# 反応例 10.2 Grignard 反応と関連反応

# アルデヒド, ケトンとの反応

H. Gilman, W.E. Catlin, Org. Synth., Coll. Vol. 1, 188 (1941).

N.L. Drake, G.B. Cooke, Org. Synth., Coll. Vol. 2, 408 (1943).

C.G. Overberger, J.H. Saunders, R.E. Allen, R. Gander, Org. Synth., Coll. Vol. 3, 200 (1955).

#### 有機リチウム化合物

SnPh<sub>3</sub> 
$$\frac{\text{PhLi/Et}_2\text{O}}{\Delta}$$
  $\frac{1}{2}$   $\frac{1}{\text{Ph}_2\text{O}}$   $\frac{\text{OH}}{\text{70~75\%}}$ 

D. Seyferth, M.A. Weiner, Org. Synth., Coll. Vol. 5, 452 (1973).

L.A. Walter, Org. Synth., Coll. Vol. 5, 452 (1973).

J.V. Hay, T.M. Harris, Org. Synth., Coll. Vol. 6, 478 (1988).

## $\alpha$ , $\beta$ -不飽和カルボニル化合物への 1, 2-付加

$$\begin{array}{c} \text{O} \\ \text{II} \\ \text{CH}_{3}\text{CH} = \text{CHCH} \\ \hline \\ 2) \text{ NH}_{4}\text{CI/H}_{2}\text{O} \\ \end{array} \begin{array}{c} \text{OH} \\ \text{CH}_{3}\text{CH} = \text{CHCHCH}_{3} \\ \text{81~86\%} \\ \end{array}$$

E.R. Coburn, Org. Synth., Coll. Vol. 3, 696 (1955).

J.C.H. Hwa, H. Sims, Org. Synth., Coll. Vol. 5, 608(1973).

L. Skattebøl, E.R.H. Jones, M.C. Whiting, Org. Synth., Coll. Vol. 4, 792(1963).

#### エステルとの反応

$$2 CH_{3}CH_{2}CH_{2}CH_{2}MgBr + HOEt \frac{1) Et_{2}O}{2) H_{2}SO_{4}/H_{2}O} (CH_{3}CH_{2}CH_{2}CH_{2})_{2}CHOH$$
83~85%

G.H.Coleman, D. Craig, Org. Synth., Coll. Vol. 2, 179 (1943).

W.E. Bachmann, H.P. Hetzner, Org. Synth., Coll. Vol. 3, 869 (1955).

$$3 C_2 H_5 MgBr + EtO OEt = 1) Et_2O (C_2 H_5)_3 C-OH 82~88\%$$

W.W. Moyer, C.S. Marvel, Org. Synth., Coll. Vol. 2, 602 (1943).

CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub> OH CH<sub>3</sub>MgBr/Et<sub>2</sub>O, 
$$\Delta$$
2) HCl/H<sub>2</sub>O, benzene CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub> OH
57%

J. Colonge, R. Marey, Org. Synth., Coll. Vol. 4, 601 (1963).

### 有機アルカリ金属化合物

P.J. Pearce, D.H. Richards, N.F. Scilly, Org. Synth., Coll. Vol. 6, 478 (1988).

CH<sub>3</sub>CH=C
$$\stackrel{\text{Br}}{\leftarrow}$$
 $\stackrel{\text{Li}}{\leftarrow}$ 
 $\stackrel{\text{CH}_3}{\leftarrow}$ 
 $\stackrel{\text{CH$ 

A.A. Morton, J.R. Myles, W.S. Emerson, *Org. Synth.*, Coll. Vol. 3, 831 (1955).

#### 二酸化炭素との反応

$$R-X$$
  $\xrightarrow{Mg}$   $R-MgX$   $\xrightarrow{1) CO_2}$   $<0$  °C  $>0$  R $-CO_2H$   $>0$  R $-CO_2H$   $>0$  R $-X=$  CI 収率:  $72\sim73\%$   $>0$  収率:  $85\%$   $>0$  R $-X=$   $>0$  R $-$ 

H. Gilman, R.H. Kirby, Org. Synth., Coll. Vol. 1, 361 (1941).

$$R-X = (CH_3)_3C-CI$$
 収率:  $69\sim70\%$ 

S.V. Puntambeker, E.A. Zoellner, Org. Synth., Coll. Vol. 1, 524 (1941).

H. Gilman, N.B.St. John, F. Schlze, Org. Synth., Coll. Vol. 2, 425 (1943).

(臭化エチルを用いないと収率は61~66%になる.)

D.M. Bowen, Org. Synth., Coll. Vol. 3, 553 (1955).

D.E. pearson, D. Cowan, Org. Synth., Coll. Vol. 5, 890 (1973).

#### 有機アルカリ金属化合物

R.B. Woodward, E.C. Komfeld, Org. Synth., Coll. Vol. 3, 413 (1955).

$$CH_{3}-C \equiv C-H \xrightarrow{\text{Na, NH}_{3}} CH_{3}-C \equiv C-\text{Na} \xrightarrow{1) CO_{2}, \text{ THF, Et}_{2}O} CH_{3}-C \equiv C-\text{CO}_{2}H$$

$$50 \sim 59\%$$

J.C. Kauer, M. Brown, Org. Synth., Coll. Vol. 5, 1043 (1973).

# アミドとの反応

G.A. Olah, M. Arvanaghi, Org. Synth., Coll. Vol. 7, 451 (1990).

#### ニトリルとの反応

PhMgBr + MeOCH<sub>2</sub>C
$$\equiv$$
N  $Et_2O$   $\Delta$  Ph OMe  $H_2SO_4/H_2O$   $DMe$  OMe  $T_1\sim78\%$ 

R.B. Moffett, R.L. Shriner, Org. Synth., Coll. Vol. 3, 567 (1955).

J.E. Callen, C.A. Donfeld, G.H. Coleman, Org. Synth., Coll. Vol. 3, 26 (1955).

PhMgBr + PhCN 
$$\xrightarrow{\text{Et}_2\text{O}}$$
  $\xrightarrow{\text{Ph}}$  NMgBr  $\xrightarrow{\text{MeOH}}$   $\xrightarrow{\text{Ph}}$  NH Ph 61~81%

P.L. Pickard, T.L. Tolbert, Org. Synth., Coll. Vol. 5, 520 (1973).

#### イミンとの反応

# エポキシドとの反応

$$CH_3(CH_2)_3MgBr + \sum_{1}^{O} \frac{1) Et_2O}{2) H_2SO_4/H_2O} CH_3(CH_2)_5OH 60~62\%$$

E.E. Dreger, Org. Synth., Coll. Vol. 1, 306 (1941).

Br 
$$\frac{Mg}{Et_2O}$$
  $MgBr$   $\frac{1)}{2) NH_4CI/H_2O}$   $78\sim90\%$ 

L.S. Hegedus, M.S. Holden, J.M. McKearin, Org. Synth., Coll. Vol. 7, 501 (1990).

A. Schwartz, P. Madan, J.K. Whitesell, R.M. Lawrence, Org. Synth., Coll. Vol. 8, 516 (1993).

#### オルトエステルとの反応:アセタールとアルデヒドの合成

$$\begin{array}{c} \text{CH}_3(\text{CH}_2)_4\text{MgBr} + \text{HC}(\text{OEt})_3 & \xrightarrow{\text{Et}_2\text{O}} & \text{CH}_3(\text{CH}_2)_4\text{CH}(\text{OEt})_2 \\ & & \nearrow \forall \cancel{P} - \cancel{N} \end{array}$$

$$\xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O}} & \text{CH}_3(\text{CH}_2)_4\text{CHO} \\ & & \text{G.B. Bachman,} \\ & & \text{Org. Synth., Coll. Vol. 2, 323 (1943).} \end{array}$$

Br MgBr 
$$CH(OEt)_2$$

$$Mg/Et_2O$$

$$A$$

$$CHO$$

$$CHO$$

$$CHO$$

$$C.A. Dornfeld, G.H. Coleman, Org. Synth., Coll. Vol. 3, 701 (1955).$$

$$40\sim42\%$$

#### Reformatsky 反応

Ph + BrCH<sub>2</sub>CO<sub>2</sub>Et 
$$\frac{1) \text{ Zn, Et}_2\text{O, benzene, } \Delta}{2) \text{ H}_2\text{SO}_4/\text{H}_2\text{O}}$$
 Ph CO<sub>2</sub>Et

C.R. Hauser, D.S. Breslow, Org. Synth., Coll. Vol. 3, 408 (1955).

K.L. Rinehart, E.G. Perkins, Org. Synth., Coll. Vol. 4, 444 (1963).

CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CN + CH<sub>3</sub>CHCO<sub>2</sub>-
$$s$$
-Bu 1) Zn, benzene,  $\Delta$  CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub> O- $s$ -Bu 50~58% CH<sub>3</sub>

K.L. Rinehart, Org. Synth., Coll. Vol. 4, 120 (1963).