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To the memory of  
Professor Louis F. Fieser  
and  
Mrs. Mary Fieser

## PREFACE

My first contact with organic chemistry was through the textbooks and experimental manual written by Professor L. F. Fieser and Mrs. M. Fieser. These works impressed me not only with their organization and lucidity, but the appearance of a compilation of reagents as an appendix really aroused my curiosity about research tools. This feature was not found in any other textbook, and was a harbinger of the famous and successful series, *Reagents for Organic Synthesis*.

The Fiesers will long be remembered for their outstanding contributions to chemical education. Their dedication to providing a quality service during the latter part of their lives played an important role in the rapid advances of organic synthesis during the past thirty years. The quick retrieval of essential information through consultation of the series must have saved uncountable man-hours in research, and in the course of such readings there must also have been occasions that a chemist became inspired to develop improved or new synthetic methods.

The "ROS" reference series is an established institution. That is the main reason Wiley & Sons decided to continue its publication. In accepting an invitation to authorship with great trepidation, I can only hope that my feeble efforts will prove to be more than merely "using a dog's tail to substitute for a mink's." (狗尾續貂)

The previous format is essentially maintained, except that more conventional reference abbreviations are used. Due to space limitations and my attempt to cover many more papers, unnecessary explanations are omitted. With the same considerations, a general transformation that can be described in a short sentence without ambiguity is deemed sufficient, and the corresponding graphics are dispensed with.

TSE-LOK HO

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## 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. Russ. Chim. Fr.
BRAS	Bull. Russ. Acad. Sci.
CB	Chem. Ber.
CC	Chem. Commun.
CCCC	Collect. Czech. Chem. Commun.
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(Pl)	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.

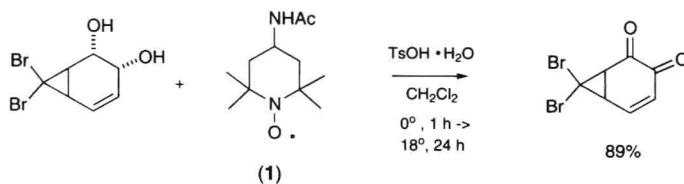
**xii Reference Abbreviations**

JOCU	J. Org. Chem. USSR (Engl. Trans.)
LA	Liebigs Ann. Chem.
MC	Mendeleev Commun.
NJC	New Journal of Chemistry
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

## 4-Acetamido-2,2,6,6-tetramethylpiperidin-1-oxyl (1).

**Glycol oxidation.**<sup>1</sup> The tosic acid salt of 4-acetamido-TEMPO is a mild oxidizing agent that converts glycols to  $\alpha$ -dicarbonyl compounds.

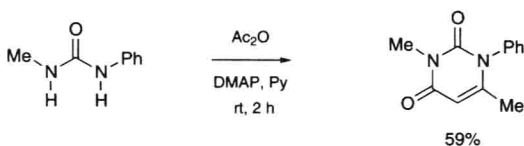


<sup>1</sup>M. G. Banwell, V. S. Bridges, J. R. Dupuche, S. L. Richards, and J. M. Walter, *JOC* **59**, 6338 (1994).

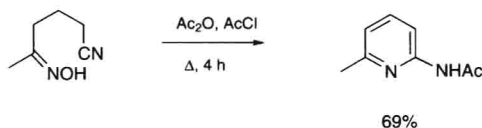
## Acetic anhydride.

**Acetylation.**<sup>1</sup> In the presence of freshly prepared MgI<sub>2</sub> (from Mg and I<sub>2</sub> in dry ether), Ac<sub>2</sub>O acetylates primary, secondary, and tertiary alcohols as well as phenols.

**Cyclization.**<sup>2</sup> Acetic anhydride provides a diketene unit on reaction with ureas in the presence of DMAP.



**Rearrangement-cyclization.**<sup>3</sup>  $\delta$ -Oximino nitriles form 2-acetamidopyridines on treatment with Ac<sub>2</sub>O-AcCl under reflux. The reaction proceeds from rearrangement of *N*-acetoxyenamines to *C*-acetoxy imines, which undergo elimination and cyclization.



**Pummerer rearrangement.**<sup>4</sup>  $\gamma$ -Sulfinyl acids give  $\gamma$ -thio- $\gamma$ -butyrolactones. In a selenium version,<sup>5</sup> the rearrangement product (with a  $\alpha,\alpha$ -difluorinated selenoxide) can react with cyclic ethers.

## 2 Acetylene

<sup>1</sup> P. K. Chowdhury, *JCR(S)* 338 (1993).

<sup>2</sup> J. Aichner, H. Egg, D. Gapp, S. Haller, D. Rakowitz, and U. Ramspacher, *H* **36**, 307 (1993).

<sup>3</sup> R. J. Vijn, H. J. Arts, P. J. Maas, and A. M. Castelijns, *JOC* **58**, 887 (1993).

<sup>4</sup> H. Su, Y. Hiwatari, M. Soenosawa, K. Sasuga, K. Shirai, and T. Kumamoto, *BCSJ* **66**, 2603 (1993).

<sup>5</sup> K. Uneyama, Y. Tokunaga, and K. Maeda, *TL* **34**, 1311 (1993).

### Acetone cyanohydrin.

**Nitrile synthesis.**<sup>1</sup> As a cyanide ion source in the preparation of alkyl nitriles by displacement of alkyl halides, it permits the reaction in an aprotic solvent.

<sup>1</sup> P. Dowd, B. K. Wilk, and M. Wlostowski, *SC* **23**, 2323 (1993).

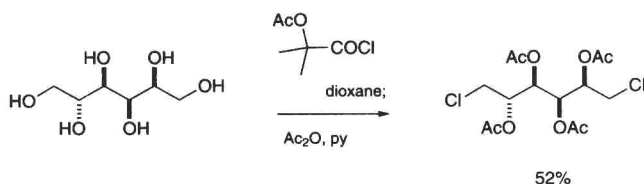
### Acetonitrile. 15, 1

**Ritter reaction.**<sup>1</sup> Benzyl alcohols are converted to amides in acetonitrile in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$ .

<sup>1</sup> H. Firouzabadi, A. R. Sardarian, and H. Badparva, *SC* **24**, 601 (1994).

### $\alpha$ -Acetoxyisobutyryl chloride. 8, 3

**Regioselective chlorination.**<sup>1</sup> Primary alcohols are converted to chlorides; thus unprotected alditols react selectively.



<sup>1</sup> M. Benazza, M. Massoui, R. Uzan, and G. Demailly, *JCC* **13**, 967 (1994).

### Acetyl chloride.

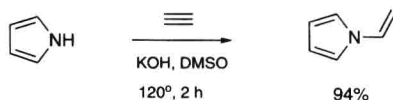
**Selective acetylation.**<sup>1</sup> Primary alcohols are selectively acetylated in the presence of secondary alcohols with acetyl chloride and various bases, such as collidine, diisopropylethylamine, or 1,2,2,6,6-pentamethylpiperidine.

<sup>1</sup> K. Ishihara, H. Kurihara, and H. Yamamoto, *JOC* **58**, 3791 (1993).

### Acetylene.

**Vinylation.**<sup>1</sup> Pyrrole undergoes *N*-vinylation with acetylene in KOH-DMSO.





<sup>1</sup> O. A. Tarasova, A. G. Mal'kina, A. I. Mikhaleva, L. Brandsma, and B. A. Trofimov, *SC* **24**, 2035 (1994).

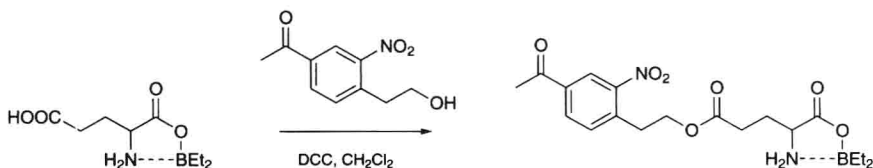
### Acetyl hypobromite.

**N-Bromination.**<sup>1</sup> Amides are brominated with AcOBr in CCl<sub>4</sub> at room temperature.

<sup>1</sup> L. Duhamel, G. Ple, and P. Angibaud, *SC* **23**, 2423 (1993).

### 2-(4-Acetyl-2-nitrophenyl)ethanol.

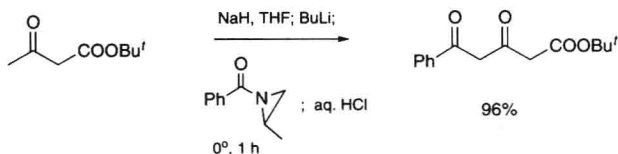
**Carboxyl group protection.**<sup>1</sup> The ω-esters of aspartic and glutamic acids are formed readily using the DCC method, after the geminal functionalities are sequestered (by reaction with Et<sub>3</sub>B). The acid can be regenerated under conditions (0.1 M Bu<sub>4</sub>NF) that do not affect an N-Boc group.



<sup>1</sup> J. Robles, E. Pedroso, and A. Grandas, *S* 1261 (1993).

### N-Acylaziridines.

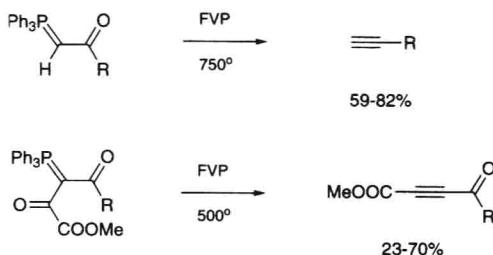
**Polyketides.**<sup>1</sup> Prepared in a one-pot reaction from RCOOH, (COCl)<sub>2</sub>, Et<sub>3</sub>N, and an aziridine (e.g., 2-methylaziridine), these reagents are suitable acyl donors for chain extension of poly-1,3-dicarbonyl compounds via reaction with their polyanions.



<sup>1</sup> B. Lygo, *TL* **35**, 5073 (1994).

**Acylmethylenetriphenylphosphoranes.**

**Acetylene precursors.** Flash vacuum pyrolysis of these stabilized Wittig reagents removes triphenylphosphine oxide to furnish acetylenes. Both terminal<sup>1</sup> and internal acetylenes<sup>2,3</sup> are accessible by this method.



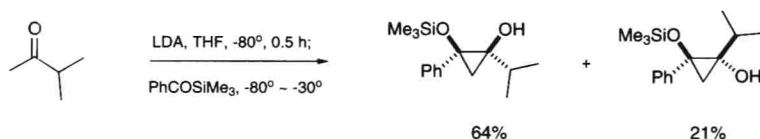
<sup>1</sup> R. A. Aitken and J. I. Atherton, *JCS(PI)* 1281 (1994).

<sup>2</sup> R. A. Aitken, H. Herion, A. Janosi, S. V. Raut, S. Seth, I. J. Shannon, and F. C. Smith, *TL* **34**, 5621 (1993).

<sup>3</sup> R. A. Aitken, C. E. R. Horsburgh, J. G. McCreadie, and S. Seth, *JCS(PI)* 1727 (1994).

**Acylsilanes. 17, 1-2**

**Cyclopropanation.**<sup>1</sup> Reaction with ketone enolates results in 1,2-cyclopropane-diol derivatives.

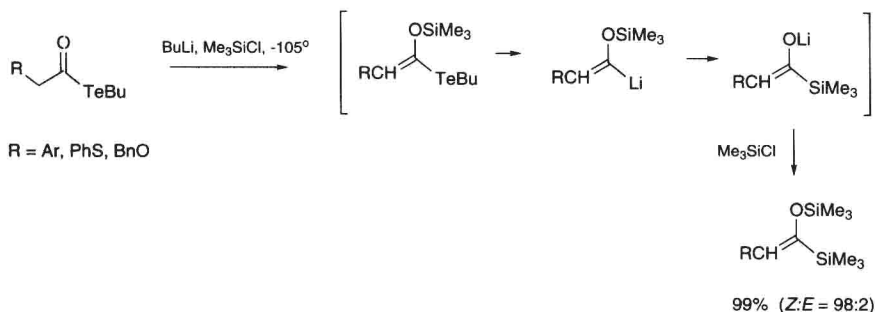


<sup>1</sup> K. Takeda, J. Nakatani, H. Nakamura, K. Sako, E. Yoshii, and K. Yamaguchi, *SL* 841 (1993).

**Acytelluranes.**

These reagents are readily obtained<sup>1</sup> from Et<sub>2</sub>AlCl-catalyzed reaction of aldehydes with diisobutylaluminum butylltelluride in THF at room temperature.

**Enol silyl ethers of acylsilanes.**<sup>2</sup> On treatment with butyllithium and trimethylsilyl chloride, these compounds undergo enol silylation, tellurium-lithium exchange, and O → C silyl migration. The lithium enolates are further silylated.

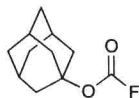


<sup>1</sup> T. Inoue, K. Takeda, N. Kambe, A. Ogawa, I. Ryu, and N. Sonoda, *JOC* **59**, 5824 (1994).

<sup>2</sup> T. Inoue, N. Kambe, I. Ryu, and N. Sonoda, *JOC* **59**, 8209 (1994).

### 1-Adamantyl fluoroformate (1).

**Phenol protection.**<sup>1</sup> The reagent (1) transforms phenols carrying strongly electron-withdrawing groups into mixed carbonates. Deprotection is accomplished by use of trifluoroacetic acid at 0–20° for 20–60 min.

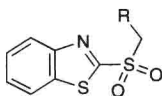


(1)

<sup>1</sup> I. Niculescu-Duvaz and C. J. Springer, *JCR(S)* 242 (1994).

### 2-Alkanesulfonylbenzothiazole (1).

**Olefination.**<sup>1</sup> The anions of (1) react with carbonyl compounds to give predominantly (*E*)-alkenes.



(1)

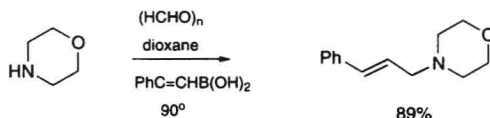
<sup>1</sup> J.-B. Baudin, G. Hareau, S. A. Julia, R. Lorne, and O. Ruel, *BSCF* 856 (1993).

**Alkenylboranes.**

**Enynes.**<sup>1</sup> The attack of lithioalkynes on alkenyldisiamylboranes followed by oxidation with iodine leads to enynes in which the original configuration of the alkenes is retained.

**Carbonylation.**<sup>2</sup> An enone that bears chirality at both  $\alpha'$  and  $\beta'$  carbon atoms can be synthesized through successive reactions of a chiral borane with an alkene and an alkyne, followed by exposure to acetaldehyde. Further treatment of the resulting alkenylborane with dichloromethyl methyl ether and  $\text{Et}_3\text{COLi}$ , and finally with  $\text{H}_2\text{O}_2$  affords the product.

**Allylamines.**<sup>3</sup> Alkeneboronic acids are converted to allylamines of defined configuration on treatment with conventional Mannich reaction components ( $\text{R}_2\text{NH}$ , paraformaldehyde). The required vinylboronic acids are available from 1-alkynes by reaction with catecholborane followed by hydrolysis.



**$\gamma,\delta$ -Unsaturated ketones.**<sup>4,5</sup> The synthesis from alkenyldiisopropoxyboranes and  $\alpha,\beta$ -unsaturated ketones is catalyzed by  $\text{BF}_3 \cdot \text{OEt}_2$ . It is suitable for reaction with substrates that are labile to organometallics (e.g., Cu reagents). The corresponding alkynyl ketones are obtained in an analogous manner.

<sup>1</sup> P. Bovicelli, P. Lupatelli, and E. Mincione, *JNP* **56**, 676 (1993).

<sup>2</sup> H. C. Brown and V. K. Mahindroo, *TA* **4**, 59 (1993).

<sup>3</sup> N. A. Petasis and I. Akritopoulou, *TL* **34**, 583 (1993).

<sup>4</sup> E.-i. Takada, S. Hara, and A. Suzuki, *TL* **34**, 7067 (1993).

<sup>5</sup> E.-i. Takada, S. Hara, and A. Suzuki, *HC* **3**, 483 (1992).

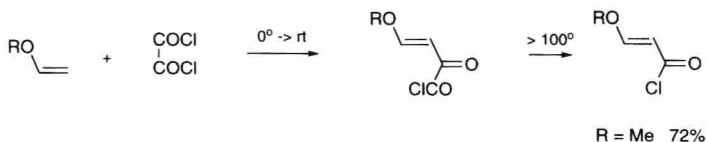
**Alkenyltriphenylphosphonium tetrafluoroborate,  $\text{Ph}_3\text{P}^+\text{CH=CHR BF}_4^-$ .**

**1,3-Dienes.**<sup>1</sup> These salts are available from the reaction of epoxides with an acid chloride ( $\text{AcCl}$  or oxalyl chloride) and  $[\text{Ph}_3\text{PH}]^+\text{BF}_4^-$ . Diene formation in moderate yields is observed when these salts are treated with  $\text{ArCHO}$  and DBU.

<sup>1</sup> K. Okuma, M. Ono, and H. Ohta, *BCSJ* **66**, 1308 (1993).

**3-Alkoxyacryloyl chlorides.**

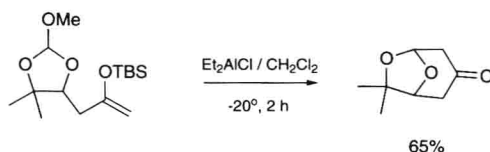
An improved preparation<sup>1</sup> involves reaction of vinyl ethers with oxalyl chloride followed by heating above  $100^\circ\text{C}$ .



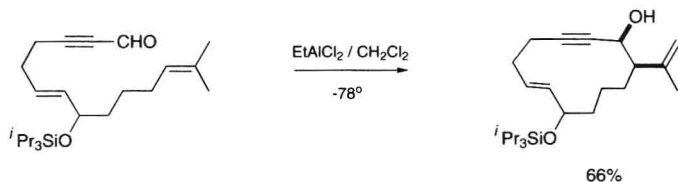
<sup>1</sup> L. F. Tietze, C. Schneider, and M. Pretor, *S* 1079 (1993).

**Alkylaluminum chlorides.** **13**, 5–8; **14**, 4–5; **15**, 2–5; **16**, 1–3; **17**, 4–7

**Mukaiyama aldolization.**<sup>1</sup> The intramolecular reaction of a dioxalenium ion with a silyl enol ether side chain gives dioxabicyclic products.



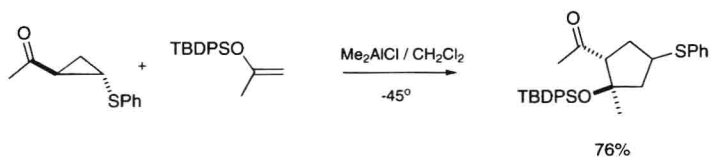
**Ene reactions.** The intramolecular version is suitable for the construction of 12-, 14-, and 16-membered ring systems.<sup>2</sup> Excellent 1,3-chirality transfer in this process is evident.<sup>3</sup>



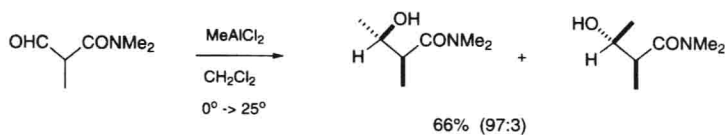
2-(Alkenylmethyl) cyclic ethers are formed by the reaction of lactols and alkenes.<sup>4</sup>

**Diels–Alder reactions.** Diethylaluminum chloride deposited on silica seems to be a superior catalyst.<sup>5</sup> Methylaluminum dichloride alone is effective in promoting intramolecular cycloadditions involving a furan ring as the diene.<sup>6</sup>

**[3+2]Cycloaddition.** Reaction of the 1,3-dipolar species derived from methyl 2-phenylthiocyclopropyl ketone with silyl vinyl ethers furnishes functionalized cyclopentanes.<sup>7</sup> A related reaction is the trapping of a fragmented cyclobutane.<sup>8</sup>

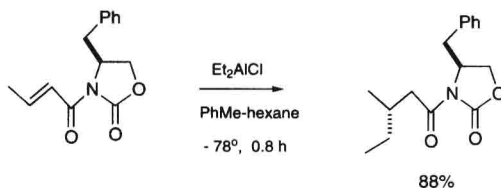


**Alkylation of enolizable carbonyl compounds.**  $\beta$ -Oxo amides react with organoaluminum chlorides stereoselectively to give alcohol products.<sup>9</sup>

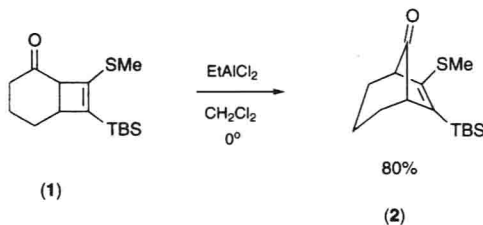


**$\gamma$ -Hydroxy esters.**<sup>10</sup> The catalyzed epoxide opening by ester enolates is stereoselective, giving predominantly the *syn* products.

**Conjugate addition.**<sup>11</sup> The addition of diethylaluminum chloride to *N*-crotonyl-4-benzyloxazolidin-2-one shows 1,5-asymmetric induction. The corresponding reaction with  $\text{Me}_2\text{AlCl}$  requires photoactivation.



**Skeletal rearrangement.**<sup>12</sup> The fused ring system (1) containing a cyclobutene unit releases its strain by rearrangement to a bridged ring skeleton (2). Thus the latter class of compounds are available in two steps, involving the initial  $\text{TiCl}_4$ -mediated [2+2]cycloaddition of the proper alkynes to cyclic enones.



<sup>1</sup> S. Leger, J. Omeara, and Z. Wang, *SL* 829 (1994).

<sup>2</sup> J. A. Marshall and M. W. Andersen, *JOC* **58**, 3912 (1993).

<sup>3</sup> K. Masuya, K. Tanino, and I. Kuwajima, *TL* **35**, 7965 (1994).

<sup>4</sup> K. Mikami and H. Kishino, *CC* 1843 (1993).

<sup>5</sup> C. Cativiela, F. Figueras, J. I. Garcia, J. A. Mayoral, E. Pires, and A. J. Royo, *TA* **4**, 621 (1993).

<sup>6</sup> C. Rogers and B. A. Keay, *CJC* **70**, 2929 (1992); **71**, 611 (1993).

<sup>7</sup> Y. Horiguchi, I. Suehiro, A. Sasaki, and I. Kuwajima, *TL* **34**, 6077 (1993).

<sup>8</sup> T. Fujiwara, T. Iwasaki, J. Miyagawa, and T. Takeda, *CL* 343 (1994).

<sup>9</sup> M. Taniguchi, H. Fujii, K. Oshima, and K. Utimoto, *BCSJ* 67, 2514 (1994).

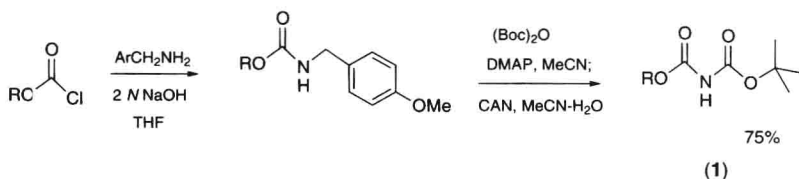
<sup>10</sup> S. K. Taylor, J. A. Fried, Y. N. Grassl, A. E. Marolewski, E. A. Pelton, T.-J. Poel, D. S. Rezanka, and M. R. Whittaker, *JOC* 58, 7304 (1993).

<sup>11</sup> K. Ruck and H. Kunz, *S* 1018 (1993).

<sup>12</sup> K. Narasaka, H. Shimadzu, and Y. Hayashi, *CL* 621 (1993).

### Alkyl *t*-butyl iminodicarbonates.

**Protected amines.**<sup>1</sup> Amines can be prepared by Gabriel and Mitsunobu syntheses using the iminodicarbonates (**1**) as nucleophiles. The reagents are available by acylation of 4-methoxybenzylamine with alkyl chloroformates, followed by introduction of the *N*-Boc group and removal of the benzyl moiety with CAN.



<sup>1</sup> J. M. Chong and S. B. Park, *JOC* 58, 7300 (1993).

### Alkyl phenyl selenides.

**Alkylating agents.**<sup>1</sup> These selenides, activated through photoinduced electron transfer, react with enol silyl ethers, forming  $\alpha$ -alkylated ketones.

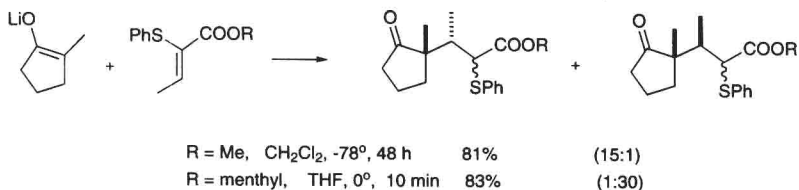


<sup>1</sup> G. Pandey and R. Sochanchingwung, *CC* 1945 (1994).

### Alkyl $\alpha$ -phenylthiocrotonates.

**Michael reactions.** The ester group exerts profound influences on the steric course of the reaction. Thus diastereocontrol<sup>1</sup> is possible by changing solvent, enolate counterion, and activating group at the  $\alpha$ -carbon of the acceptor. The phenylthio group increases reactivity, but electron-withdrawing substituents at this position tend to erode the diastereoselectivity. Temperature effects are also dramatic.

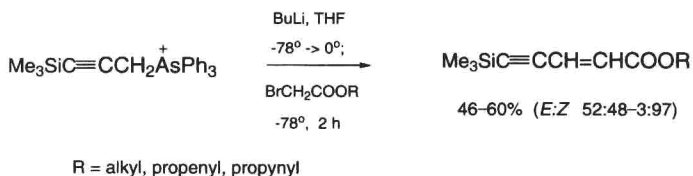
## 10 Allylboranes



<sup>1</sup>E. J. Corey and I. N. Houpis, *TL* **34**, 2421 (1993).

### Alkyltriphenylarsonium salts.

**Unsaturated esters.**<sup>1</sup> Alkylation of the corresponding ylides with a bromoacetic ester generates conjugated esters directly.



<sup>1</sup>Y. Shen and Y. Xiang, *HC* **3**, 547 (1992).

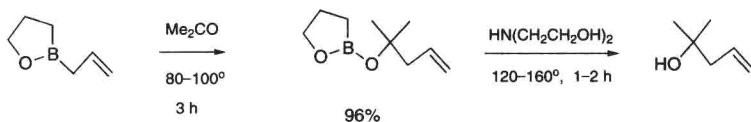
### Allenyl(triphenyl)lead.

***1-Alkyn-4-ols.***<sup>1</sup> Propargylation of carbonyl compounds is achieved in a reaction catalyzed by  $\text{BF}_3 \cdot \text{OEt}_2$ . The reagent is prepared from  $\text{Ph}_3\text{PbMgBr}$  and propargyl bromide.

<sup>1</sup>D. Seyferth, D. Y. Son, and S. Shah, *OM* **13**, 2105 (1994).

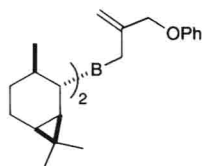
### Allylboranes. **14**, 11–12; 139–141; **16**, 6

**Allylation.**<sup>1</sup> 2-Allyl-1,2-oxaborolane is an allylating agent prepared from reaction of 2-allyloxy-1,2-oxaborolane with allylmagnesium bromide. Allylation is carried out without solvent, between  $0^\circ\text{C}$ . to room temperature with aldehydes and at  $80$ – $100^\circ\text{C}$  with ketones. Conjugated aldehydes undergo 1,2-addition.





*B*-Allylbis(isocaranyl)boranes (**1**)<sup>2</sup> can deliver the allyl group to carbonyl substrates to give chiral homoallylic alcohols.



(1)

<sup>1</sup> W. Zhou, S. Liang, S. Yu, and W. Luo, *JOMC* **452**, 13 (1993).

<sup>2</sup> T. A. J. van der Heide, J. van der Baan, E. A. Bijpost, F. J. J. de Kanter, F. Bickelhaupt, and G. W. Klumpp, *TL* **34**, 4655 (1993).

### Allyl chloroformate. 13, 9

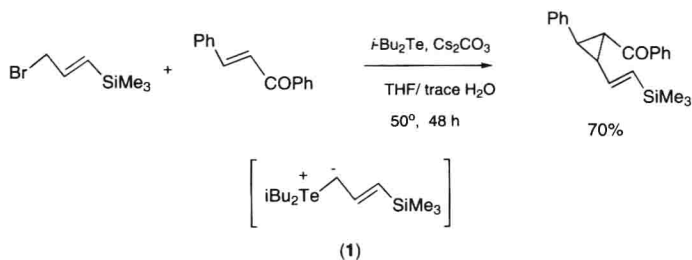
*N*<sup>ε</sup>-Protection of lysine.<sup>1</sup> Reaction with the copper chelate of lysine furnishes the derivative quantitatively. The method is suitable for large-scale preparation.

<sup>1</sup> A. Crivici and G. Lajoie, *SC* **23**, 49 (1993).

### Allyldiisobutyltelluronium bromide.

*Heteroatom allylation.* Diisobutyl telluride is a good leaving group; therefore phenols,<sup>1</sup> thiophenols,<sup>2</sup> and anilines<sup>3</sup> are readily allylated by this salt.

*Cyclopropanation.*<sup>4</sup> The derived ylide (**1**) is able to participate in cyclopropane ring formation with enones. It is not necessary to use the salt stoichiometrically as diisobutyl telluride can be made catalytic.



<sup>1</sup> C. Xu, S. Lu, and X. Huang, *SC* **23**, 2527 (1993).

<sup>2</sup> S.-M. Lu, C.-D. Xu, and X. Huang, *YH* **14**, 545 (1994).

<sup>3</sup> C. Xu, S. Lu, and X. Huang, *HC* **5**, 7 (1994).

<sup>4</sup> Y.-Z. Huang, Y. Tang, Z.-L. Zhou, W. Xia, and L.-P. Shi, *JCS(PI)* 893 (1994).