alternatively:





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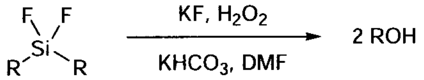
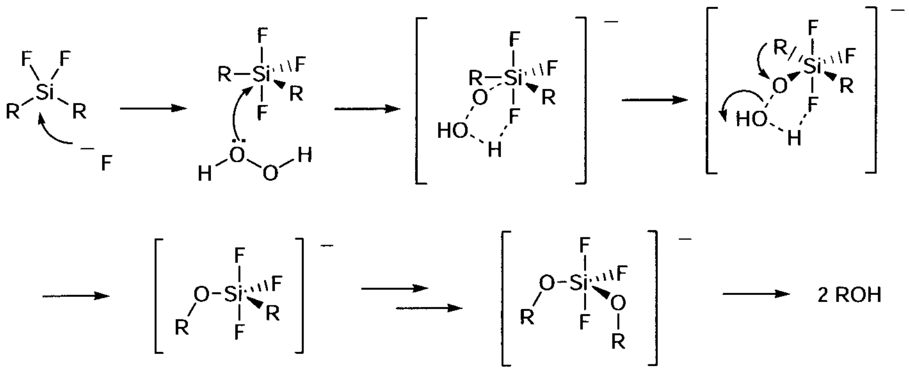
Tamao–Kumada oxidation

Oxidation of alkyl fluorosilanes to the corresponding alcohols.
Cf. Fleming oxidation.





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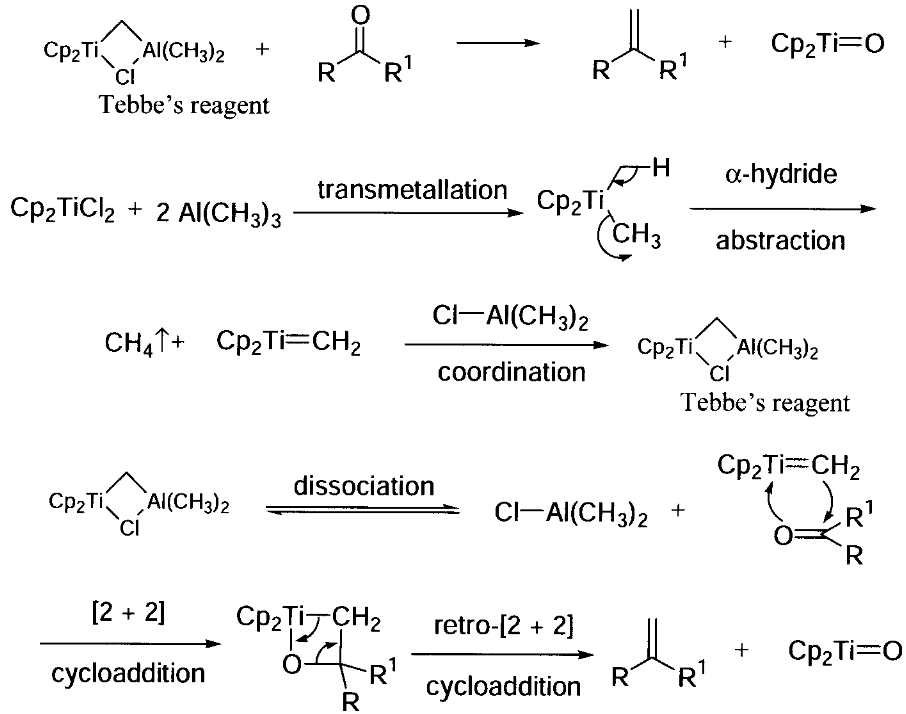
Tebbe olefination (Petasis alkenylation)



The Petasis reagent (Me_2TiCp_2, dimethyltitanocene) undergoes similar olefination reactions with ketones and aldehydes [5]. However, the mechanism is very different.

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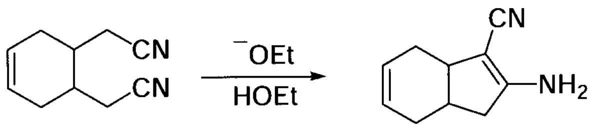
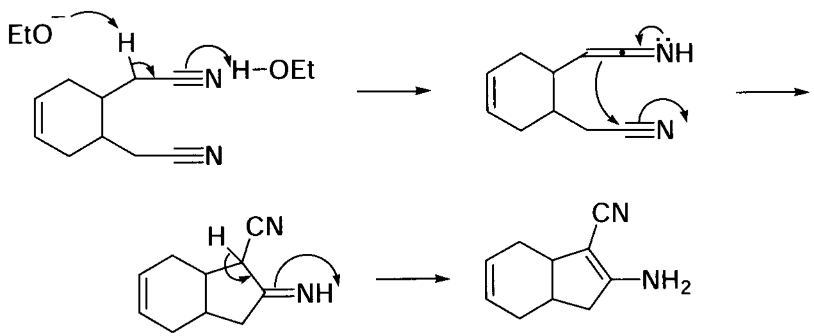
Thorpe–Ziegler reaction

The intramolecular version of the Thorpe reaction.





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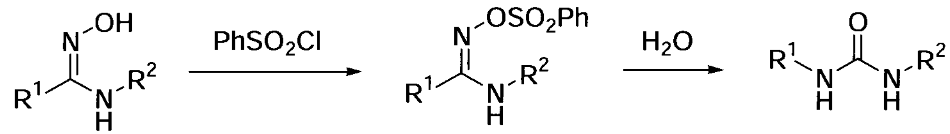
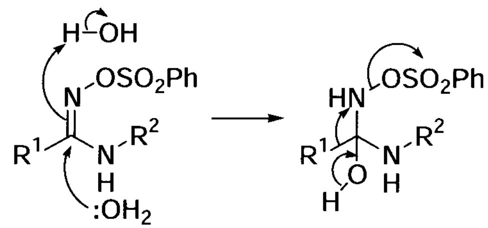
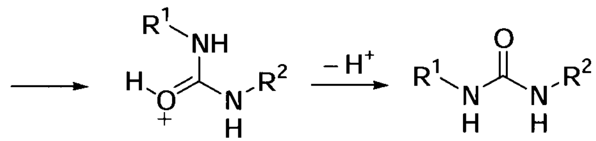
Tiemann rearrangement



amidoxime urea



The substituent *anti* to the leaving group ($^-OSO_2Ph$) migrates.



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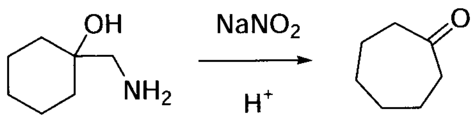
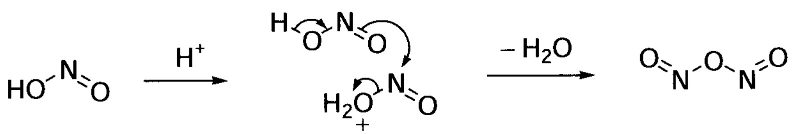
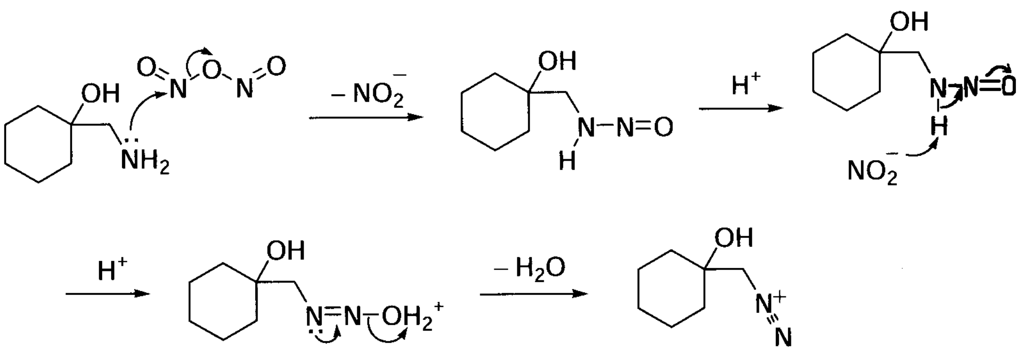
Tiffeneau–Demjanov rearrangement



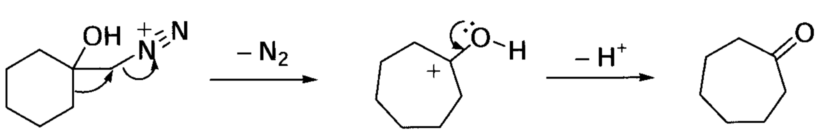
Step 1, Generation of N_2O_3



Step 2, Transformation of amine to diazonium salt



Step 3, Ring-expansion *via* rearrangement



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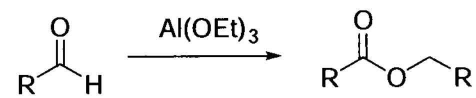
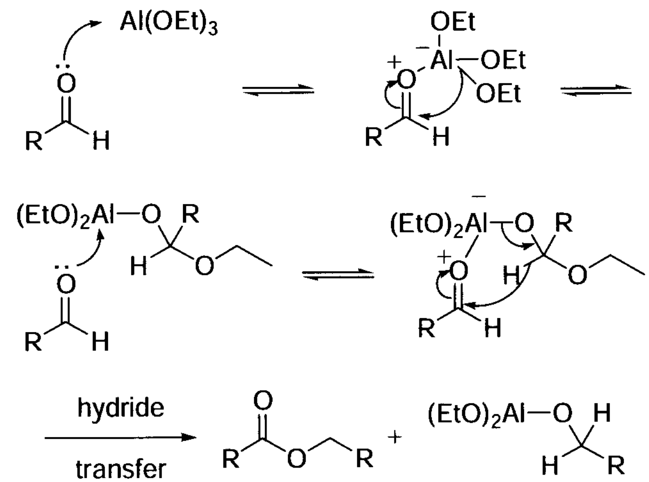
Tishchenko reaction

Esters from the corresponding aldehydes and $Al(OEt)_3$.





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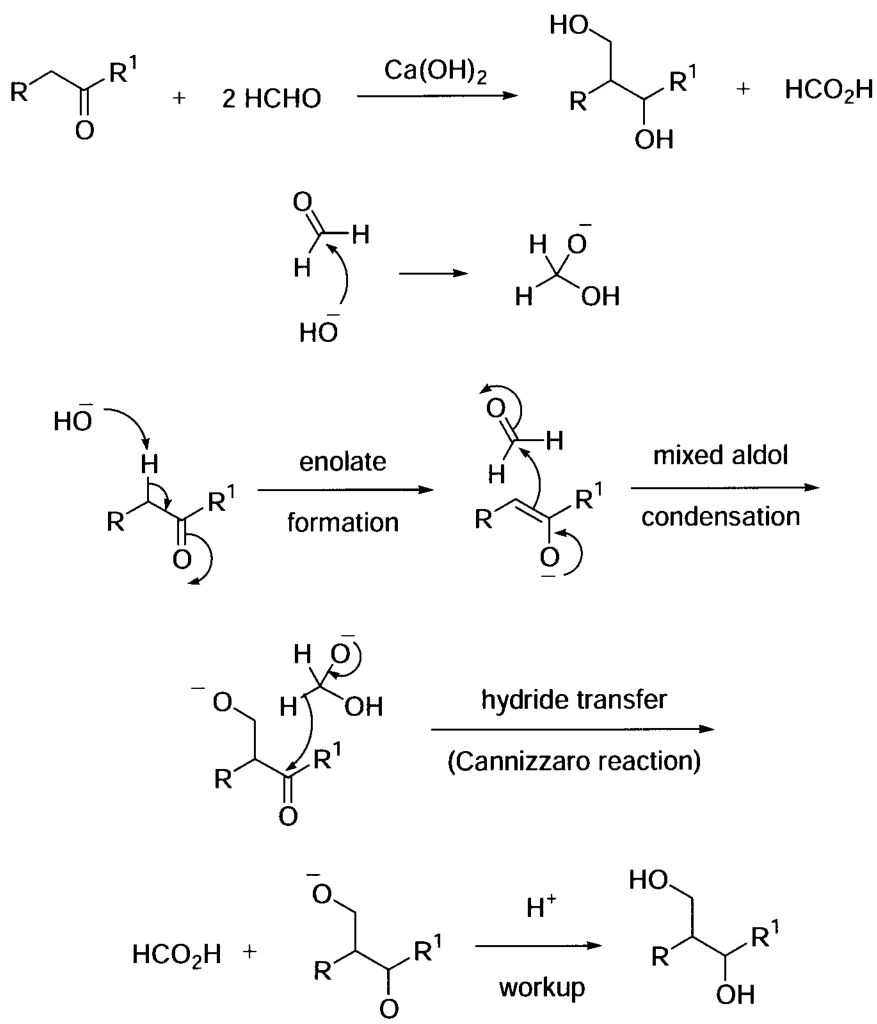
Tollens reaction



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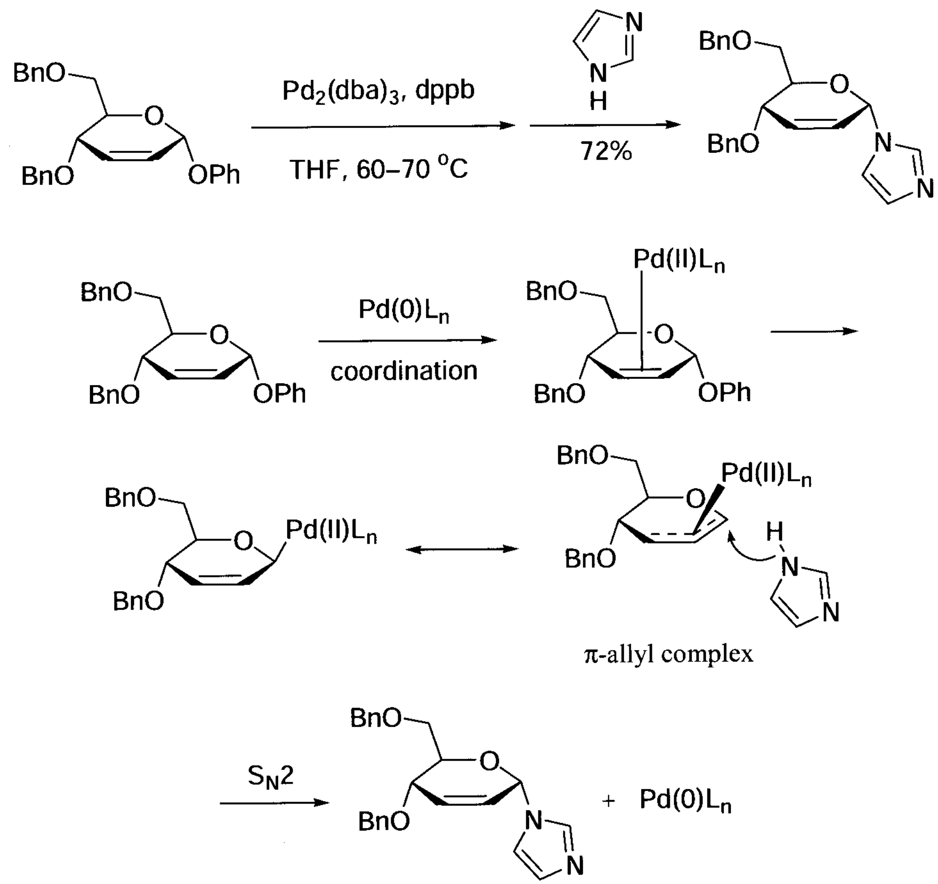
Tsuji–Trost reaction



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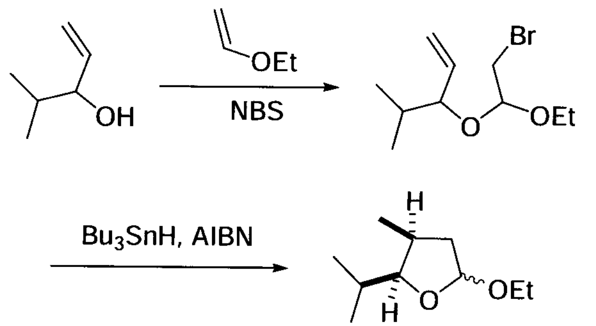
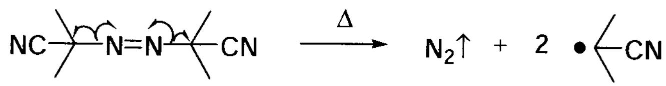
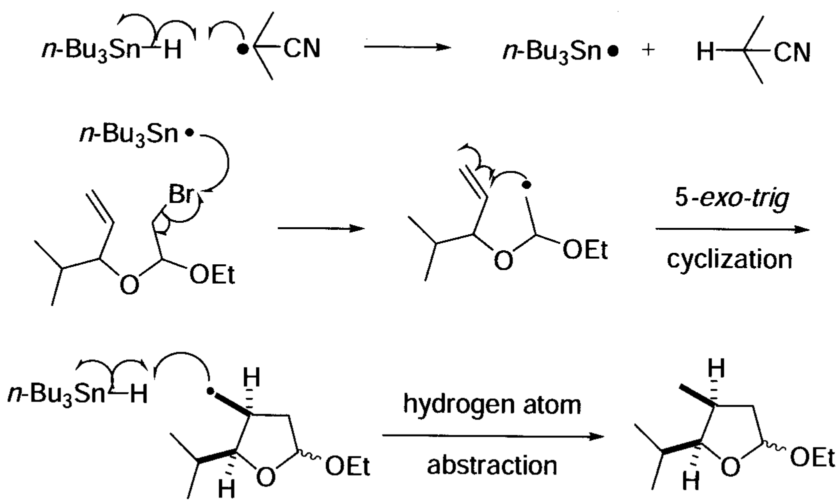
Ueno–Stork cyclization





2,2'-azobisisobutyronitrile (AIBN)



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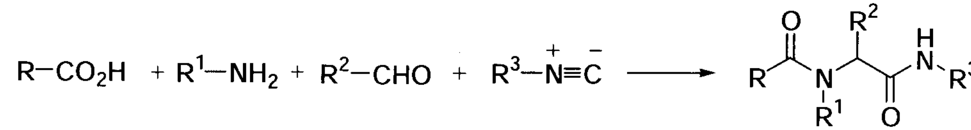
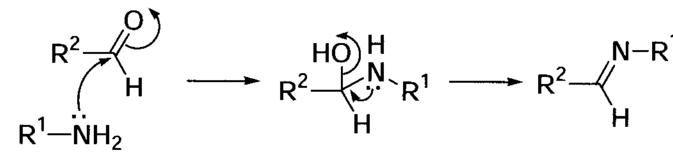
Ugi reaction

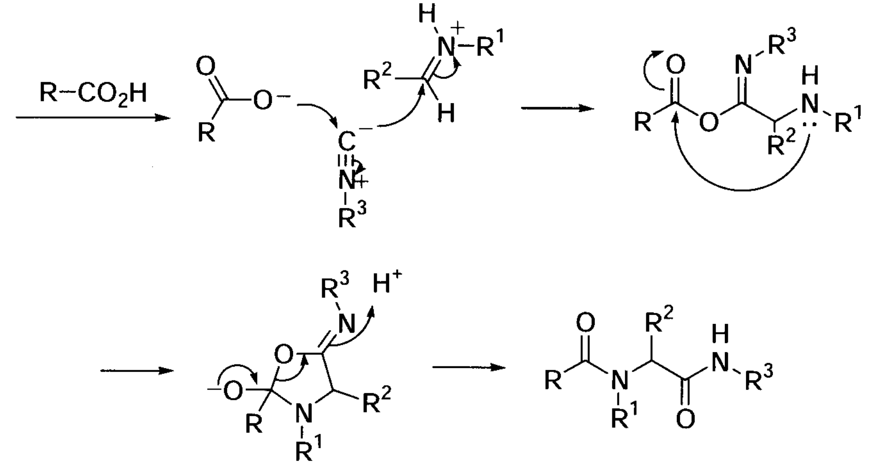
Four-component condensation (4CC) of carboxylic acids, *C*-isocyanides, amines, and oxo compounds to afford peptides. *Cf.* Passerini reaction.



isocyanide



imine



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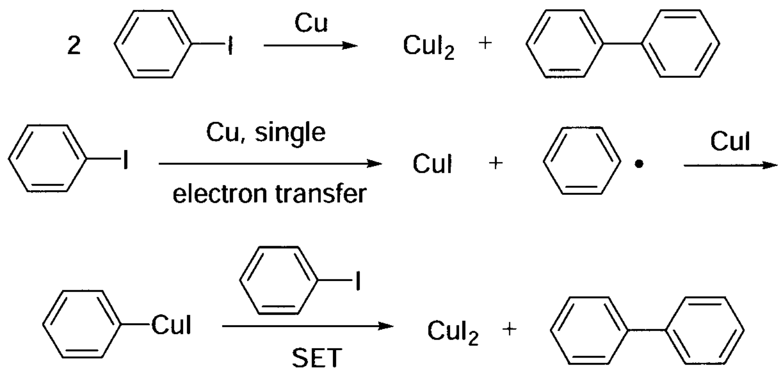
Ullmann reaction

Homocoupling of aryl iodide in the presence of Cu.



The overall transformation of PhI to PhCuI is an oxidative addition process.

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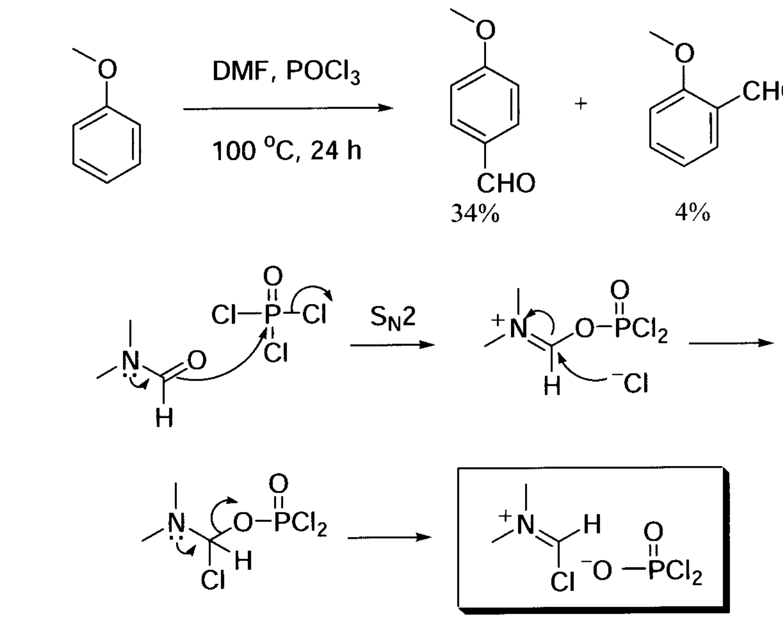
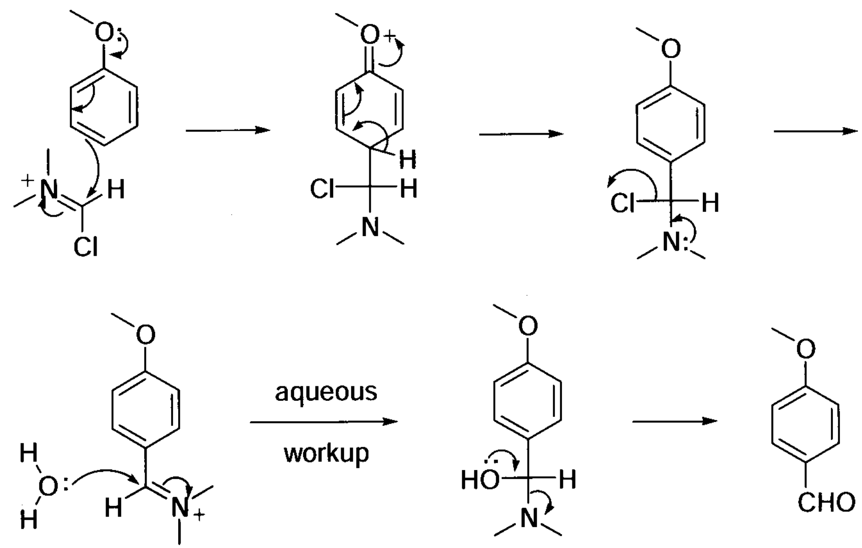
Vilsmeier–Haack reaction



Vilsmeier–Haack reagent



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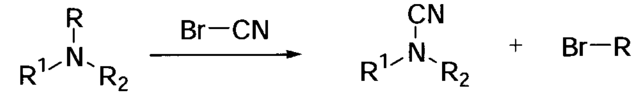
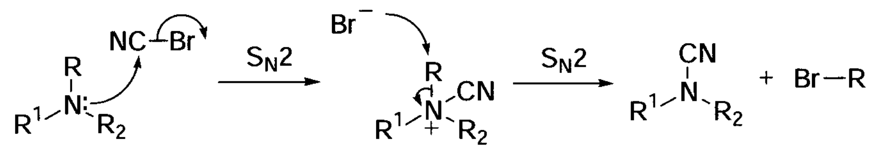
von Braun reaction

Treatment of tertiary amines with cyanogen bromide, resulting in cyanamide and alkyl halides.



Cyanogen bromide (BrCN) is a ***counterattack reagent.***



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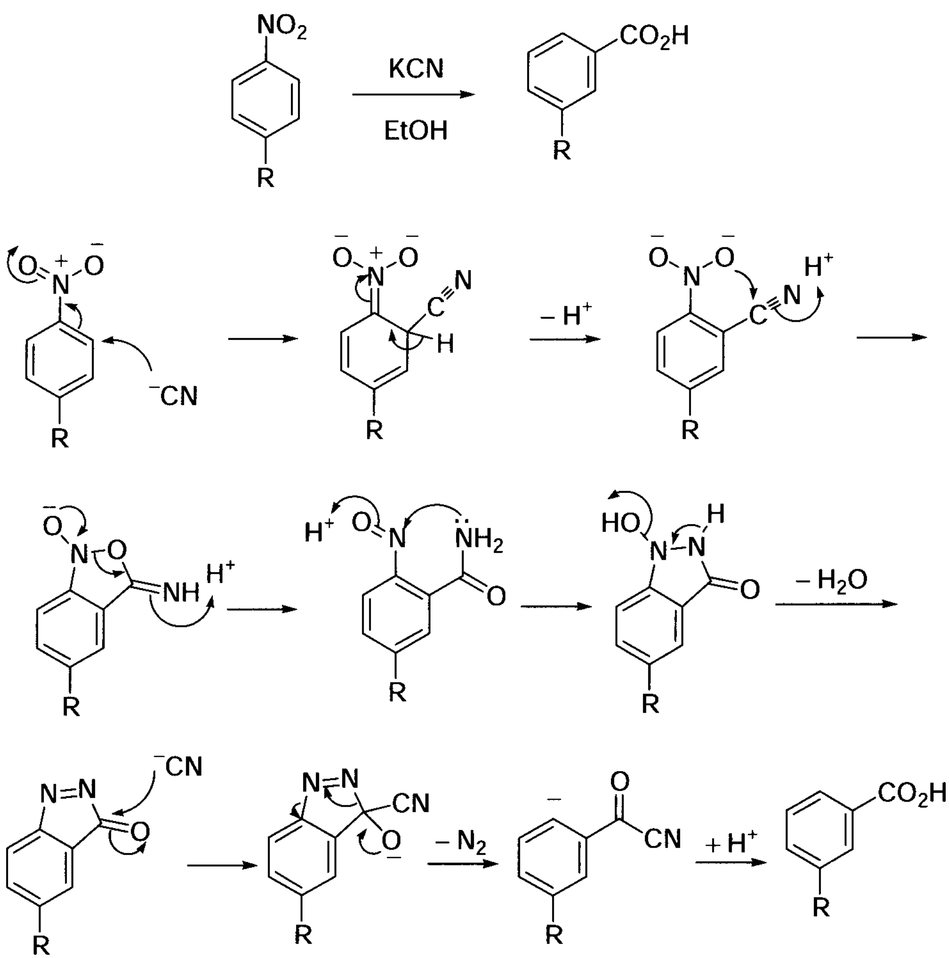
von Richter reaction



pyrazolone intermediate

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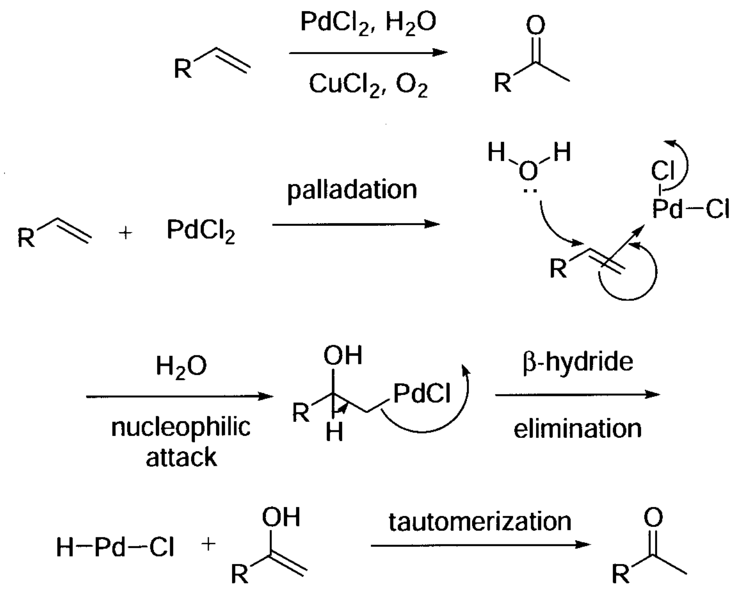
Wacker oxidation



$$H{-}Pd{-}Cl \longrightarrow Pd(0) + HCl$$

Regeneration of Pd(II):

$$Pd(0) + 2\ CuCl_2 \longrightarrow PdCl_2 + 2\ CuCl$$

Regeneration of Cu(II):

$$CuCl + O_2 \longrightarrow CuCl_2 + H_2O$$

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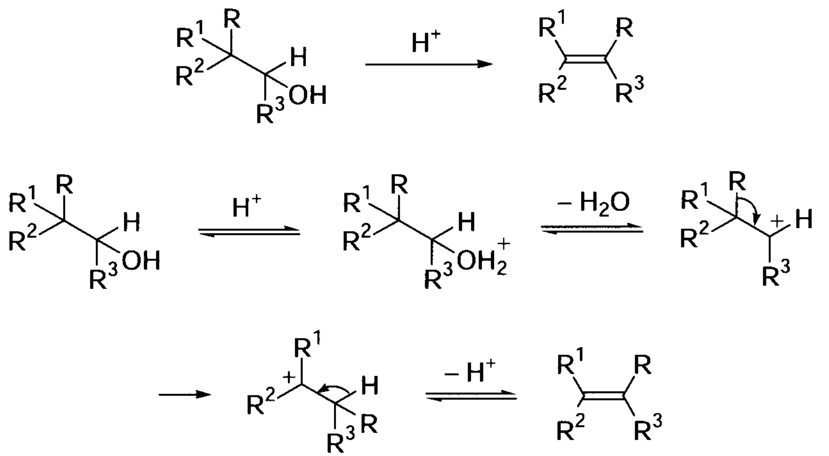
Wagner–Meerwein rearrangement



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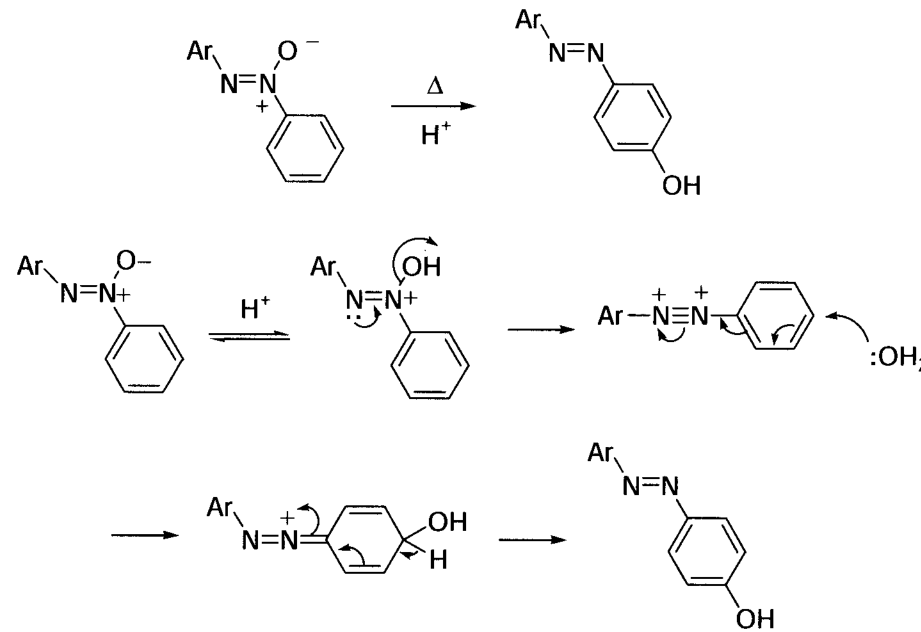
Wallach rearrangement



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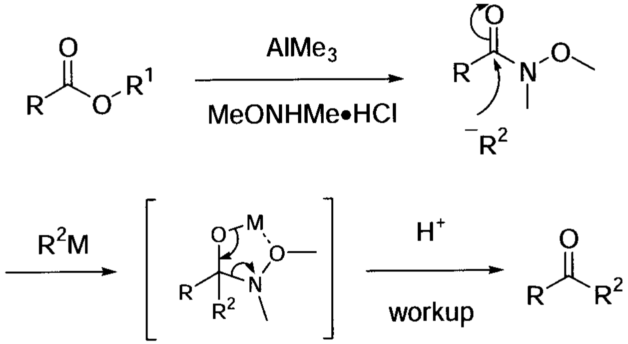
Weinreb amide



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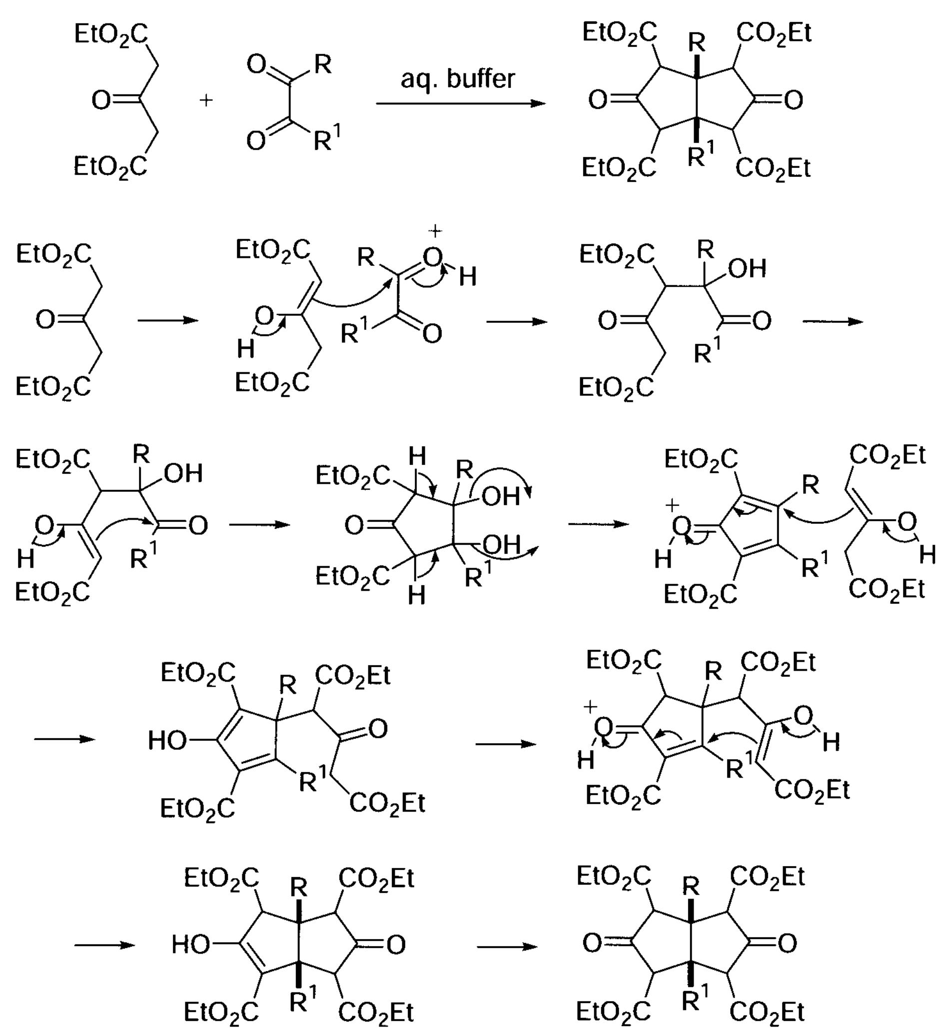
Weiss reaction

Synthesis of *cis*-bicyclo[3.3.0]octane-3,7-dione.



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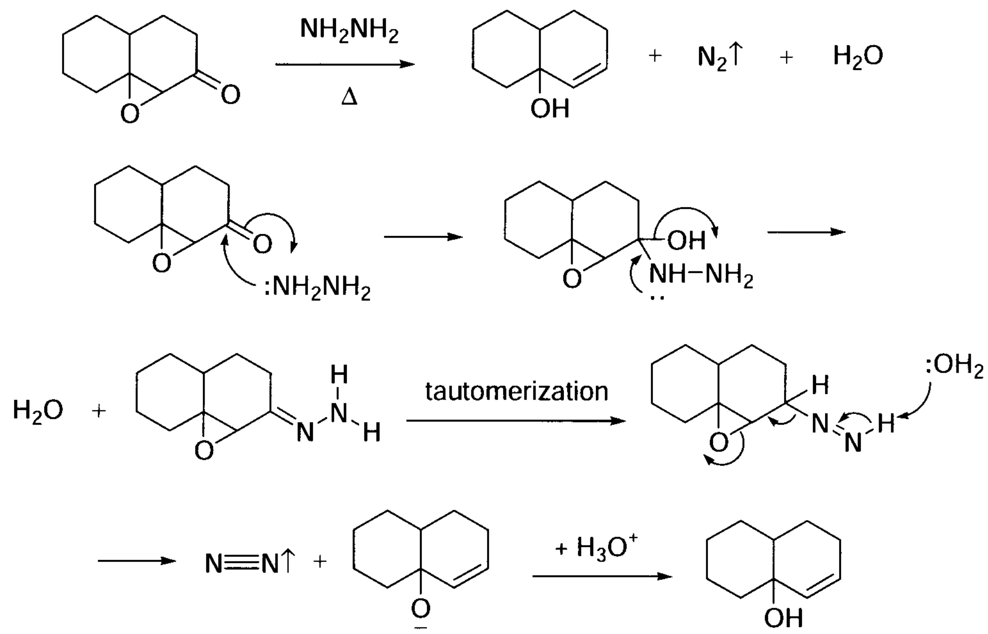
Wharton oxygen transposition reaction

Reduction of α,β-epoxy ketones by hydrazine to allylic alcohols.



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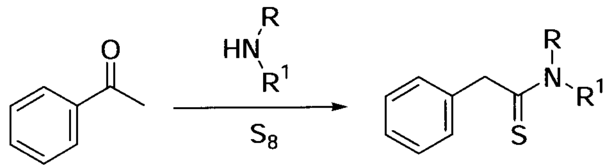
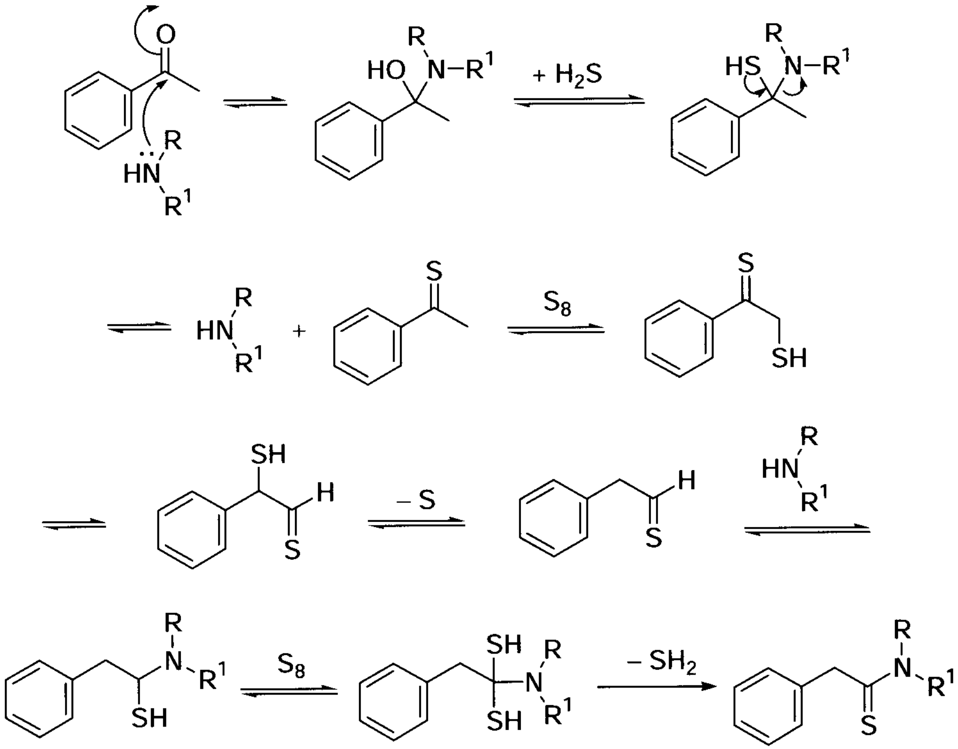
Willgerodt–Kindler reaction

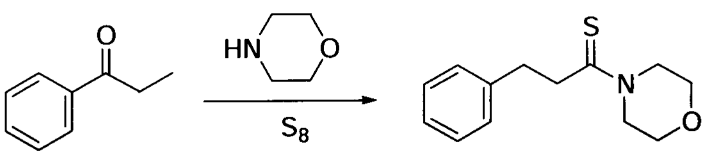
Conversion of ketones to the corresponding thioamide and/or ammonium salt.



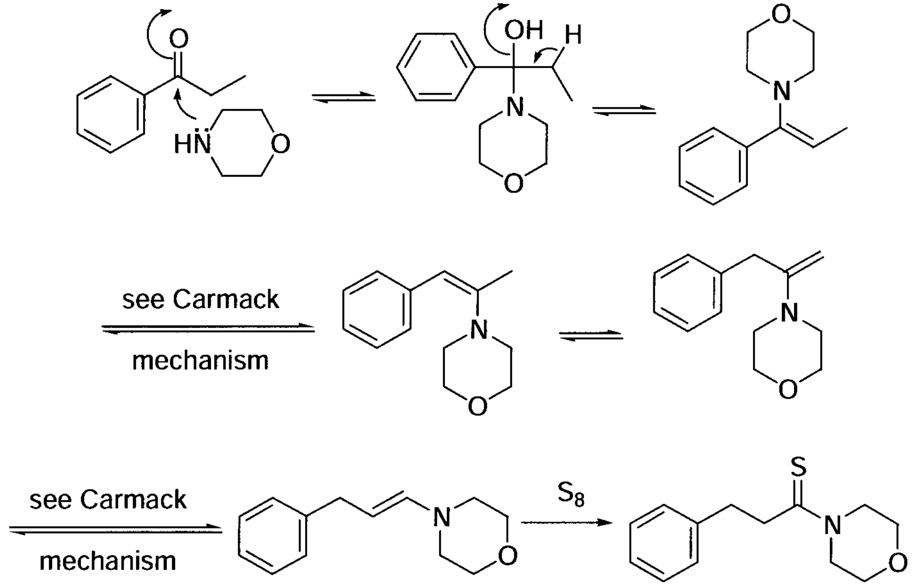
thioamide



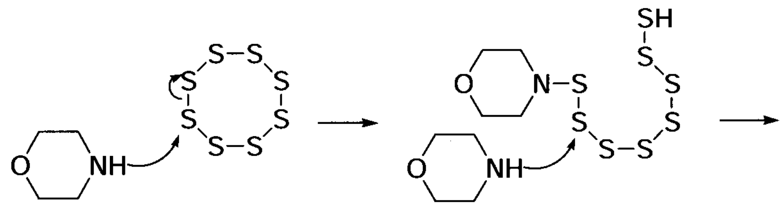
A slightly different mechanism has also been proposed:



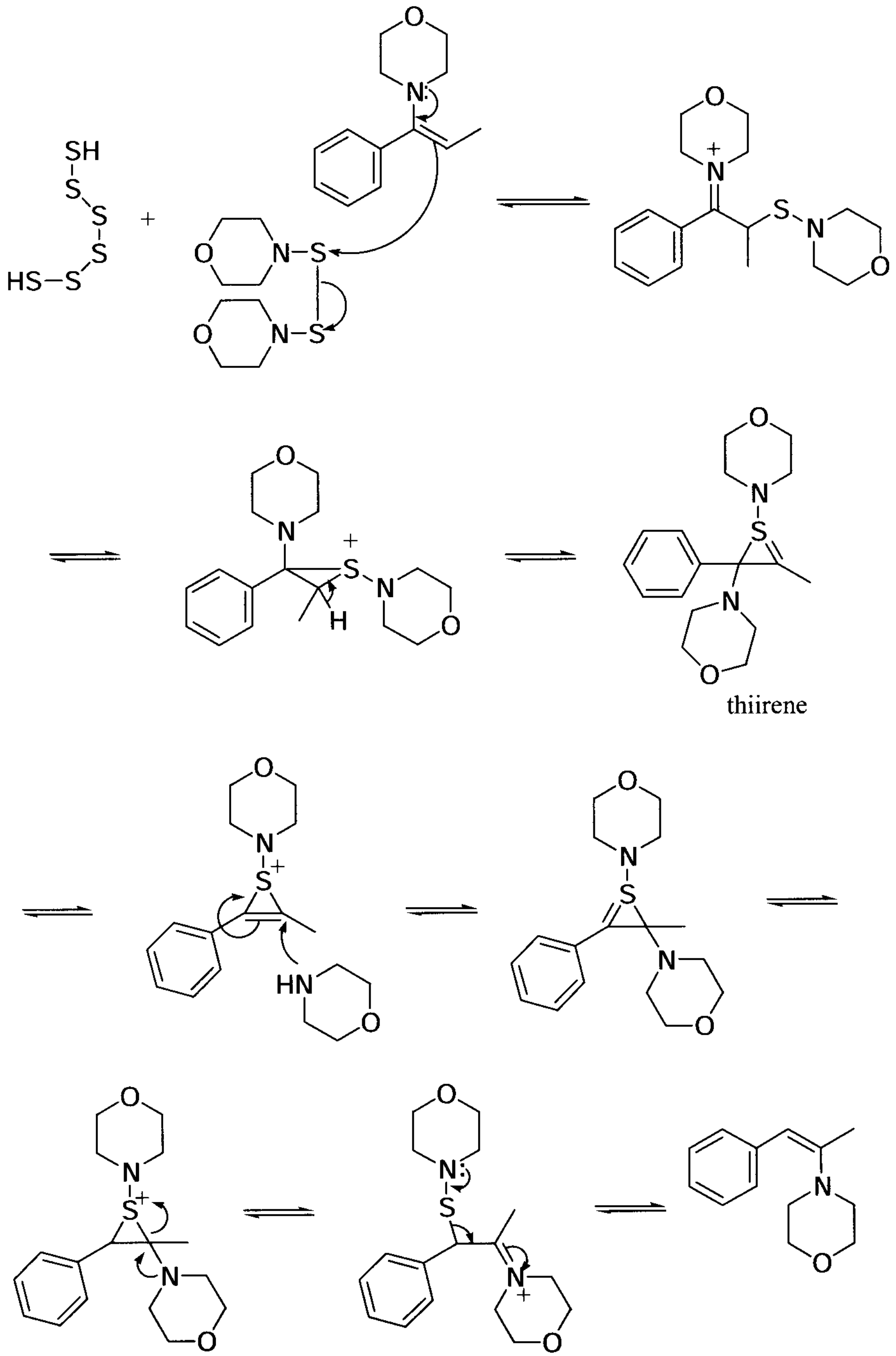
thioamide



In Carmack's mechanism [5], the most unusual movement of a carbonyl group from methylene carbon to methylene carbon was proposed to go through an intricate pathway *via* a highly reactive intermediate with a sulfur-containing heterocyclic ring. The sulfenamide serves as the isomerization catalyst:



sulfenamide



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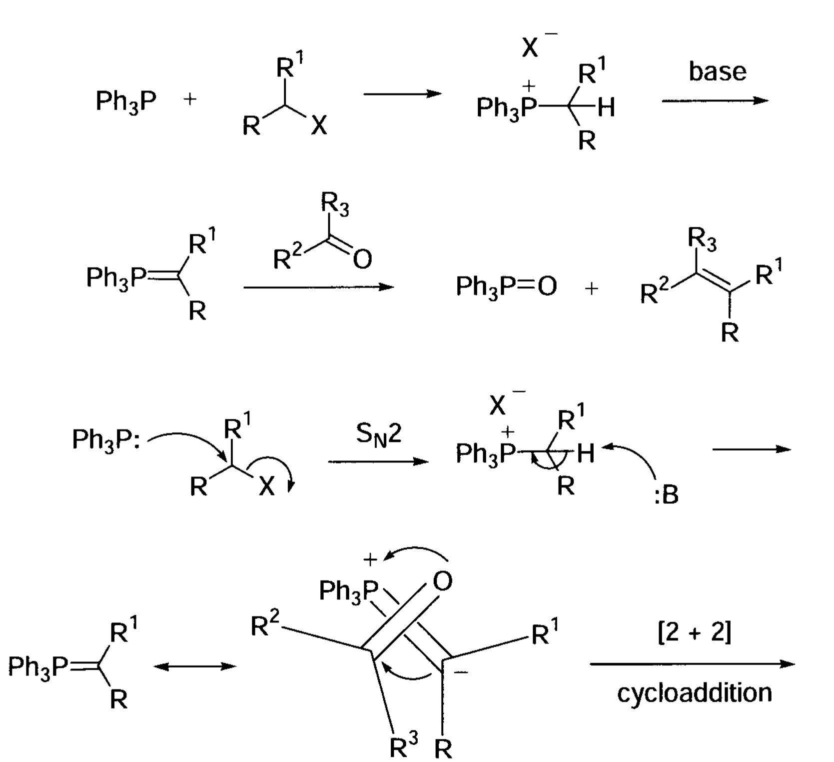
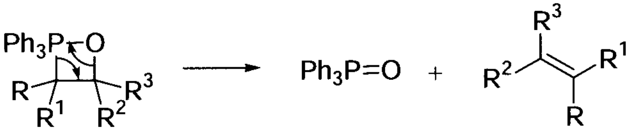
Wittig reaction

Olefination of carbonyls using phosphorus ylides.



"puckered" transition state, irreversible and concerted



oxaphosphetane intermediate

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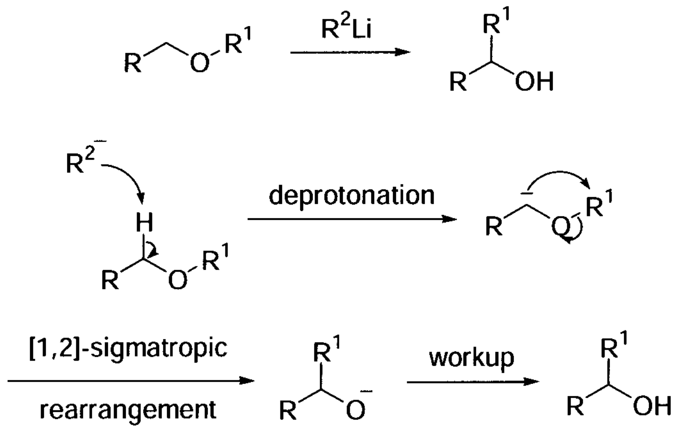
[1,2]-Wittig rearrangement

Treatment of ethers with alkyl lithium results in alcohols.



The radical mechanism is also possible as radical intermediates have been identified.

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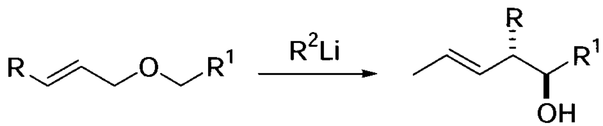
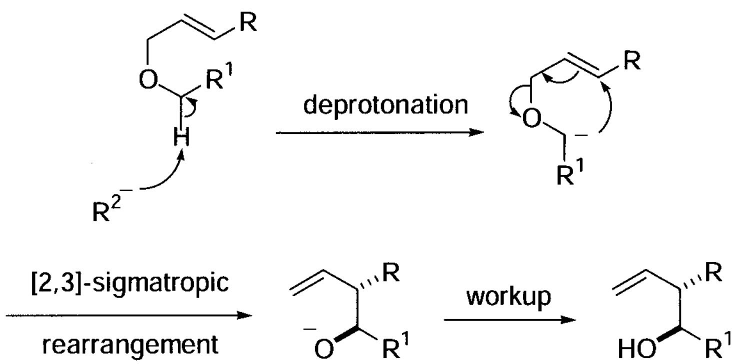
[2,3]-Wittig rearrangement

Transformation of allyl ethers into homoallylic alcohols by treatment with base. Also known as Still–Wittig rearrangement.



R^1 = alkynyl, alkenyl, Ph, COR, CN.



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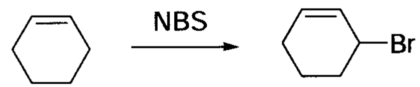
Wohl–Ziegler reaction

Allylic bromination.



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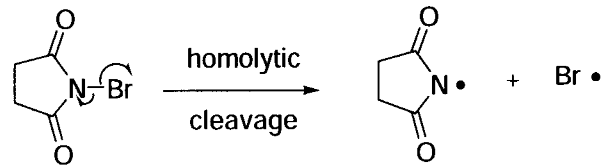

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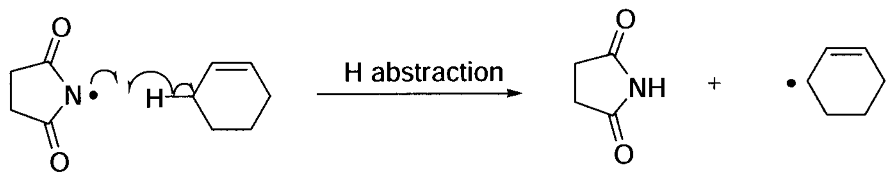

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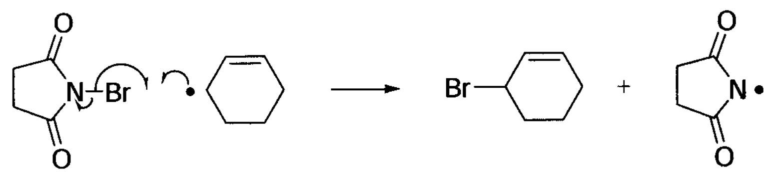

The succinimidyl radical now is available for the next cycle of the radical chain reaction

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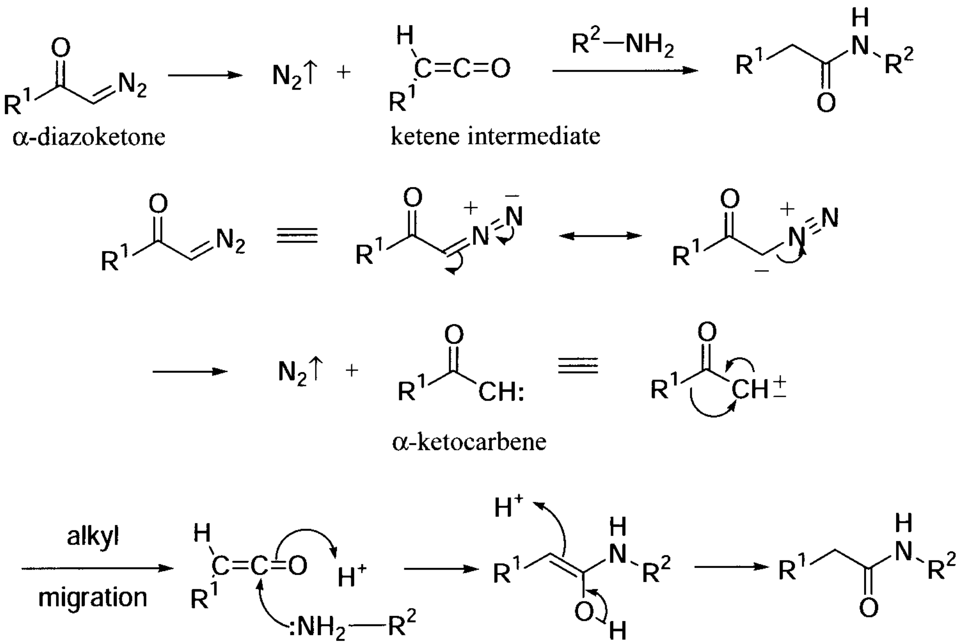
Wolff rearrangement



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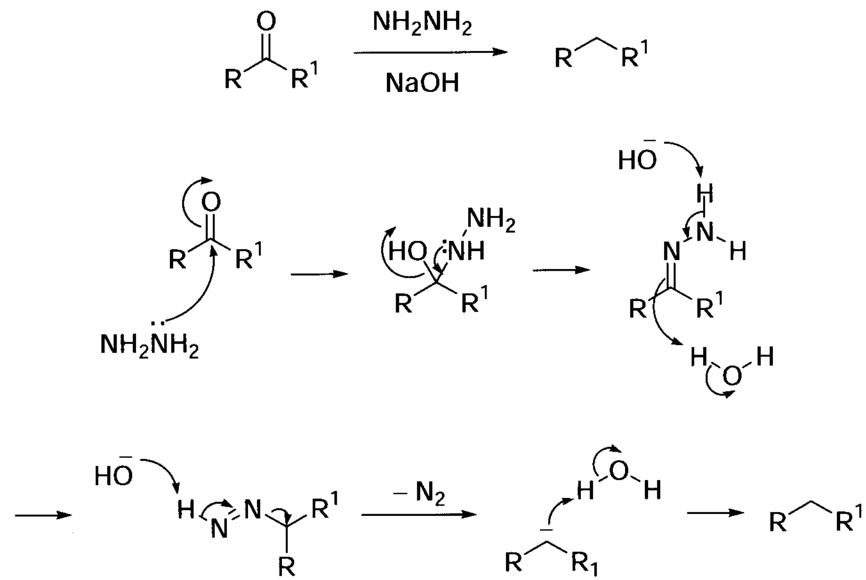
Wolff–Kishner reduction

Carbonyl reduction to methylene using basic hydrazine.



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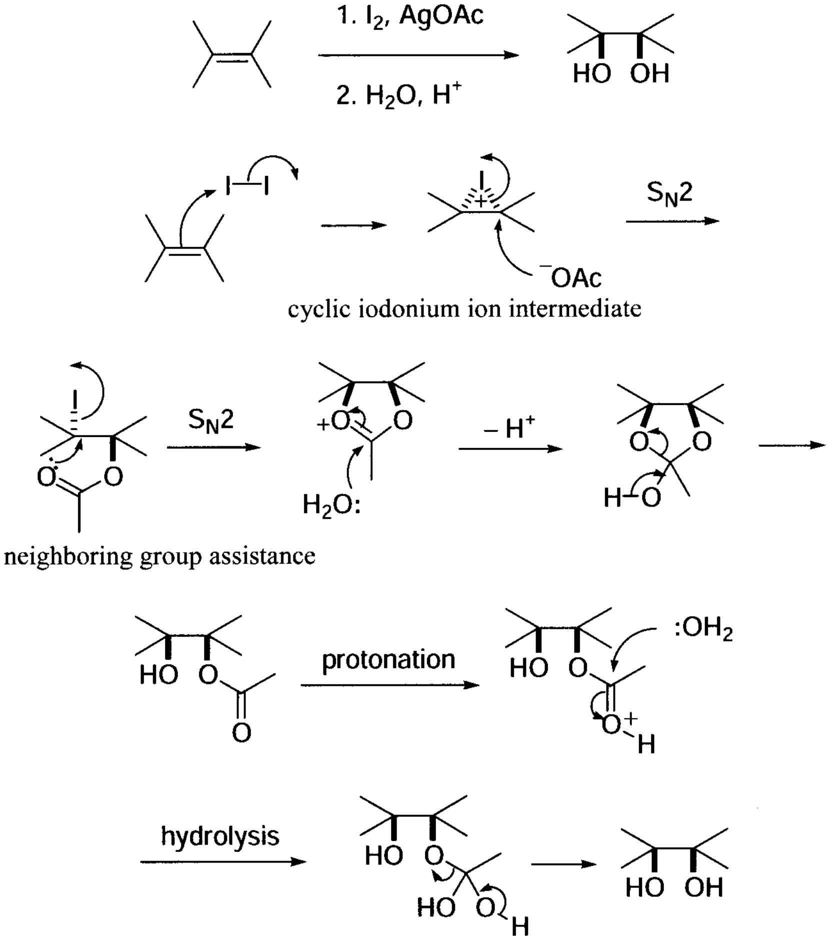
Woodward *cis*-dihydroxylation

Cf. Prévost *trans*-dihydroxylation



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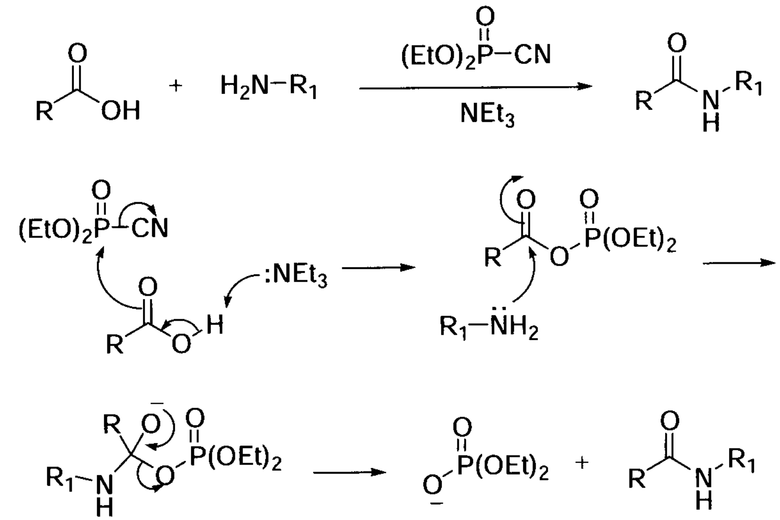
Yamada coupling reagent

The use of diethyl phosphoryl cyanide (diethyl cyanophosphonate) for the activation of carboxylic acids.



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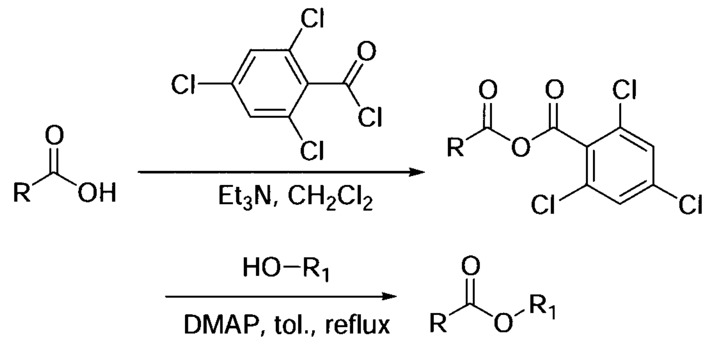
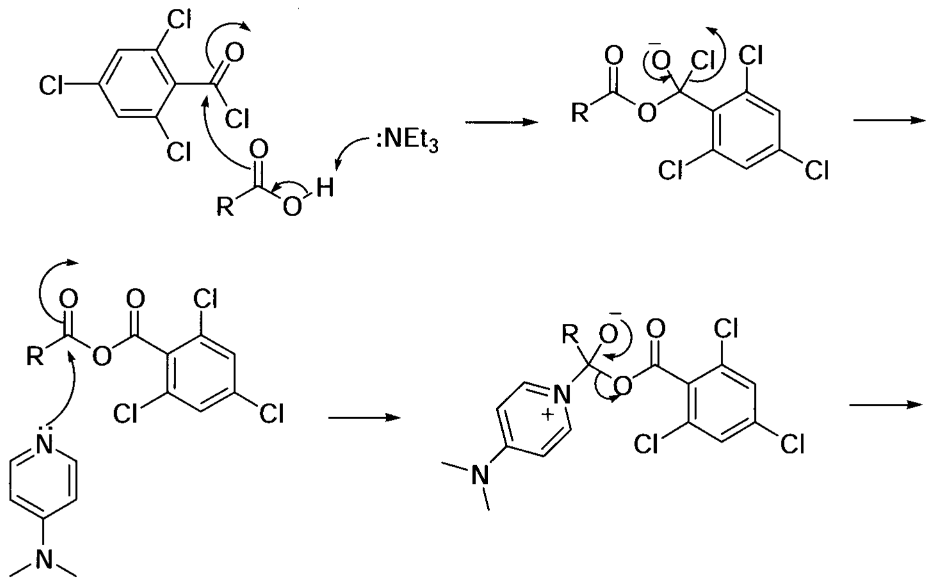
Yamaguchi esterification

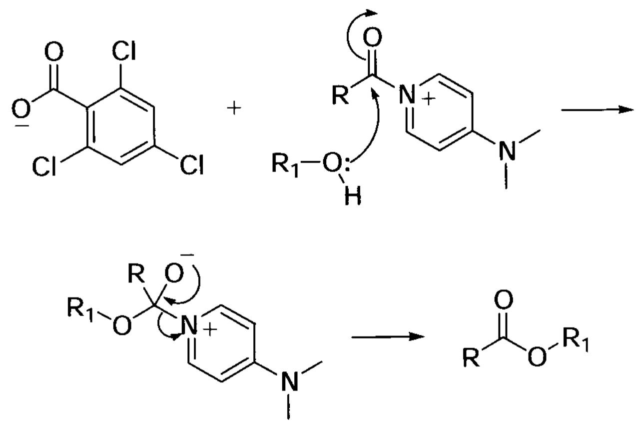
Esterification using 2,4,6-trichlorobenzoyl chloride (Yamaguchi reagent).





DMAP (Dimethylaminopyridine)

Steric hindrance of the chloro substituents blocks attack of the other carbonyl.



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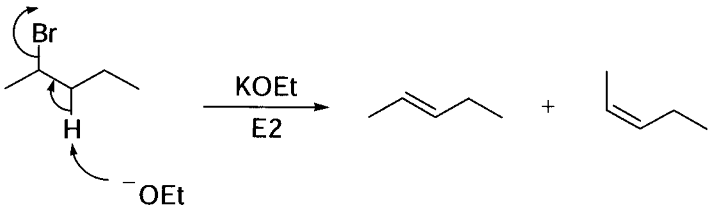
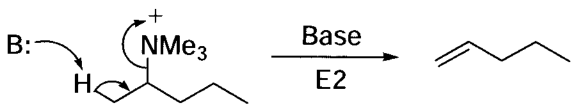
Zaitsev elimination

E2 elimination to give the more substituted olefin.



major minor

Hofmann elimination, on the other hand, furnishes the least highly substituted olefins.



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Zaitsev elimination

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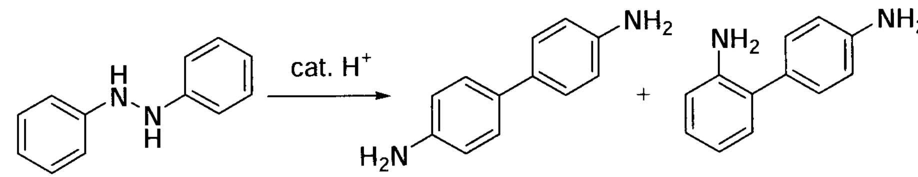
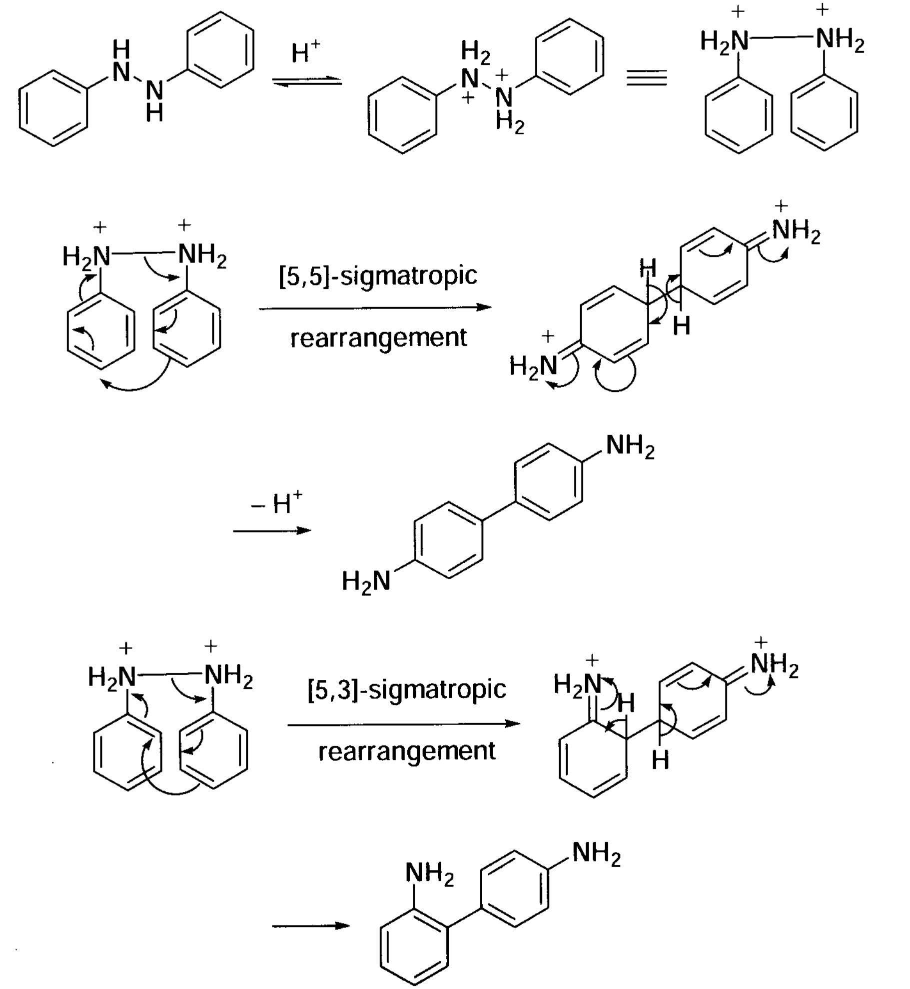
Zinin benzidine rearrangement (semidine rearrangement)



70% 30%



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Subject Index