Fiesers'

Reagents for Organic Synthesis

VOLUME TWENTY FIVE

Tse-Lok Ho

WILEY

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PREFACE

In the Preface of ROS-24 I mentioned Ji Hsiao-Lan with the profoundest of admiration because of his role in editing the encyclopedic “Four Libraries of Books”. During preparation of the present volume I happened to be reading “The Meaning of Everything. The Story of the Oxford English Dictionary” by Simon Winchester. The heart-wrenching journey that lasted 71 years for the completion of the first edition of the chef-d’oeuvre strikes a resonance in my heart.

This volume covers chemical literature from the beginning of 2007 to the end of June, 2008. From this period the most glaring mosaic of chemical vision scintillates with an aura of aurum.

GENERAL ABBREVIATIONS

Ac	acetyl
acac	acetylacetonate
ADDP	1,1′-(azodicarbonyl)dipiperidine
AIBN	2,2′-azobisisobutyronitrile
An	*p*-anisyl
aq	aqueous
Ar	aryl
ATPH	aluminum tris(2,6-diphenylphenoxide)
9-BBN	9-borabicyclo[3.3.1]nonane
BINOL	1,1′-binaphthalene-2,2′-diol
Bn	benzyl
Boc	*t*-butoxycarbonyl
bpy	2,2′-bipyridyl
BSA	*N*,*O*-bis(trimethylsilyl)acetamide
Bt	benzotriazol-1-yl
Bu	*n*-butyl
Bz	benzoyl
18-c-6	18-crown-6
c-	cyclo
CAN	cerium(IV)ammonium nitrate
Cap	caprolactamate
cat	catalytic
Cbz	benzyloxycarbonyl
Chx	cyclohexyl
cod	1,5-cyclooctadiene
cot	1,3,5-cyclooctatriene
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
CSA	l0-camphorsulfonic acid
Cy	cyclohexyl
cyclam	1,4,8,11-tetraazacyclotetradecane
DABCO	1,4-diazobicyclo[2.2.2]octane
DAST	(diethylamino)sulfur trifluoride
dba	dibenzylideneacetone
DBN	1,5-diazobicyclo[4.3.0]non-5-ene
DBU	1,8-diazobicyclo[5.4.0]undec-7-ene

DCC	*N*,*N*′-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
de	diastereomer excess
DEAD	diethyl azodicarboxylate
DIAD	diisopropyl azodicarboxylate
Dibal-H	diisobutylaluminum hydride
DMA	*N*,*N*-dimethylacetamide
DMAD	dimethyl acetylenedicarboxylate
DMAP	4-dimethylaminopyridine
DMD	dimethyldioxirane
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMPU	*N*,*N*′-dimethylpropyleneurea
DMSO	dimethyl sulfoxide
dpm	dipivaloylmethane
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,2-bis(diphenylphosphino)ferrocene
dppp	l,3-bis(diphenylphosphino)propane
dr	diastereomer ratio
DTTB	4,4′-di-*t*-butylbiphenyl
E	COOMe
ee	enantiomer excess
en	ethylenediamine
er	enantiomer ratio
Et	ethyl
EVE	ethyl vinyl ether
Fc	ferrocenyl
Fmoc	9-fluorenylmethoxycarbonyl
Fu	furanyl
HMDS	hexamethyldisilazane
HMPA	hexamethylphosphoric amide
hv	light
Hx	*n*-hexyl
i	iso
Ipc	isopinocampheyl
kbar	kilobar
L	ligand
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilazide

LTMP	lithium 2,2,6,6-tetramethylpiperidide
LN	lithium naphthalenide
lut	2,6-lutidine
M	metal
MAD	methylaluminum bis(2,6-di-*t*-butyl-4-methylphenoxide)
MCPBA	*m*-chloroperoxybenzoic acid
Me	methyl
MEM	methoxyethoxymethyl
Men	menthyl
Mes	mesityl
Mexyl	3,5-dimethylphenyl
MOM	methoxymethyl
Ms	methanesulfonyl (mesyl)
MS	molecular sieves
MTO	methyltrioxorhodium
MVK	methyl vinyl ketone
nbd	norbornadiene
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide
NMO	*N*-methylmorpholine *N*-oxide
NMP	*N*-methylpyrrolidone
Np	naphthyl
Ns	*p*-nitrobenzenesulfonyl
Nu	nucleophile
Oc	octyl
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PEG	poly(ethylene glycol)
Ph	phenyl
phen	1,10-phenenthroline
Pht	phthaloyl
Piv	pivaloyl
PMB	*p*-methoxybenzyloxymethyl
PMHS	poly(methylhydrosiloxane)
PMP	*p*-methoxyphenyl
Pr	*n*-propyl
py	pyridine
Q^+	quaternary onium ion
RAMP	(*R*)-1-amino-2-methoxymethylpyrrolidine
RaNi	Raney nickel

RCM	ring closure metathesis
R^f	perfluoroalkyl
ROMP	ring opening metathesis polymerization
s-	secondary
(s)	solid
salen	*N*,*N*′-ethylenebis(salicylideneiminato)
SAMP	(*S*)-1-amino-2-methoxymethylpyrrolidine
sc	supercritical
SDS	sodium dodecyl sulfate
sens.	sensitizer
SEM	2-(trimethylsilyl)ethoxymethyl
SES	2-[(trimethylsilyl)ethyl]sulfonyl
TASF	tris(dimethylamino)sulfur(trimethylsilyl)difluoride
TBAF	tetrabutylammonium fluoride
TBDPS	*t*-butyldiphenylsilyl
TBDMS	*t*-butyldimethylsilyl
TBS	*t*-butyldimethylsilyl
TEMPO	2,2,6,6-tetramethylpiperidinooxy
Tf	trifluoromethanesulfonyl
THF	tetrahydrofuran
THP	tetrahydropyranyl
Thx	*t*-hexyl
TIPS	triisopropylsilyl
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TMS	trimethylsilyl
Tol	*p*-tolyl
TON	turn over numbers
Tp	tris(1-pyrazolyl)borato
tpp	tetraphenylporphyrin
Ts	tosyl (*p*-toluenesulfonyl)
TSE	2-(trimethylsilyl)ethyl
TTN	thallium trinitrate
Z	benzyloxycarbonyl
Δ	heat
))))	microwave

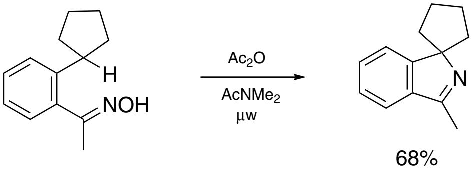
REFERENCE ABBREVIATIONS

ACIEE	Angew. Chem. In. Ed. Engl.
ACR	Acc. Chem. Res.
BCSJ	Bull. Chem. Soc. Jpn.
CB	Chem. Ber.
CC	Chem. Commun.
CEJ	Chem. Eur. J.
CL	Chem. Lett.
EJOC	Eur. J. Org. Chem.
JACS	J. Am. Chem. Soc.
JCCS(T)	J. Chin. Chem. Soc. (Taipei)
JOC	J. Org. Chem.
JOMC	J. Organomet. Chem.
OBC	Org. Biomol. Chem.
OL	Organic Letters
OM	Organometallics
S	Synthesis
SC	Synth. Commun.
SL	Synlett.
T	Tetrahedron
TA	Tetrahedron: Asymmetry
TL	Tetrahedron Lett.

A

Acetic anhydride.

Dehydration.[1] Ketoximes of alkyl aryl ketones afford pyrrolines on heating with Ac_2O in dimethylacetamide. Cyclization probably proceeds via H-abstraction after the nitrenium ions are formed.



[1] Savarin, C.G., Grise, C., Murry, J.A., Reamer, R.A., Hughes, D.L. *OL* **9**, 981 (2007).

Acetylacetonato(1,5-cyclooctadiene)rhodium(I).

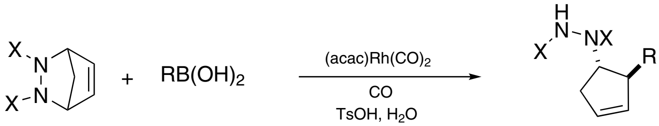
Aryltrialkoxysilanes. Preparation of $ArSi(OR)_3$ from ArX and $HSi(OR)_3$ is readily accomplished with the aid of (acac)Rh(cod) in DMF.[1]

[1] Murata, M., Yamasaki, H., Ueta, T., Nagata, M., Ishikura, M., Watanabe, S., Masuda, Y. *T* **63**, 4087 (2007).

Acetylacetonato(dicarbonyl)rhodium(I).

Alkynylation. Addition of 1-alkynes to α-keto esters is catalyzed by $(acac)Rh(CO)_2$ in the presence of a hindered phosphine ligand [e.g., 2-(di-*t*-butylphosphino)biphenyl].[1] Complexes containing more electron-rich analogues of the acetylaetonato ligand favor the reaction.

Coupling. Allylic carbonylation and coupling with boronic acids transform 2,3-diazabicyclo[2.2.1]hept-5-enes into 5-hydrazinyl-2-cyclopentenyl ketones.[2]



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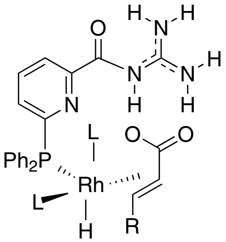
Addition to α-dicarbonyl compounds.[3] α-Diketones and α-keto esters react in aqueous DME with $ArB(OH)_2$ to produce the monadducts.

Reduction. Conjugated acids are converted to saturated aldehydes by syngas at room temperature, using $(acac)Rh(CO)_2$ in conjunction with a special guanidine as catalyst.[4] Only CO is liberated as stoichiometric side product. Furthermore, conditions for this highly selective reaction do not disturb acetals, esters, carbamates, ethers, silyl ethers, sulfides and many other functional groups.



Hydroformylation. With the Rh complex as catalyst (and a phosphite ligand) enamides and *N*-vinylimides are converted under syngas to α-amidoacetaldehydes.[5]

[1] Dhondi, P.K., Carberry, P., Choi, L.B., Chisholm, J.D. *JOC* **72**, 9590 (2007).
[2] Menard, F., Weise, C.F., Lautens, M. *OL* **9**, 5365 (2007).
[3] Ganci, G.R., Chisholm, J.D. *TL* **48**, 8266 (2007).
[4] Smejkal, T., Breit, B. *ACIE* **47**, 3946 (2008).
[5] Saidi, O., Ruan, J., Vinci, D., Wu, X., Xiao, J. *TL* **49**, 3516 (2008).

Acetyl chloride.

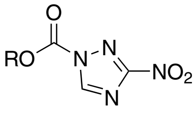
Nitration of arylamines. Nitration is performed by treatment of the $[ArNHR_2]NO_2$ salts with two equivalents of AcCl.[1] Apparently, the active nitrating agent, $AcONO_2$, is formed.

[1] Zhang, P., Cedilote, M., Cleary, T.P., Pierce, M.E. *TL* **48**, 8659 (2007).

N-Alkoxycarbonylazoles.

Allyl carbonates. 1-Allyloxycarbonylimidazole is an allyloxycarbonylating agent for enolate ions (e.g., generated from ketones and NaHMDS in DME, −78°).[1] *O*-Allylation occurs under the influence of $BF_3 \cdot OEt_2$. Substituted allyl groups are similarly transferred from homologous reagents.

Carbamates, carbonates, and thiocarbonates are also readily prepared from the highly stable, nonhygroscopic, and usually crystalline mixed carbamates **1** of 3-nitro-1,2,4-triazole.[2]

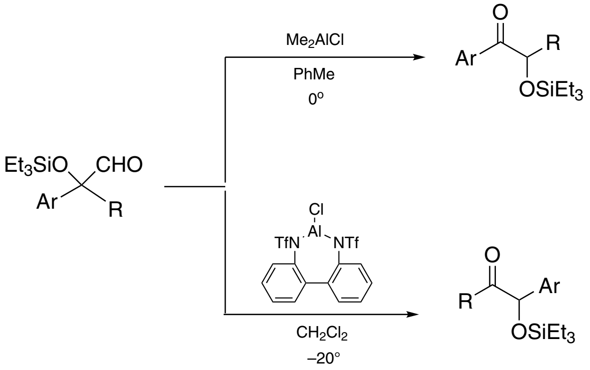


(1)

[1] Trost, B.M., Xu, J. *JOC* **72**, 9372 (2007).
[2] Shimizu, M., Sodeoka, M. *OL* **9**, 5231 (2007).

Alkylaluminum chlorides.

Rearrangement. α-Siloxyarylacetaldehydes give aryl ketones on treatment with Me_2AlCl. On the other hand, chloroaluminum biphenyl-2,2′-bis(triflylamide) catalyzes an alternative rearrangement pathway.[1]



[1] Ohmatsu, K., Tanaka, T., Ooi, T., Maruoka, K. *ACIE* **47**, 5203 (2008).

S-Alkylisothiouronium salts.

Thiol surrogates. These readily available compounds (RX + thiourea) release RSH in the presence NaOH for conjugate addition. Essentially they are odorless thiolating agents.[1]

[1] Zhao, Y., Ge, Z.-M., Cheng, T.-M., Li, R.-T. *SL* 1529 (2007).

η^3-Allyl(1,5-cyclooctadiene)palladium tetrafluoroborate.

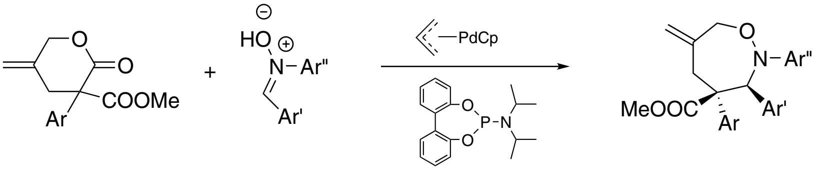
Allylation.[1] The Pd salt in the presence of 6-diphenylphosphino-2-pyridone catalyzes *C*-allylation of indoles (at C-3) and pyrroles (at C-2) with allyl alcohol in toluene at 50°, generating water as the only byproduct. The key to activation of the allylating agent is by H-bonding.

Nucleophilic substitution.[2] Benzylic acetates react with nucleophiles such as amines, sodium arenesulfonates, and malonic esters under the influence of the title reagent together with DPPF and a mild base [Et_3N in EtOH or K_2CO_3 in *t*-AmOH].

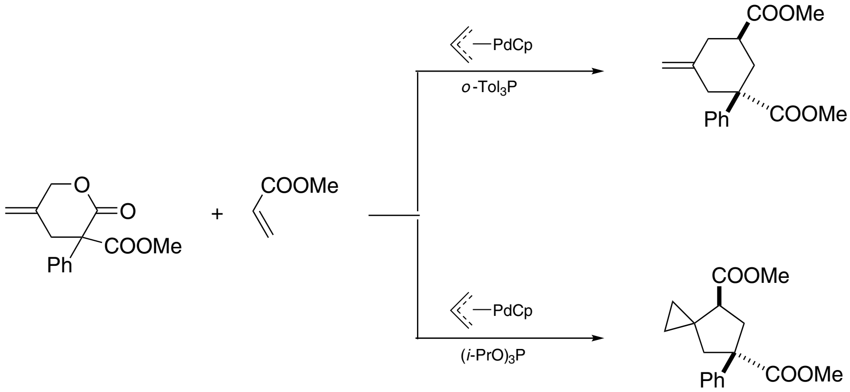
[1] Usui, I., Schmidt, S., Keller, M., Breit, B. *OL* **10**, 1207 (2008).
[2] Yokogi, M., Kuwano, R. *TL* **48**, 6109 (2007).

η³-Allyl(cyclopentadienyl)palladium.

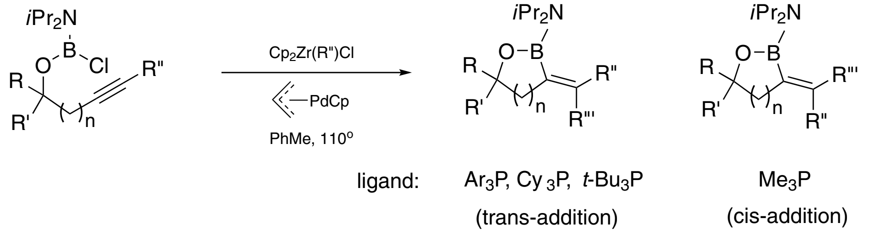
Cycloaddition. The Pd complex is useful for generating internal salts containing a π-allylpalladium complex from (ω-1)-methylene lactones. Trapping of the intermediates by other 1,3-dipoles such as nitrones results in the products of different types of heterocycles (with larger ring size).[1]



The subtle ligand effects are manifested in the reaction of dipolar species with acrylic esters, apparently due to different number of P-ligands on the π-allylpalladium complex. With two additional ligands (phosphites) on Pd the π-allyl segment suffers attack at the central carbon to eventually generate spiro[2.4]heptanes, whereas only one additional ligand (phosphine) engenders an electronic bias toward bond formation at the terminus.[2]



Carboboration.[3] An alkyl group is delivered from (alkyl)zirconocene chlorides to a triple bond accompanied by the formation of an oxaborolidine unit. Remarkably, Me_3P (vs. other phosphine ligands) has a unique stereochemical influence.

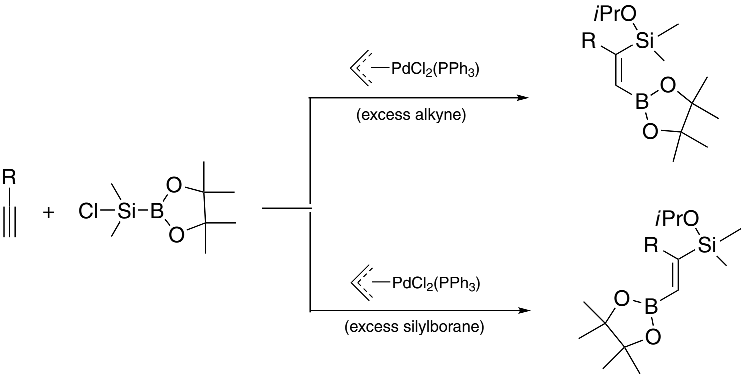


Elimination.[4] *o*-Quinodimethane is generated from (*o*-trimethylsilylmethyl)benzyl methyl carbonate on heating with the Pd complex and DPPE in DMSO at 120°.

[1] Shintani, R., Murakami, M., Hayashi, T. *JACS* **129**, 12356 (2007).
[2] Shintani, R., Park, S., Hayashi, T. *JACS* **129**, 14866 (2007).
[3] Daini, M., Yamamoto, A., Suginome, M. *JACS* **130**, 2918 (2008).
[4] Giudici, R.E., Hoveyda, A.H. *JACS* **129**, 3824 (2007).

η^3-Allyldichloro(triphenylphosphine)palladium.

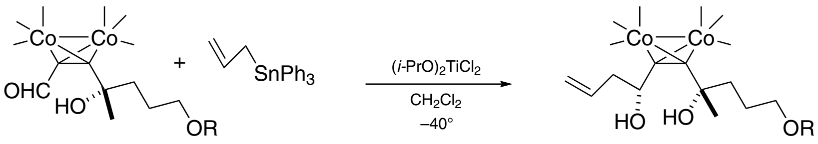
Borylsilylation.[1] (Chlorodimethylsilyl)pinacolatoborane adds to 1-alkynes to give 1-pinacolatoboryl-2-silylalkenes. The relative amount of the addends is the determinant factor in the stereochemical outcome of the reaction



[1] Ohmura, T., Oshima, K., Suginome, M. *CC* 1416 (2008).

Allylstannanes.

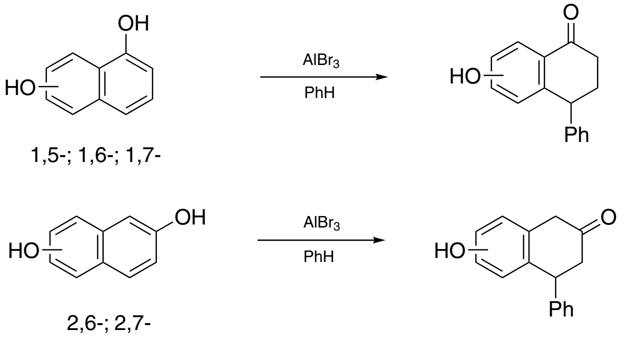
Allyl addition.[1] Diastereoselectivity for the addition of an allyl group to hexacarbonyldicobalt complexes of 4-hydroxy-2-alkynals is much higher using allyltriphenylstannane instead of the tributyl congener.



[1] Hayashi, Y., Yamaguchi, H., Toyoshima, M., Okado, K., Toyo, T., Shoji, M. *OL* **10**, 1405 (2008).

Aluminum bromide.

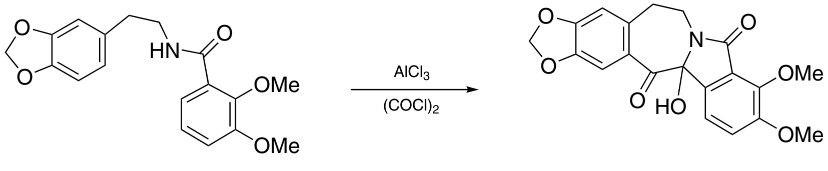
Reductive phenylation.[1] Naphthalenediols and benzene combine to afford hydroxytetralones. The transformation occurs when the mixtures of the aromatic compounds are treated with an excess of $AlBr_3$.



[1] Koltunov, K.Yu. *TL* **49**, 3891 (2008).

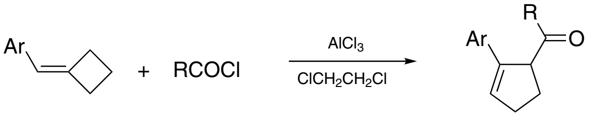
Aluminum chloride.

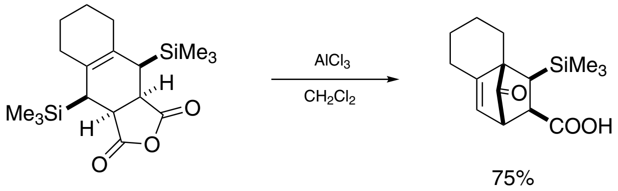
Friedel–Crafts acylation. A synthesis of chilenine is completed by a two-fold Friedel–Crafts acylation of an *N*-(arylethyl)amide with oxalyl chloride.[1]



chilenine

Acylation of arylidenecyclobutanes is accompanied by ring expansion.[2] A route to norbornen-7-ones entails an intramolecular desilylative Friedel–Crafts acylation.[3] Such compounds are not directly accessible by a Diels–Alder reaction.





Carbimination. Thiophene and *N*-substituted pyrroles and indoles undergo electrophilic substitution with ArNC at room temperature. The reaction gives imines as products.[4]

Aromatization. Treatment of 6-hydroxy-1,2,3,6-tetrahydro-*N*-tosyl-3-pyridones with $AlCl_3$ in $MeNO_2$ at −78° brings about dehydration and *O*-tosylation to give 3-tosyloxypyridines.[5]

[1] Kim, G., Jung, P., Tuan, L.A. *TL* **49**, 2391 (2008).
[2] Jiang, M., Shi, M. *OL* **10**, 2239 (2008).
[3] Li, D., Liu, G., Hu, Q., Wang, C., Xi, Z. *OL* **9**, 5433 (2007).
[4] Tobisu, M., Yamaguchi, S., Chatani, N. *OL* **9**, 3351 (2007).
[5] Hodgson, R., Kennedy, A., Nelson, A., Perry, A. *SL* 1043 (2007).

Aluminum dimethylamide.

Transamination.[1] Tertiary amides are converted to secondary amides on reaction with secondary amines in the presence of $Al_2(NMe_2)_6$.

[1] Hoerter, J.M., Otte, K.M., Gellman, S.H., Cui, Q., Stahl, S.S. *JACS* **130**, 647 (2008).

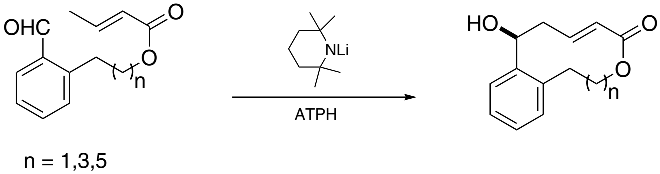
Aluminum iodide.

Baylis–Hillman reaction. Ethyl propynoate apparently undergoes iodoalumination to generate a nucleophilic species that adds onto carbonyl compounds. (*Z*)-β-Iodoacrylic esters are produced.[1]

[1] Lee, S.I., Hwang, G.-S., Ryu, D.H. *SL* 59 (2007).

Aluminum tris(2,6-diphenylphenoxide), ATPH.

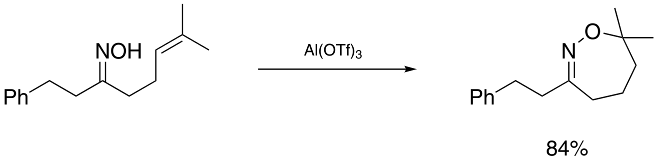
Macrolide synthesis.[1] By way of an intramolecular aldol reaction using ATPH and LiTMP, macrocyclic (10-, 12-, and 14-membered) lactones are formed.



[1] Abramite, J.A., Sammakia, T. *OL* **9**, 2103 (2007).

Aluminum triflate.

Cycloisomerization.[1] An oxime function is liable to add to a double bond at an appropriate distance and the reaction is realized by heating unsaturated oximes with $Al(OTf)_3$ in $MeNO_2$.



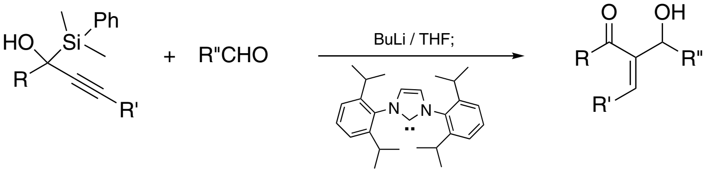
[1] Cheminade, X., Chiba, S., Narasaka, K., Dunach, E. *TL* **49**, 2384 (2008).

Aminocarbenes.

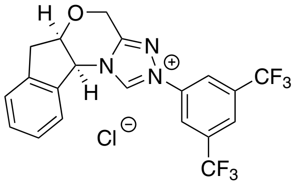
Reviews.[1,2] Applications of heterocyclic carbenes in organic synthesis have been reviewed.

Aldol reactions. Enolization of ketones at room temperature (and ensuing silylation) is readily effected by 1,3-bis(1-adamantyl)imidazol-2-ylidene.[3] Accordingly, Mukaiyama aldol reaction is accomplished under the appropriate conditions.[4]

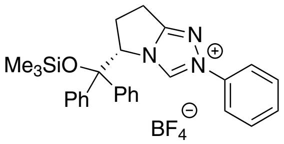
Baylis–Hillman reaction products are obtained in an unconventional manner from α-silylpropargyl alcohols and aldehydes, using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene as catalyst.[5]



Acyloin condensation. Carbene species (for promoting intramolecular acyloin condensation) are more readily generated from 1,2,4-triazolium salts when one of the *N*-substituents is highly electron-deficient (e.g., **1**).[6] The bicyclic triazolium salt **2** derived from pyroglutamic acid catalyzes benzoin condensation in modest yields, in which electron-rich ArCHO is less reactive but better asymmetric induction is observed.[7]



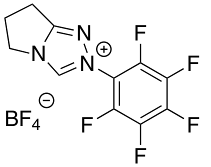
(1)



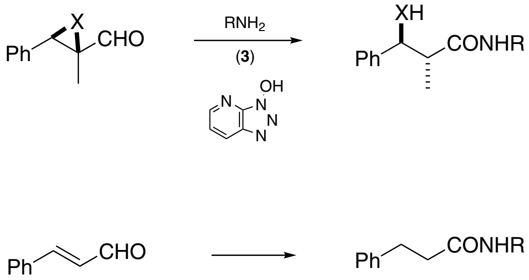
(2)

Analogous condensation of ArCHO and aldimines gives α-amino ketones.[8]

Carboxylic derivatives. A mixture of an aldehyde and a nitrosoarene is converted into an *N*-arylhydroxamic acid on treatment with **3** and DBU,[9] whereas α,α-dichloro aldehydes gives α-chloro carboxamides in the presence of amines under similar conditions.[10] A mild organic base is needed to generate the carbene (and a slight variation of the catalyst system for the same reaction comprises the *N*-mesitytriazolium chloride and imidazole base.[11])

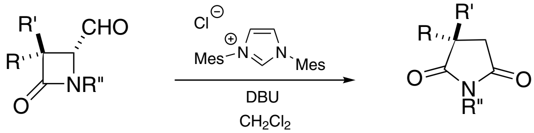


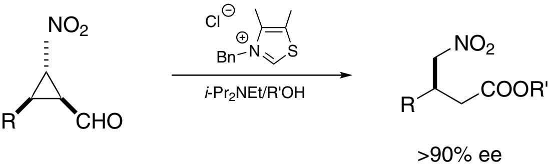
(3)



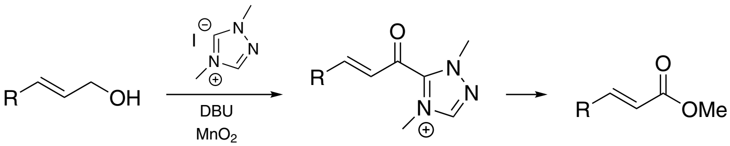
There is a significant difference in reaction profile for the reaction of enals with nitrosoarenes. Isoxazolidin-5-ones are formed and alcoholysis of which leads to β-arylamino esters.[12] With the nitroarenes replaced by arylazo carbonyl compounds to perform the reaction 3-oxopyrazoldinones result.[13]

As a redox process, the ring expansion of β-formyl-β-lactams to furnish succinimides[14] and the ring scission of 2-nitrocyclopropanecarbaldehydes[15] are also mediated by an azocarbene.





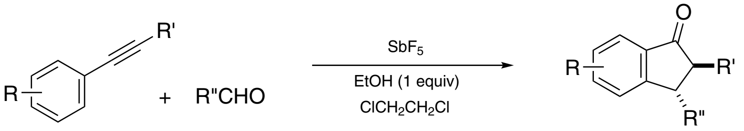
Enals generated by oxidation of allylic alcohols with MnO_2 in the presence of azolium ylides are trapped to form secondary allylic alcohols. These are subject to further oxidation and the resulting ketones undergo alcoholysis in situ.[16]



[1] Hahn, F.E., Jahnke, M.C. *ACIE* **47**, 3122 (2008).
[2] Marion, N., Diez-Gonzalez, S., Nolan, S.P. *ACIE* **46**, 2988 (2007).
[3] Song, J.J., Tan, Z., Reeves, J.T., Fandrick, D.R., Yee, N.K., Senanayake, C.H. *OL* **10**, 877 (2008).
[4] Song, J.J., Tan, Z., Reeves, J.T., Yee, N.K., Senanayake, C.H. *OL* **9**, 1013 (2007).
[5] Reynolds, T.E., Stern, C.A., Scheidt, K.A. *OL* **9**, 2581 (2007).
[6] Takikawa, H., Suzuki, K. *OL* **9**, 2713 (2007).
[7] Enders, D., Han, J. *TA* **19**, 1367 (2008).
[8] Li, G.-Q., Dai, L.-X., You, S.-L. *CC* 852 (2007).
[9] Wong, F.T., Patra, P.K., Seayad, J., Zhang, Y., Ying, J.Y. *OL* **10**, 2333 (2008).
[10] Vora, H.U., Rovis, T. *JACS* **129**, 13796 (2007).
[11] Bode, J.W., Sohn, S.S. *JACS* **129**, 13798 (2007).
[12] Seayad, J., Patra, P.K., Zhang, Y., Ying, J.Y. *OL* **10**, 953 (2008).
[13] Chan, A., Scheidt, K.A. *JACS* **130**, 2740 (2008).
[14] Li, G.-Q., Li, Y., Dai, L.-X., You, S.-L. *OL* **9**, 3519 (2007).
[15] Vesely, J., Zhao, G.-L., Bartoszewicz, A., Cordova, A. *TL* **49**, 4209 (2008).
[16] Maki, B.E., Chan, A., Phillips, E.M., Scheidt, K.A. *OL* **9**, 371 (2007).

Antimony(V) chloride.

Indanones.[1] *trans*-2,3-Disubstituted indanones are produced in reasonably good yields from a mixture of arylalkynes and aldehydes with EtOH (1 equiv.) as additive, by treatment with $SbCl_5$.



[1] Saito, A., Umakoshi, M., Yagyu, N., Hanzawa, Y. *OL* **10**, 1783 (2008).

Arylboronic acids.

Amide formation. *o*-Halophenylboronic acids catalyze the Diels–Alder reaction of acrylic acid as well as condensation of carboxylic acids with amines at room temperature (in the presence of 4A-molecular sieves).[1]

A thorough study indicates that (1-methyl-4-pyridinio)boronic acid iodide is a superior catalyst for amidation under azeotropic conditions, and esterification of 2-hydroxyalkanoic acids.[2]

[1] Al-Zoubi, R.M., Marion, O., Hall, D.G. *ACIE* **47**, 2876 (2008).
[2] Maki, T., Ishihara, K., Yamamoto, H. *T* **63**, 8645 (2007).

N-Arylsulfinylimines.

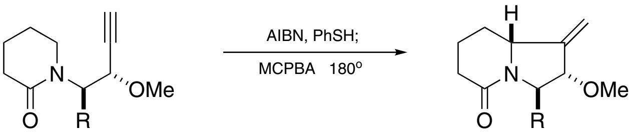
Imido transfer.[1] Aldehydes are converted into RCH=NAr on reaction with ArN=S=O, using catalysts such as $VOCl_3$, $MoOCl_3$, and MoO_2Cl_2.

[1] Zhizhin, A.A., Zarubin, D.N., Ustynyuk, N.A. *TL* **49**, 699 (2008).

Azobisisobutyronitrile.

Deallylation. Allyl carboxylates are hydrolyzed under neutral conditions on treatment with AIBN (10 mol%) and water. This radical deallylation generally proceeds in high yields.[1]

Oxidative cyclization. Alkynyllactams cyclize by reaction with PhSH and AIBN, involving carbon radical shuffle.[2]

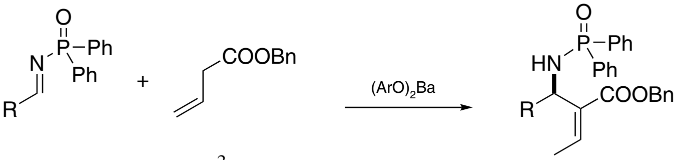


[1] Perchyonok, V.T., Ryan, S.J., Langford, S.J., Hearn, M.T., Tuck, K.L. *SL* 1233 (2008).
[2] Denes, F., Beaufis, F., Renaud, P. *OL* **9**, 4375 (2007).

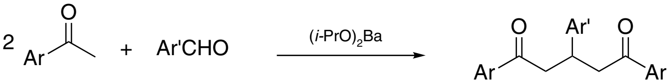
B

Barium alkoxides.

Aminoalkylation.[1] The use of $(ArO)_2Ba$ in THF to deprotonate 3-butenoic esters for reaction with *N*-phosphinylaldimines gives α-substituted crotonates.



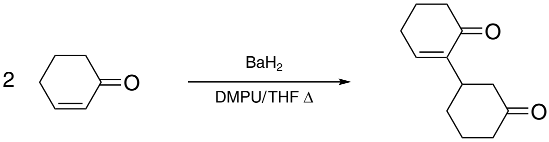
Aldol + Michael reactions.[2] A 2 : 1 condensation between ArCOMe and Ar′CHO is observed when the mixtures are treated with $(i\text{-}PrO)_2Ba$.

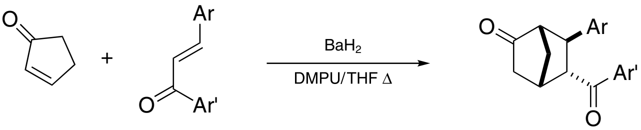


[1] Yamaguchi, A., Aoyama, N., Matsunaga, S., Shibasaki, M. *OL* **9**, 3387 (2007).
[2] Yanagisawa, A., Takahashi, H., Arai, T. *T* **63**, 8581 (2007).

Barium hydride.

Michael reaction.[1] 2-Cycloalkenones dimerize in the presence of BaH_2. However, 2-cyclopentenone condenses with chalcone to form a bicyclo[2.2.1]heptanone.





[1] Yanagisawa, A., Shinohara, A., Takahashi, H., Arai, T. *SL* 141 (2007).

Fiesers' Reagents for Organic Synthesis, Volume 25. By Tse-Lok Ho

Benzenesulfonic anhydride.

Amide formation.[1] Activation of carboxylic acids by $(PhSO_2)_2O$ (with catalytic DMAP) as mixed anhydrides for acylation of R_2NH is a very simple operation.

[1] Funasaka, S., Kato, K., Mukaiyama, T. *CL* **36**, 1456 (2007).

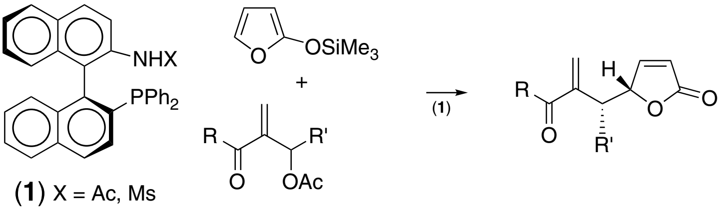
Benzyl *N*-phenyl-2,2,2-trifluoroacetimidate.

O-Benzylation.[1] Benzyl ethers of base-sensitive hydroxy esters and hindered alcohols are formed by reaction with the title reagent (Me_3SiOTf as catalyst). The reagent is more stable than the trichloro analogue and it can be prepared from $CF_3C(=NPh)Cl$ and BnOH.

[1] Okada, Y., Ohtsu, M., Bando, M., Yamada, H. *CL* **36**, 992 (2007).

1,1′-Binaphthalene-2-amine-2′-phosphines.

Substitution reactions. An S_N2 reaction between 2-trimethylsiloxyfuran and acetylated Baylis–Hillman adducts is induced by the amine/phosphine **1**.[1]



Actually the *N*-acetyl derivative catalyzes the aza-Baylis–Hillman reaction.[2]

[1] Jiang, Y.-Q., Shi, Y.-L., Shi, M. *JACS* **130**, 7202 (2008).
[2] Qi, M.-J., Ai, T., Shi, M., Li, G. *T* **64**, 1181 (2008).

1,1′-Binaphthalene-2,2′-bis(*p*-toluene sulfoxide).

Michael reaction. The title compound is a bidentate S,S-ligand for Rh. Complexes of the sort are used in mediating aryl transfer from $ArB(OH)_2$ to 2-cycloalkenones and conjugated lactones under basic conditions.[1]

[1] Mariz, R., Luan, X., Gatti, M., Linden, A., Dorta, R. *JACS* **130**, 2172 (2008).

1,1′-Binaphthalene-2,2′-diamine derivatives.

Aldol reaction. Asymmetric aldol reaction of chloroacetone with electron-deficient ArCHO gives mainly the *anti*-3-chloro-4-hydroxy-2-butanones, in the presence of **1**.[1] The