

Fiesers' Reagents for Organic Synthesis

VOLUME NINETEEN

Tse-Lok Ho

National Chaio Tung University
Republic of China



A WILEY-INTERSCIENCE PUBLICATION
JOHN WILEY & SONS, INC.
NEW YORK / CHICHESTER / WEINHEIM / BRISBANE / SINGAPORE / TORONTO

Chem
55
R287
068x
v. 19

PREFACE

This volume examines literature of mostly the 1995–1996 period. Due to the proliferation of publications, I have decided not to cite full papers extending from those preliminary communications already included in previous volumes of the series and containing sufficient details for synthetic applications of the reagents. Deciding what to cover is always a dilemma, but my policy is to report the newest and significant reagents and reactions when they first appear. For less significant work or an old reagent with a single new use, I might delay the discussion until a later volume. As I have mentioned previously, I shall strive to amend my mistakes in missing important work. In volumes prepared by the Fiesers, the nomenclature of compounds does not always conform to the IUPAC or the CA system, probably for the sake of convenience to the reader. My arrangement is in the same spirit, and actually, I have tried to place cognate reagents near each other so that related information becomes more immediately available to a browser. Thus, azidotrimethylsilane, chlorotrimethylsilane, and other Me_3SiX are grouped under T, near trimethylsilyl triflate. Similarly, titanocenes with modified ligands are assembled together.

TSE-LOK HO

noted in any form
wise, except as
either the
appropriate
A 1923, (978)
addressed to the
NY 10158-0012,

CONTENTS

General Abbreviations	ix
Reference Abbreviations	xiii
Reagents	1
Author Index	417
Subject Index	467

GENERAL ABBREVIATIONS

Ac	acetyl
acac	acetylacetonate
ADDP	1,1'-(azodicarbonyl)dipiperidine
AIBN	2,2'-azobisisobutyronitrile
aq	aqueous
Ar	aryl
Bn	benzyl
Boc	t-butoxycarbonyl
Bu	<i>n</i> -butyl
Bz	benzoyl
18-c-6	18-crown-6
c-	cyclo
cat	catalytic
Cp	cyclopentadienyl
Cy	cyclohexyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DAST	(diethylamino)sulfur trifluoride
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DCC	N,N'-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
de	diastereomer excess
DIBALH	diisobutylaluminum hydride
DMAP	4-(dimethylamino)pyridine
DMD	dimethyldioxirane
DME	1,2-dimethoxyethane
DMF	N,N-dimethylformamide
DMPU	N,N'-dimethylpropyleneurea
DMSO	dimethyl sulfoxide
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,2-bis(diphenylphosphino)ferrocene
dppp	1,2-bis(diphenylphosphino)propane
E	COOMe
ee	enantiomer excess
Et	ethyl
EVE	ethyl vinyl ether
HMPA	hexamethylphosphoric triamide

x General Abbreviations

hv	light
Ipc	isopinocampheyl
iPr	isopropyl
kbar	kilobar
L	ligand
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LTMP	lithium 2,2,6,6-tetramethylpiperidide
lut	2,6-lutidine
M	metal (alkali)
MCPBA	m-chloroperoxybenzoic acid
Me	methyl
Ms	mesyl (methanesulfonyl)
MTO	methylrhodium trioxide
MVK	methyl vinyl ketone
NBS	N-bromosuccinimide
NCS	N-chlorosuccinimide
NIS	N-iodosuccinimide
NMO	N-methylmorpholine oxide
Nu	nucleophile
Ctc	octyl
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PEG	polyethylene glycol
Ph	phenyl
Pht	phthaloyl
Piv	pivaloyl
Pr	<i>n</i> -propyl
py	pyridine
Q ⁺	quaternary onium ion
RAMP	(R)-1-amino-2-methoxymethylpyrrolidine
RaNi	Raney nickel
R ^f	perfluoroalkyl
(s)	solid
SAMP	(S)-1-amino-2-methoxymethylpyrrolidine
sens.	photosensitizer
TBAF	tetrabutylammonium fluoride
TBS	=TBDMS, <i>t</i> -butyldimethylsilyl
TEMPO	2,2,6,6,-tetramethylpiperidinoxy
TES	triethylsilyl
THF	tetrahydrofuran

TIPS triisopropylsilyl
 TMEDA N,N,N',N'-tetramethylethylenediamine
 TMS trimethylsilyl
 Tolu tosyl (*p*-toluenesulfonyl)
 Δ heat
 μ microwave

TIPS	triisopropylsilyl
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	trimethylsilyl
Ts	tosyl (<i>p</i> -toluenesulfonyl)
Δ	heat
)))	microwave

REFERENCE ABBREVIATIONS

ACR	Acc. Chem. Res.
ACS	Acta Chem. Scand.
ACIEE	Angew. Chem. Int. Ed. Engl.
AJC	Aust. J. Chem.
AOMC	Appl. Organomet. Chem.
BBB	Biosc. Biotech. Biochem.
BCSJ	Bull. Chem. Soc. Jpn.
BSCB	Bull. Soc. Chim. Belg.
BSCF	Bull. Soc. Chim. Fr.
BRAS	Bull. Russ. Acad. Sci.
CB	Chem. Ber.
CC	Chem. Commun.
CCCC	Collect. Czech. Chem. Commun.
CEJ	Chem. Eur. J.
CJC	Can. J. Chem.
CL	Chem. Lett.
CPB	Chem. Pharm. Bull.
CR	Carbohydr. Res.
DC	Dokl. Chem. (Engl. Trans.)
G	Gazz. Chim. Ital.
H	Heterocycles
HC	Heteroatom Chem.
HCA	Helv. Chim. Acta
HX	Huaxue Xuebao
IJC(B)	Indian J. Chem., Sect. B
IJS(B)	Int. J. Sulfur Chem., Part B
JACS	J. Am. Chem. Soc.
JCC	J. Carbohydr. Chem.
JCCS(T)	J. Chin. Chem. Soc. (Taipei)
JCR(S)	J. Chem. Res. (Synopsis)
JCS(P1)	J. Chem. Soc. Perkin Trans. 1
JFC	J. Fluorine Chem.
JHC	J. Heterocycl. Chem.
JMC	J. Med. Chem.
JNP	J. Nat. Prod.
JOC	J. Org. Chem.
JOMC	J. Organomet. Chem.

JOCU	J. Org. Chem. USSR (Engl. Trans.)
LA	Liebigs Ann. Chem.
MC	Mendeleev Commun.
NKK	Nippon Kagaku Kaishi
OM	Organometallics
PAC	Pure Appl. Chem.
PSS	Phosphorus Sulfur Silicon
RJOC	Russian J. Org. Chem.
RTC	Recl. Trav. Chim. Pays-Bas
S	Synthesis
SC	Synth. Commun.
SL	Synlett
SOC	Synth. Org. Chem. (Jpn.)
T	Tetrahedron
TA	Tetrahedron:Asymmetry
TL	Tetrahedron Lett.
YH	Youji Huaxue

A

Acetic acid.

Cleavage of *p*-methoxybenzyl ethers.¹ Alcohols are liberated from the ethers on warming with HOAc (7 examples, 88–96%).

Hodgetts, K.J., Wallace, T.W. *SC* **24**, 1151 (1994).

Acetone cyanohydrin.

Nitriles from alcohols.¹ Using this reagent as a donor in the Mitsunobu reaction successfully completes the preparation of alkyl nitriles.

Aesa, M.C., Baan, G., Novak, L., Szantay, C. *SC* **26**, 909 (1996).

Acetonitrile. 15, 1; 18, 2

β -Hydroxy nitriles.¹ Acetonitrile protonates acyllithium species, which are formed from RLi and CO. Subsequent reaction of the aldehydes with the cyanomethyl anion affords the β -hydroxy nitriles.

Li, N.-S., Yu, S., Kabalka, G.W. *JOC* **60**, 5973 (1995).

N-Acetyl-*N*-acyl-3-aminoquinazolinones.

Acetylation of primary amines.¹ Secondary amines are not affected by these reagents.

Atkinson, R.S., Barker, E., Sutcliffe, M.J. *CC* 1051 (1996).

Acetyl chloride. 18, 2

β -Chlorosulfides.¹ Sulfenyl chlorides (RSCl) are formed when sulfenate esters (RSOR') are treated with acetyl chloride (or other acid chlorides). The reactive species functionalize olefins in situ.

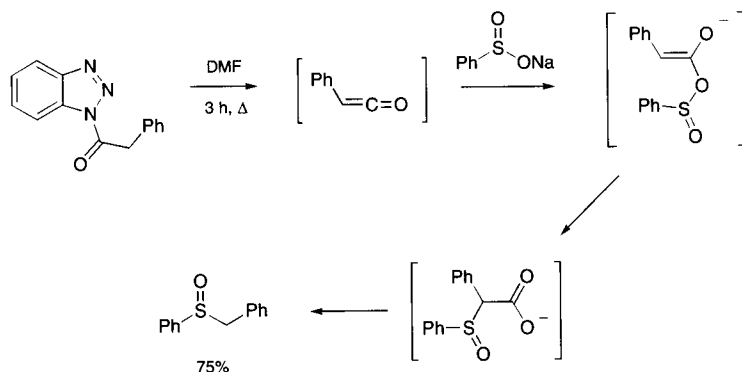
Deprotection of α -halo aldehyde dimethyl acetals.² Acetyl chloride in combination with acetic anhydride and sodium acetate regenerates the aldehydes (9 examples, 83–98%).

Brown, C., Evans, G.R. *TL* **37**, 679 (1996).

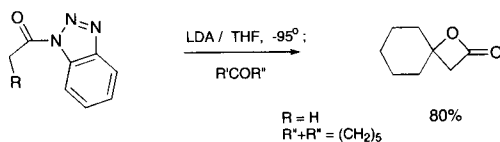
Benincasa, M., Boni, M., Ghelfi, F., Pagnoni, U.M. *SC* **25**, 1843 (1995).

***N*¹-Acylbenzotriazoles.**

Sulfoxides.¹ Reaction of the activated amides with arenesulfinate anions results in sulfoxides. α -Sulfinyl carboxylic acids are likely the intermediates.



β -Lactones.² The amides undergo aldolization with ketones and aldehydes, furnishing β -lactones in one step. Both transformations imply ketene formation in the initial step.

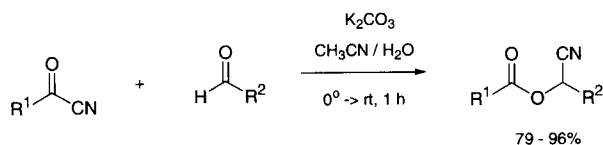


¹Katritzky, A.R., Yang, B., Qian, Y. *SL* 701 (1996).

²Wedler, C., Kleiner, K., Kunath, A., Schick, H. *LA* 881 (1996).

Acyl cyanides.

Cyanohydrin esters.¹ Reaction of acyl cyanides with aldehydes in the presence of K₂CO₃ in aqueous acetonitrile leads to α -cyanohydrin esters.



¹Okimoto, M., Chiba, T. *S* 1188 (1996).

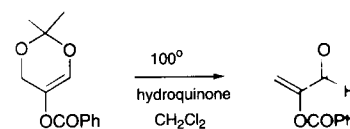
***N*-Acyl-2-methylimidazoles.**

Acylsilanes.¹ Acylimidazoles are electrochemically reduced on a Pt cathode, and the ensuing acyl anion equivalents can be trapped with Me₃SiCl.

¹Kise, N., Kaneko, H., Unemoto, N., Yoshida, J. *TL* 36, 8839 (1995).

2-Acyloxyacroleins.

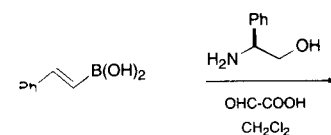
Dienophiles.¹ These compounds on enolacylation and thermolysis of dienophiles in Diels-Alder reactions.



Funk, R.L., Yost, K.J. *JOC* 61, 2598 (1996).

Alkenylboronic acids.

α -Amino acids.¹ A three-component reaction of an alkenylboronic acid, an amine, and an α -oxo acid produces natural substitution patterns are formed.



Petasis, N.A., Zavalov, I.A. *JACS* 119, 445 (1997).

1-[*N*-(Alkoxyoxalyl)-*N*-methylamino]

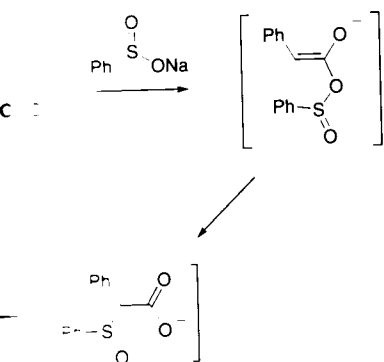
α -Keto esters.¹ A general method for the synthesis of α -keto esters via the reaction of the salts.

De las Heras, M.A., Vaquero, J.J., Garcia-Nieto, P. *JOC* 61, 2598 (1996).

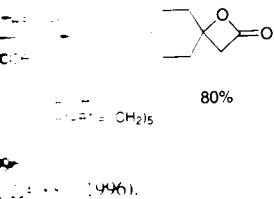
Alkynyl triflones.

Alkynylation.¹ The introduction of an alkynyl carbon skeleton is a remarkable achievement. The use of a radical initiator, good yields of α -alkynyl ketones, the corresponding ethers and adamantane derivatives to give β -trifluoromethylalkyl alkynes.

and amides with arenedisulfonate anions results in
like the intermediates.

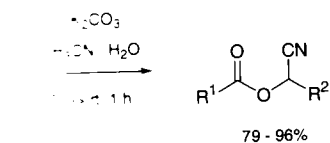


ization with ketones and aldehydes,
formations imply ketene formation in the initial



(1996).

amides with aldehydes in the presence of
hydrin esters.

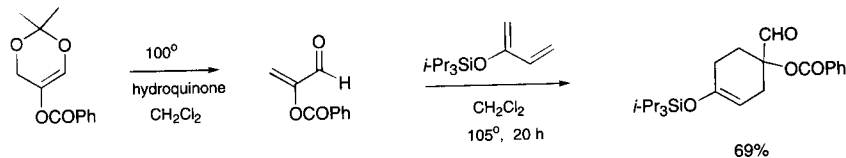


electronically reduced on a Pt cathode, and the
product with Me3SiCl.

J. Org. Chem. 36, 8839 (1995).

2-Acyloxyacroleins.

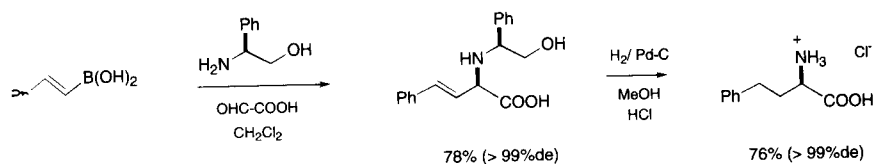
Dienophiles.¹ These compounds are available from 2,2-dimethyl-1,3-dioxan-5-one on enolacetylation and thermolysis of the resulting enol esters at 100°. They serve as dienophiles in Diels-Alder reactions.



Funk, R.L., Yost, K.J. *JOC* 61, 2598 (1996).

Alkenylboronic acids.

α -Amino acids.¹ A three-component condensation involving an alkenylboronic acid, an amine, and an α -oxo acid proceeds in uniformly good yields. Products having a natural substitution pattern are formed by using benzylic amines and glyoxylic acid.



Petasis, N.A., Zavialov, I.A. *JACS* 119, 445 (1997).

1-[N-(Alkoxyoxalyl)-N-methylamino]-3-methylimidazolium salts.

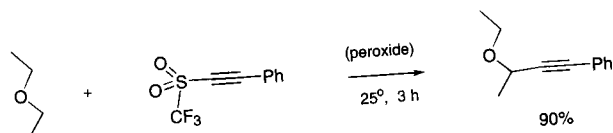
α -Keto esters.¹ A general method for the synthesis of α -keto esters is by Grignard reaction of the salts.

De las Heras, M.A., Vaquero, J.J., Garcia-Navio, J.L., Alvarez-Builla, J. *JOC* 61, 9009 (1996).

Alkynyl triflones.

Alkynylation.¹ The introduction of an alkynyl group to an unactivated position in a carbon skeleton is a remarkable achievement. With alkynyl triflones in the presence of a radical initiator, good yields of α -alkynyl ethers or 1-alkynyladamantanes are formed from the corresponding ethers and adamantane, respectively. Alkenes mainly undergo addition to give β -trifluoromethylalkyl alkynes.

4 Allylbarium reagents



Alkenyl triflates.² The (Z)-alkenyl triflates can be made from alkynyl triflates by the addition of HI followed by Stille coupling. Some other alkenyl triflates are available from organocopper reactions.

Alkenyl and dienyl triflates also insert into unactivated C-H bonds.

¹Gong, J., Fuchs, P.L. *JACS* **118**, 4486 (1996).

²Xiang, J., Fuchs, P.L. *JACS* **118**, 11986 (1996).

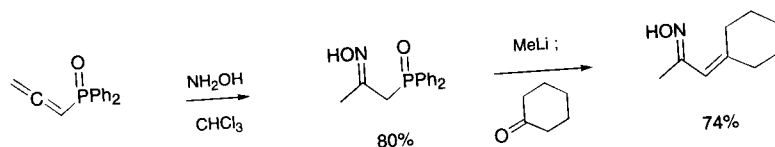
Allenyl *n*-butyl telluride.

Homopropargylic alcohols.¹ On successive treatment with BuLi and an aldehyde, the telluride transfers its allenyl group as a propargyl residue to the latter compound.

¹Dabdoub, M.J., Rotta, J.C.G. *SL* 526 (1996).

Allenyldiphenylphosphine oxide.

α,β -Unsaturated oximes.¹ The addition of hydroxylamine to the allenylphosphine oxides affords oximes of α -phosphinoyl ketones, which may be used to olefinate ketones.



¹Palacios, F., Aparicio, D., de los Santos, J.M., Rodriguez, E. *TL* **37**, 1289 (1996).

Allyl *N*-arenesulfonyloxy carbamates.

Allyl carbamates.¹ Allyl carbamates are formed by displacement of the *N*-arenesulfonyloxy group of the reagents with organocopper compounds.

¹Greck, C., Bischoff, L., Ferreira, F., Genet, J.P. *JOC* **60**, 7010 (1995).

Allylbarium reagents.

Homoallylic amines.¹ The regioselectivity for the addition of γ -substituted allylic reagents to imines is dependent on reaction temperatures. γ -Adducts are formed at -78° , whereas α -adducts are obtained at 0° .

1,5-Dienes.² The coupling of 2,2,2-trifluoroethylphosphates proceeds that of Grignard reagents (α,γ' cross coupling) use of the allylic phosphate esters in these

Yanagisawa, A., Ogasawara, K., Yasue, K., Yamagisawa, A., Yasue, K., Yamamoto, H. *SL*

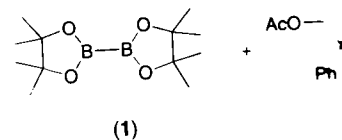
Allyl benzotriazol-1-yl carbonate.

Allyl carbonates.¹ Mixed carbonates prepared from this reagent in the presence of copper(I) salts preferentially.

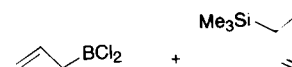
Harada, T., Yamada, H., Tsukamoto, H., Takahashi, T. *TL* 1289 (1996).

Allylboranes and allylboronic acid derivatives.

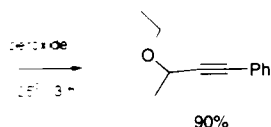
Preparation.¹ One method of preparation is the Pd(0)-catalyzed replacement of allylic acetates with allylboranes.



Allylation. γ -Selective allylation from tartrate esters and allyldiisopropylphosphine oxides. The reaction with allylic silanes follows a γ -selective pathway, and primary alcohols are obtained.



Ishiyama, T., Ahiko, T., Miyaura, N., Yamamoto, Y., Hara, S., Suzuki, A. *TL* 1289 (1996).
Singleton, D.A., Waller, S.C., Zhang, Z.

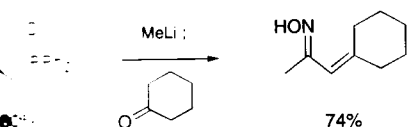


triflates can be made from alkenyl triflates by
ing. Some other alkenyl triflates are available

nt: unactivated C-H bonds.

cessive treatment with BuLi and an aldehyde,
p-allyl residue to the latter compound.

hydroxylamine to the allenylphosphine
nes which may be used to olefinate ketones.



R. *TL* 37, 1289 (1996).

es are formed by displacement of the
n organocopper compounds.

(1995).

for the addition of γ -substituted allylic
temperatures. γ -Adducts are formed at -78° ,

1,5-Dienes.² The coupling of allylbarium reagents with allylic bis-(2,2,2-trifluoroethyl)phosphates proceeds at α and α' positions and is thus different from that of Grignard reagents (α,γ' cross coupling). Hence, little transposition occurs with the use of the allylic phosphate esters in these reactions.

Yanagisawa, A., Ogasawara, K., Yasue, K., Yamamoto, H. *CC* 367 (1996).

Yanagisawa, A., Yasue, K., Yamamoto, H. *SL* 842 (1996).

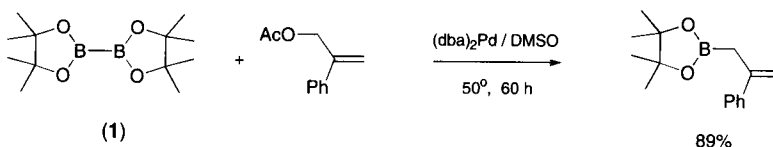
Allyl benzotriazol-1-yl carbonate.

Allyl carbonates.¹ Mixed carbonates derived from carbohydrates are readily prepared from this reagent in the presence of Et₃N. Primary hydroxyl groups react preferentially.

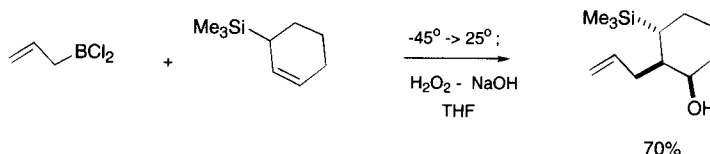
Harada, T., Yamada, H., Tsukamoto, H., Takahashi, T. *JCC* 14, 165 (1995).

Allylboranes and allylboronic acid derivatives.

Preparation.¹ One method of preparation of allylboronates involves the Pd(0)-catalyzed replacement of allylic acetate with bis(pinacolato)diboron (1).



Allylation. γ -Selective allylation of aldehydes using chiral reagents formed in situ from tartrate esters and allyldiisopropoxyboranes² shows 37–85% ee. On the other hand, the reaction with allylic silanes follows a pathway leading to hydroxyallylation of the double bond, and primary alcohols are obtained from 5-silyl-1,3-dienes.³



Ishiyama, T., Ahiko, T., Miyaura, N. *TL* 37, 6889 (1996).

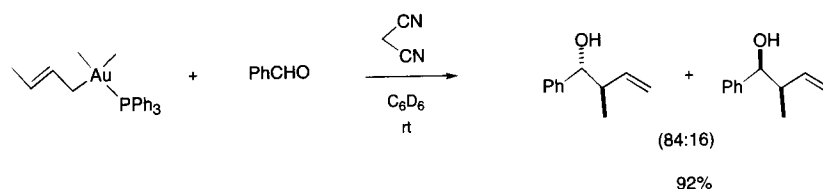
Yamamoto, Y., Hara, S., Suzuki, A. *SL* 883 (1996).

Singleton, D.A., Waller, S.C., Zhang, Z., Frantz, D.E., Leung, S.-W. *JACS* 118, 9986 (1996).

6 Allylmanganese reagents

(η^1 -Allyl)dimethylgold complexes.

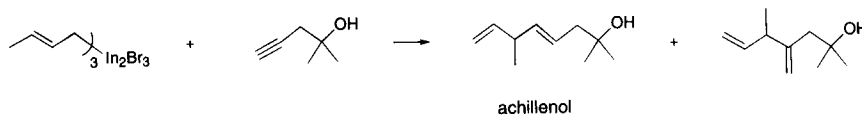
Allylation.¹ These allylating agents react with aromatic aldehydes in a γ - and *anti*-selective manner.



¹Sone, T., Ozaki, S., Kasuga, N.C., Fukuoka, A., Komiya, S. *BCSJ* **68**, 1523 (1995).

Allylindium reagents.

Carbonindation of alkynes.¹ The reaction of allylindium reagents with propargyl or homopropargyl alcohols shows regio- and stereoselectivities, leading to (*E*)-allylic or -homoallylic alcohols.



¹Araki, S., Imai, A., Shimizu, K., Yamada, M., Mori, A., Butsugan, Y. *JOC* **60**, 1841 (1995).

Allyl isothiocyanate.

***N*-Allyl carboxamides.**¹ These amides are formed in good yields by heating fatty acids with $\text{CH}_2=\text{CHCH}_2\text{N}=\text{C}=\text{S}$ in the presence of Amberlyst A26-OH resin at 100°. The formation of adducts that liberate COS is implicated.

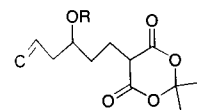
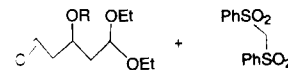
¹Delaveau, V., Mouloungui, Z., Gaset, A. *SC* **26**, 2341 (1996).

Allylmanganese reagents.

Homoallylic alcohols.¹ The reagents are formed in situ by treating allylic phenyl sulfides with lithium 4,4'-di-*t*-butylbiphenylide and then MnCl_2 . Reaction with aldehydes gives the alcohols.

¹Ahn, Y., Doubleday, W.W., Cohen, T. *SC* **25**, 33 (1995).

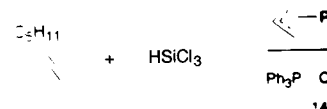
(π -Allyl)palladium chloride dimer
Alkenes.¹ With a bidentate ligand, it promotes the addition of carbon to an intramolecular reaction which forms



R = TBDPS

Hydrosilylative dimerization

1,3-butadienes with good stereoselectivity. Products are isolated after Grignard

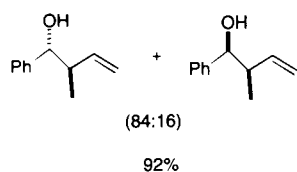


Trost, B.M., Gerusz, V.J. *JACS* **117**, 1177 (1995)
Kawanami, Y., Yamamoto, K. *SL* **1**, 14 (1995)

Allylphosphine oxides and allylphosphonates

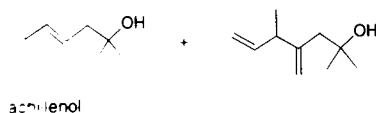
1,3-Dienes. The Horner-Wadsworth-Emmons reaction is *E*-selective.¹ However, different allylphosphonates, and therefore the allyl group is critical.² Thus, NaH and $t\text{-BuOK}$ for those bearing a quaternary ammonium group like pentamethyldiethylenepentamine

react with aromatic aldehydes in a γ - and



K. ... S. *BCSJ* **68**, 1523 (1995).

... of allylindium reagents with propargyl or
... stereoselectivities, leading to (*E*)-allylic or



... A. Butsugan, Y. *JOC* **60**, 1841 (1995).

... are formed in good yields by heating fatty
... of Amberlyst A26-OH resin at 100°. The
... indicated

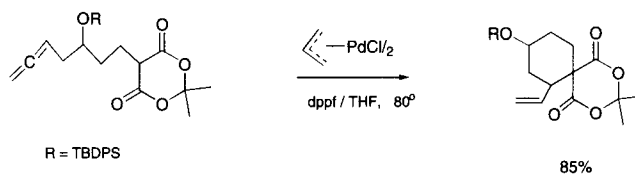
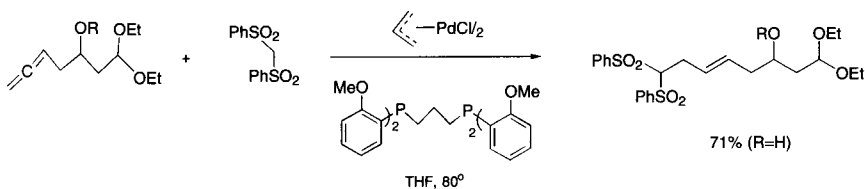
...

... are formed in situ by treating allylic phenyl
... and then MnCl₂. Reaction with aldehydes

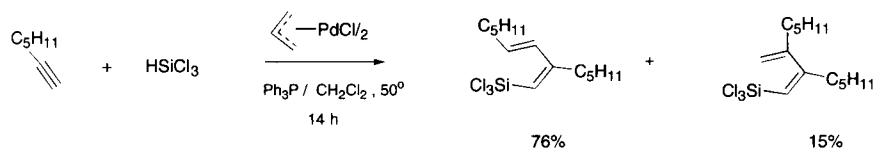
...

(π -Allyl)palladium chloride dimer.

Alkenes.¹ With a bidentate ligand and in the presence of *t*-BuOK, the Pd catalyst promotes the addition of carbon acids to a terminal carbon of an allene, except for intramolecular reaction which forms a cyclohexane.



Hydrosilylative dimerization of 1-alkynes.² A synthesis of 2,4-dialkyl-1-silyl-1,3-butadienes with good stereocontrol is realized. With the use of HSiCl₃ as reagent, the products are isolated after Grignard reactions (Cl₃SiR → (EtO)₃SiR).



¹Trost, B.M., Gerusz, V.J. *JACS* **117**, 5156 (1995).

²Kawanami, Y., Yamamoto, K. *SL* 1232 (1995).

Allylphosphine oxides and allylphosphonates.

1,3-Dienes. The Horner-Wittig reactions of allyl(diphenyl)phosphine oxides are (*E*)-selective.¹ However, different bases may change the outcome of the reactions with allylphosphonates, and therefore, a judicious choice according to the nature of the allyl group is critical.² Thus, NaH is employed for phosphonates bearing a *P*-allyl group, *t*-BuOK for those bearing 2-methylallyl and prenyl groups, and BuLi-pentamethyldiethylenepentamine for crotylphosphonates.

¹Liu, R.-Q., Schlosser, M. *SL* 1195 (1996).

²Liu, R.-Q., Schlosser, M. *SL* 1197 (1996).

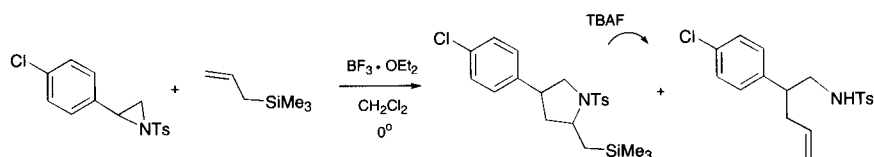
Allylsamarium bromide.

Homoallylic amines.¹ Displacement of benzotriazole from the readily available *N*-aminoalkylbenzotriazoles proceeds rapidly to afford the products (8 examples, 72–93%).

¹Wang, J., Zhou, J., Zhang, Y. *SC* 26, 3395 (1996).

Allylsilanes. 13, 11–13; 14, 18–19; 15, 8; 18, 14, 15–16

***N*-Tosyl-2-aryl-4-pentenylamines.**¹ Lewis acid-catalyzed opening of *N*-tosyl-2-arylaziridines in the presence of allyltrimethylsilane gives a mixture of the pentenylamines and 4-aryl-2-trimethylsilylmethylpyrrolidines. A homogeneous product is obtained on treating such a mixture with TBAF.



Allylation of α -diketones.² Allyltrifluorosilanes react with α -diketones in the presence of Et_3N at room temperature. *syn*-Diols are obtained as the major products. γ,γ -Disubstituted allylsilanes give α -ketols under the same conditions.

Allyltriarylbismuthonium salts.³ These compounds are prepared by Lewis acid-catalyzed reaction of allylsilanes with Ar_3BiF_2 at -78° . They are thermally unstable, decomposing into allylarenes at room temperature.

Allylsilylation. The distributive addition of the allyl and silyl moieties to a double⁴ or triple bond⁵ is catalyzed by AlCl_3 . Results from the latter reaction show that these are both regio- and stereoselective and that *syn*-addition is indicated.

¹Schneider, M.-R., Mann, A., Taddei, M. *TL* 37, 8493 (1996).

²Gewald, R., Kira, M., Sakurai, H. *S* 111 (1996).

³Matano, Y., Yoshimune, M., Suzuki, H. *TL* 36, 7475 (1995).

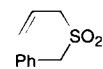
⁴Yeon, S.H., Lee, B.W., Yoo, B.R., Suk, M.-Y., Jung, I.N. *OM* 14, 2361 (1995).

⁵Yeon, S.H., Han, J.S., Hong, E., Do, Y., Jung, I.N. *JOMC* 499, 159 (1995).

Allyl tolyl sulfone.

Extrusion of sulfur dioxide.¹ Allyl tolyl sulfone acts as a scavenger for the free radicals derived from alkyl allyl sulfones ($\text{R-SO}_2\text{-CH}_2\text{CH=CH}_2$) such that extrusion of SO_2 to give $\text{R-CH}_2\text{CH=CH}_2$ becomes a synthetically useful process. In other words, processes other than SO_2 extrusion and radical recombination are suppressed.

The addition of R- and allyl radicals is possible. The relay allyl tolyl sulfone is about five fold excess.

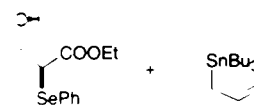


...et-Sire, B., Zard, S.Z. *JACS* 118,

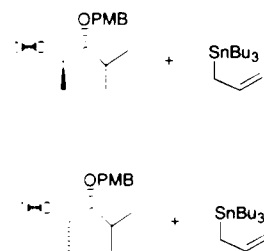
Allyltributylstannane. 13, 10; 14,

Preparation.¹ From allyl aldehyde and reaction with Bu_3SnLi . Various yields to quantitative.

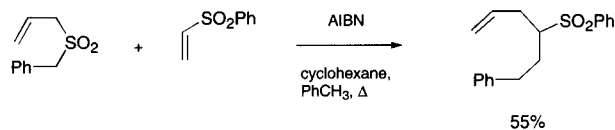
Displacement of activated halides. Radical allylation, which is initiated by displacement of α -seleno esters (e.g., SePh) with Lewis acid (e.g., Me_3Al) to give a



Allylation of aldehydes. The reaction of aldehydes with allyltributylstannane. Besides Lewis acids, other



The addition of R· and allyl radical generated from R-SO₂-CH₂CH=CH₂ to alkenes is feasible. The relay allyl tolyl sulfone is omitted in these cases, but the allyl sulfone is added in about five fold excess.

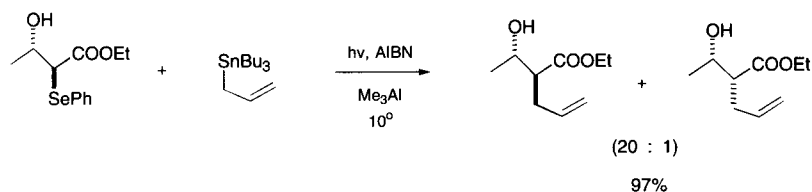


Quiclet-Sire, B., Zard, S.Z. *JACS* **118**, 1209 (1996).

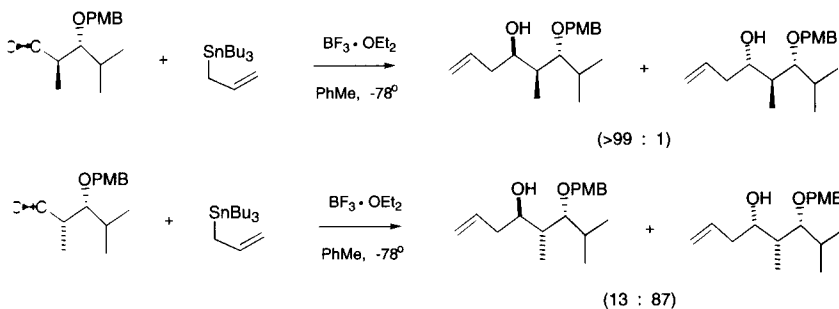
Allyltributylstannane. 13, 10; 14, 14-17; 16, 7-9; 17, 12-13

Preparation.¹ From allyl alcohol, the preparation involves mesylation (BuLi; MsCl) and reaction with Bu₃SnLi. Various substituted analogs are obtained in yields ranging from 71% to quantitative.

Displacement of activated halides. α-Halo esters,² amides,³ and acetals⁴ undergo radical allylation, which is initiated by AIBN or light. A related transformation, such as displacement of α-seleno esters (e.g., that of β-hydroxy-α-phenylseleno esters)⁵ requires a Lewis acid (e.g., Me₃Al) to give a high *anti*-selectivity.



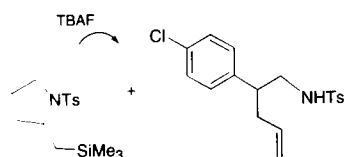
Allylation of aldehydes. The allylation is discriminatory between an aldehyde and a ketone.⁶ Besides Lewis acids,⁷ other catalysts include (Ph₃P)₂PtCl₂.⁸



benzotriazole from the readily available
to afford the products (8 examples, 72-93%).

8, 4, 15-16

Lewis acid-catalyzed opening of
dimethylsilane gives a mixture of the
pyrrolidines. A homogeneous product is
3,3,3-



Allyl sulfones react with α-diketones in the
presence of Lewis acids to give allylated
products as the major products.
under the same conditions.

Allyl sulfones are prepared by Lewis
acid catalysis. At BF₃ at -78°. They are thermally unstable,
decompose

the allyl and silyl moieties to a double
bond. The latter reaction show that these are both
indicated.

1, 1, 1-

1, 1, 1-

JACS **117**, 2361 (1995).

JACS **117**, 159 (1995).

Allyl sulfone acts as a scavenger for the free
radical (R-SO₂-CH₂CH=CH₂) such that extrusion of
allyl sulfone is a synthetically useful process. In other words,
radical recombination are suppressed.

Homoallylic amines. The reaction of aldimines with allyltributylstannane is catalyzed by Me_3SiCl ⁹ and by the π -allylpalladium chloride dimer.¹⁰

[Note that sulfonyl azides and azidoformate esters form *N*-allyl sulfonamides and carbamates, respectively, in the free-radical reactions (using $\text{Ph}_3\text{SnCH}_2\text{CH}=\text{CH}_2$ as the allyl donor).¹¹]

¹Weigand, S., Brückner, R. *S* 475 (1996).

²Landais, Y., Planchenault, D. *T* 51, 12097 (1995).

³Hanessian, S., Yang, H., Schaum, R. *JACS* 118, 2507 (1996).

⁴Nagano, H., Azuma, Y. *CL* 845 (1996).

⁵Gerster, M., Audergon, L., Moufid, N., Renaud, P. *TL* 37, 6335 (1996).

⁶Kim, S., Kim, S.H. *TL* 36, 3723 (1995).

⁷Evans, D.A., Dart, M.J., Duffy, J.L., Yang, M.G., Livingston, A.B. *JACS* 117, 6619 (1995).

⁸Nakamura, H., Asao, N., Yamamoto, Y. *CC* 1273 (1995).

⁹Wang, D.-K., Dai, L.-X., Hou, X.-L. *TL* 36, 8649 (1995).

¹⁰Nakamura, H., Iwama, H., Yamamoto, Y. *CC* 1459 (1996).

¹¹Dang, H.-S., Roberts, B.P. *JCS(P1)* 1493 (1996).

Alumina. 14, 20–21; 16, 9–10; 18, 16–17

Aroyldiazomethanes.¹ Diaroyldiazomethanes decompose at room temperature to generate aroyldiazomethanes in the presence of alumina.

Wittig reactions.² The synthesis of unsaturated esters is conveniently performed.

Piperazines.³ Twofold *N*-alkylation of *N*-arylamines with carbamates of bis(2-bromoethyl)amine on basic alumina at 150° forms *N*-arylpiperazines. The *N*-protecting group is also removed during the reaction.

Friedel–Crafts acylation.⁴ An improved procedure for the acylation of aromatic ethers is to carry it out with acids in the presence of $(\text{CF}_3\text{CO})_2\text{O}$ on an alumina surface.

¹Korneev, S., Richter, C. *S* 1248 (1995).

²Dhavale, D.D., Sindkhedkar, M.D., Mali, R.S. *JCR(S)* 414 (1995).

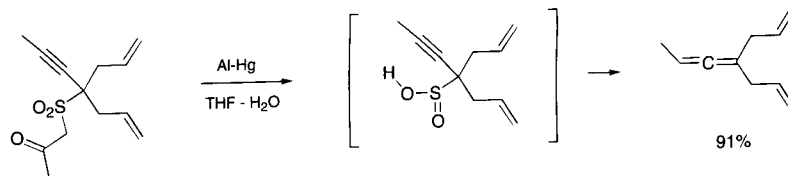
³Mishani, E., Dence, C.S., McCarthy, T.J., Welch, M.J. *TL* 37, 319 (1996).

⁴Ranu, B.C., Ghosh, K., Jana, U. *JOC* 61, 9546 (1996).

Aluminum. 18, 17–18

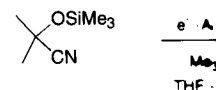
1,2-Diols and 1,2-diamines. Aromatic carbonyl compounds and imines are rapidly converted to 1,2-diols¹ and 1,2-diamines,² respectively, with Al-KOH in methanol (ArCHO , 15 examples, 52–93%; ArCOR , 9 examples, 65–93%; $\text{ArCH}=\text{NAr}'$, 12 examples, 65–90%).

Trisubstituted allenes.³ Propargylic sulfones undergo reductive elimination with Al/Hg in aqueous THF (11 examples, 74–92%).



Reductive alkylation of styrenes.⁴ Electrochemical reductive alkylation of styrenes at the β -carbon. If proper α,ω -dihalogenated cycloalkanes are formed.

α,N,N -Tris(trimethylsilyl) enamine. Sacrificing aluminum anode in the presence of examples, 59–82%).



Kurana, J.M., Sehgal, A., Gogia, A., Manu...
Brah, B., Prajapati, D., Sandhu, J.S. *TL* 36...
Edwin, J.E., Adlington, R.M., Crouch, N...
Enel, E., Paugam, J.P., Nedelec, J.-Y., Per...
stantieux, T., Picard, J.-P. *OM* 15, 1604

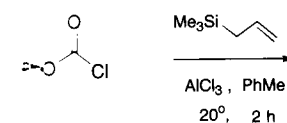
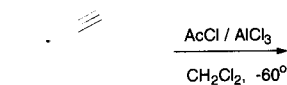
Aluminum bis(triflamide).

Acetylation. The triflamide is a...
phenols and aliphatic alcohols (10 exam...
and triflates are also effective.

Mami, K., Kotera, O., Motoyama, Y., Sak...

Aluminum chloride. 13, 15–17; 14, 21

Acylation. Some noteworthy...
chloro- α -allenyl ketones,¹ phenyl...
pentenones.³



aldimines with allyltributylstannane is aluminum chloride dimer.¹⁰

formate esters form *N*-allyl sulfonamides and reactions (using $\text{Ph}_3\text{SnCH}_2\text{CH}=\text{CH}_2$ as the

18 (1996).

37, 6335 (1996).

Angston, A.B. *JACS* **117**, 6619 (1995).

12 (1995).

12 (1995).

12 (1996).

decompose at room temperature to alumina.

separated esters is conveniently performed.

N-arylamines with carbamates of at 150° forms *N*-arylpiperazines. The reaction.

procedure for the acylation of aromatic presence of $(\text{CF}_3\text{CO})_2\text{O}$ on an alumina surface.

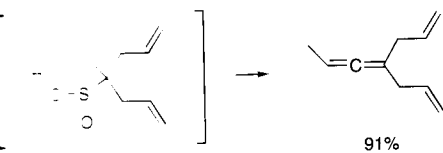
414 (1995).

TL **37**, 319 (1996).

carbonyl compounds and imines are rapidly respectively, with Al-KOH in methanol (ArCHO , examples, 65–93%; $\text{ArCH}=\text{NAr}'$, 12 examples,

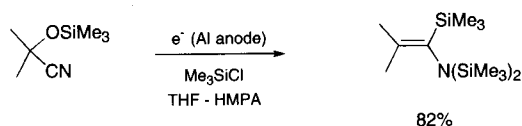
ketones undergo reductive elimination with

42



Reductive alkylation of styrenes.⁴ Using a sacrificing aluminum anode, the electrochemical reductive alkylation of styrenes with alkyl halides in DMF (60°) takes place at the β -carbon. If proper α,ω -dihaloalkanes are used as the alkylating agents, arylcycloalkanes are formed.

α,N,N -Tris(trimethylsilyl) enamines.⁵ Electrolysis of α -siloxy nitriles with a sacrificing aluminum anode in the presence of Me_3SiCl results in reductive silylation (8 examples, 59–82%).



Khurana, J.M., Sehgal, A., Gogia, A., Manian, A., Maikap, G.C. *JCS(P1)* 2213 (1996).

Baruah, B., Prajapati, D., Sandhu, J.S. *TL* **36**, 6747 (1995).

Baldwin, J.E., Adlington, R.M., Crouch, N.P., Hill, R.L., Laffey, T.G. *TL* **36**, 7925 (1995).

Leonel, E., Paugam, J.P., Nedelec, J.-Y., Perichon, J. *JCR(S)* 278 (1995).

Constantieux, T., Picard, J.-P. *OM* **15**, 1604 (1996).

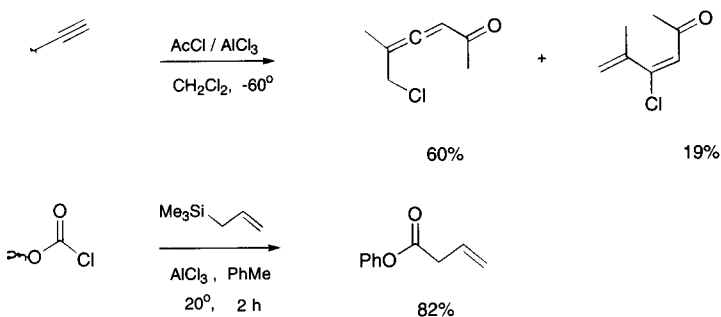
Aluminum bis(triflamide).

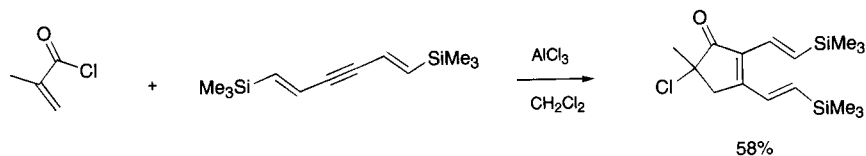
Acetylation. The triflamide is a highly efficient catalyst for the acetylation of phenols and aliphatic alcohols (10 examples, 90–99%). But some other metal triflamides and triflates are also effective.

Mikami, K., Kotera, O., Motoyama, Y., Sakaguchi, H., Maruta, M. *SL* 171 (1996).

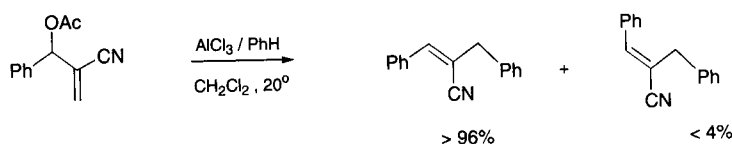
Aluminum chloride. 13, 15–17; 14, 21–22; 15, 10; 16, 10–11; 17, 15; 18, 18–20

Acylation. Some noteworthy examples of acylation are the formation of δ -chloro- α -allyl ketones,¹ phenyl esters of β,γ -unsaturated acids,² and substituted cyclopentenones.³





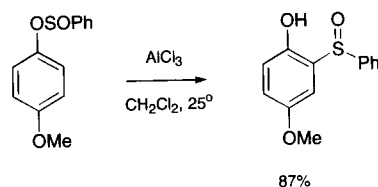
Friedel–Crafts alkylations. α -(1-Acetoxyalkyl)acrylic acid derivatives that are readily obtained via the Baylis–Hillman reaction are good alkylating agents. The substitution follows predominantly an $\text{S}_{\text{N}}2'$ pattern.⁴ Alkylation of aromatic hydrocarbons with benzalazines provides unsymmetrical diarylmethanes (10 examples, 63–73%).⁵



Formyldestannylation. A trimethylstannyl group attached to an aromatic ring⁶ or an alkenyl position⁷ is liable to replacement on reaction with dichloromethyl methyl ether. Aldehydes are formed.

Hydrosilylation.⁸ Alkynes react with hydrosilanes to give (*Z*)-silylalkenes as a result of *anti*-addition.

Thia–Fries rearrangement.⁹ Benzenesulfinylphenols are obtained on treatment of the aryl benzenesulfinates with AlCl_3 in CH_2Cl_2 at room temperature.



¹Santelli-Rouvier, C., Lefrere, S., Santelli, M. *JOC* **61**, 6678 (1996).

²Mayr, H., Gabriel, A.O., Schumacher, R. *LA* 1583 (1995).

³Fiandanese, V., Marchese, G., Punzi, A., Ruggieri, G. *TL* **37**, 8455 (1996).

⁴Basavaiah, D., Pandiaraju, S., Padmaja, K. *SL* 393 (1996).

⁵Mathew, F., Bhattacharjee, S., Myrboh, B. *SC* **25**, 1795 (1995).

⁶Niestroj, M., Neumann, W.P. *CB* **129**, 45 (1996).

⁷Niestroj, M., Neumann, W.P., Mitchell, T.N. *JOMC* **519**, 45 (1996).

⁸Asao, N., Sudo, T., Yamamoto, Y. *JOC* **61**, 7654 (1996).

⁹Jung, M.E., Lazarova, T.I. *TL* **37**, 7 (1996).

Aluminum isopropoxide—trifluoroacetic acid
Meerwein–Ponndorf–Verley reduction.

the reduction.¹ Both reagents are used in catalytic

Akamanchi, K.G., Varalakshmy, N.R. *TL* **36**, 3571 (1995).

Akamanchi, K.G., Noorani, V.R. *TL* **36**, 5085 (1995).

Aluminum tris(2,6-diphenylphenoxide). [A]

Conjugate addition to carbonyl compounds.

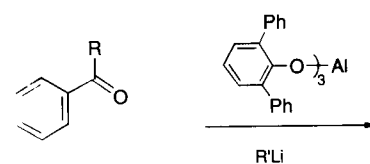
prevents attack at the carbonyl group, and the

aromatic aldehydes and ketones.¹ With relative

i-BuLi, products from addition in the *p*-position

Nonaromatic conjugate carbonyl compounds

4-reduction² with *i*-BuAlH–BuLi at -78° affords

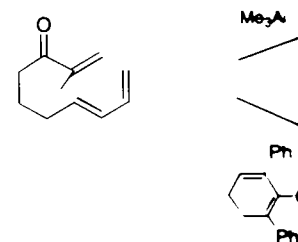


Diels–Alder reactions.³ The stereoselective

addition of diene and conjugate ketones and aldehydes

in the presence of ATPH. The bulky complex

controls the orientation. The difference in an intramolecular



Claisen rearrangement. Complexation

of the allyl vinyl ether ensures a high (*E*):(*Z*) ratio

of the product. The bulky complex

of aluminum tris(2,6-diphenylphenoxide) with

the allyl vinyl ether [2- α -naphthyl-6-phenyl]phenoxide]. The