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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

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	*n*-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
DIBAH	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

$h\nu$	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	*n*-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, *t*-butyldimethylsilyl
TEMPO	2,2,6,6,-tetramethylpiperidinoxy
TES	triethylsilyl
THF	tetrahydrofuran

TIPS	triisopropylsilyl
TMEDA	*N*,*N*,*N*,*N*′-tetramethylethylenediamine
TMS	trimethylsilyl
Ts	tosyl (*p*-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

CONTENTS

A

Acetic acid.

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

[1] 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.

[1] 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.

[1] 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.

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

Acetyl chloride. 18, 2

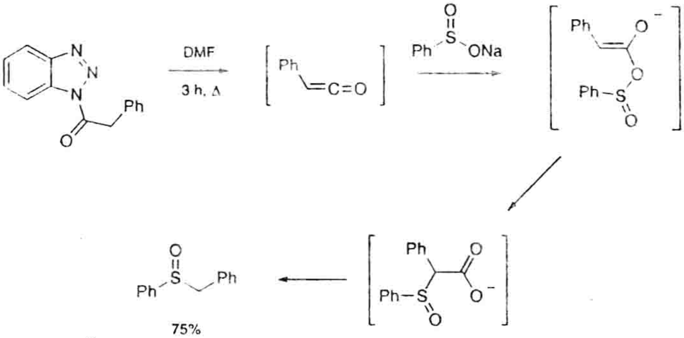
β-Chlorosulfides.[1] Sulfenyl chlorides (RSCl) are formed when sulfenate esters (RSOR′) are treated with acetyl chloride (or other acid chlorides). The reactive species functionalize olefins in situ.

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%).

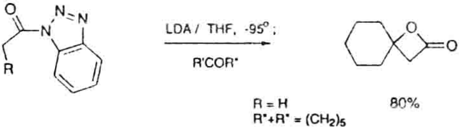
[1] Brown, C., Evans, G.R. *TL* **37**, 679 (1996).
[2] Benincasa, M., Boni, M., Ghelfi, F., Pagnoni, U.M. *SC* **25**, 1843 (1995).

N^1-Acylbenzotriazoles.

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



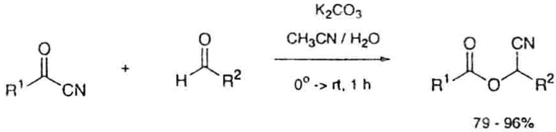
β-Lactones.[2] The amides undergo aldolization with ketones and aldehydes, furnishing β-lactones in one step. Both transformations imply ketene formation in the initial step.



[1] Katritzky, A.R., Yang, B., Qian, Y. *SL* 701 (1996).
[2] Wedler, 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 K_2CO_3 in aqueous acetonitrile leads to α-cyanohydrin esters.



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

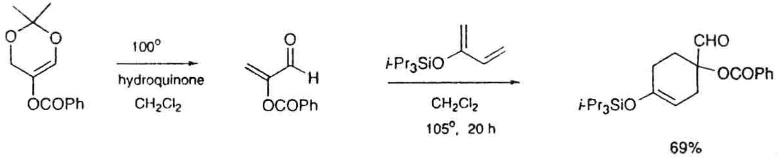
N-Acyl-2-methylimidazoles.

Acylsilanes.[1] Acylimidazoles are electrochemically reduced on a Pt cathode, and the ensuing acyl anion equivalents can be trapped with Me_3SiCl.

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

2-Acyloxyacroleins.

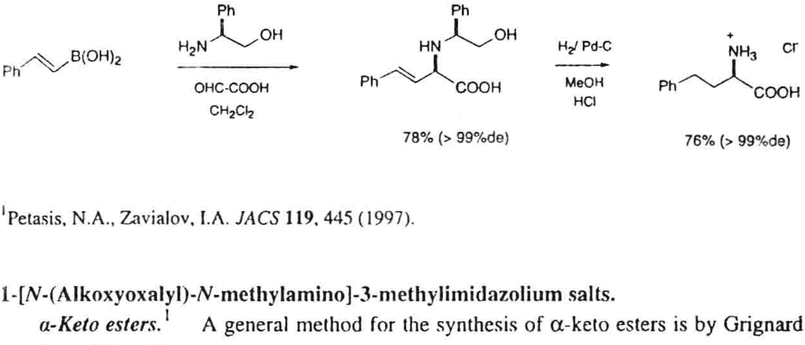
Dienophiles.[1] These compounds are available from 2,2-dimethyl-1,3-dioxan-5-one on enolacetylation and thermolysis of the resulting enol esters at 100°. They serve as dienophiles in Diels–Alder reactions.



[1] 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.



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

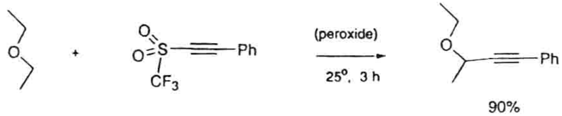
1-[*N*-(Alkoxyoxalyl)-*N*-methylamino]-3-methylimidazolium salts.

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

[1] 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.



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

Alkenyl and dienyl triflones also insert into unactivated C–H bonds.

[1] Gong, J., Fuchs, P.L. *JACS* **118**, 4486 (1996).
[2] Xiang, J., Fuchs, P.L. *JACS* **118**, 11986 (1996).

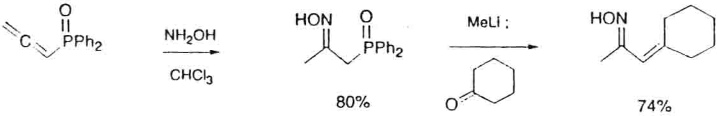
Allenyl *n*-butyl telluride.

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.

[1] Dabdoub, 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.



[1] Palacios, 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.

[1] Greck, 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 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.

[1] Yanagisawa, A., Ogasawara, K., Yasue, K., Yamamoto, H. *CC* 367 (1996).
[2] Yanagisawa, A., Yasue, K., Yamamoto, H. *SL* 842 (1996).

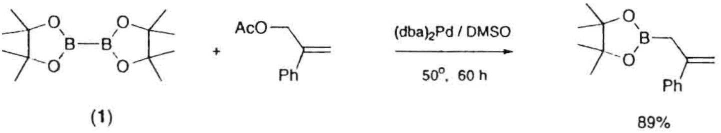
Allyl benzotriazol-1-yl carbonate.

Allyl carbonates.[1] Mixed carbonates derived from carbohydrates are readily prepared from this reagent in the presence of Et_3N. Primary hydroxyl groups react preferentially.

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

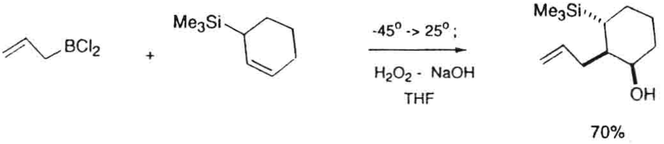
Allylboranes and allylboronic acid derivatives.

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



(**1**)

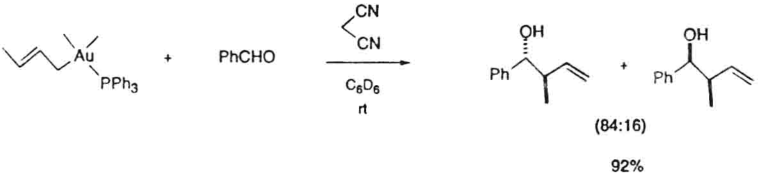
Allylation. γ-Selective allylation of aldehydes using chiral reagents formed in situ from tartrate esters and allyldiisopropoxyboranes[2] shows 37–85% ee. On the other hand, the reaction with allylic silanes follows a pathway leading to hydroxyallylation of the double bond, and primary alcohols are obtained from 5-silyl-1,3-dienes.[3]



[1] Ishiyama, T., Ahiko, T., Miyaura, N. *TL* **37**, 6889 (1996).
[2] Yamamoto, Y., Hara, S., Suzuki, A. *SL* 883 (1996).
[3] Singleton, D.A., Waller, S.C., Zhang, Z., Frantz, D.E., Leung, S.-W. *JACS* **118**, 9986 (1996).

(η^1-Allyl)dimethylgold complexes.

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



[1] Sone, 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.

achillenol

[1] Araki, 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 $CH_2{=}CHCH_2N{=}C{=}S$ in the presence of Amberlyst A26–OH resin at 100°. The formation of adducts that liberate COS is implicated.

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

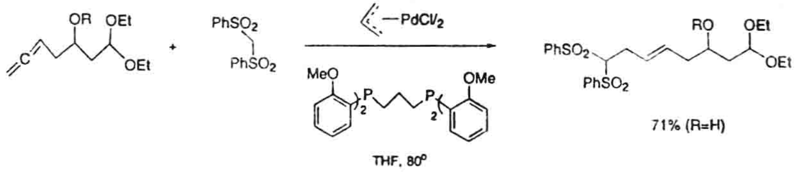
Allylmanganese reagents.

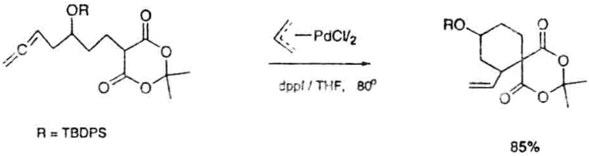
Homoallylic alcohols.[1] The reagents are formed in situ by treating allylic phenyl sulfides with lithium 4,4′-di-*t*-butylbiphenylide and then $MnCl_2$. Reaction with aldehydes gives the alcohols.

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

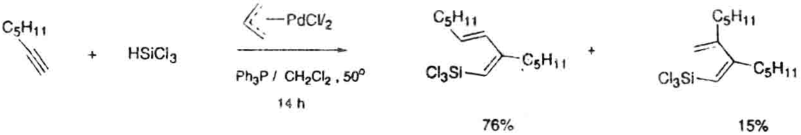
(π-Allyl)palladium chloride dimer.

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 $HSiCl_3$ as reagent, the products are isolated after Grignard reactions ($Cl_3SiR \rightarrow (EtO)_3SiR$).



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[1] Trost, B.M., Gerusz, V.J. *JACS* **117**, 5156 (1995).
[2] Kawanami, 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-methallyl and prenyl groups, and BuLi-pentamethyldiethylenepentamine for crotylphosphonates.