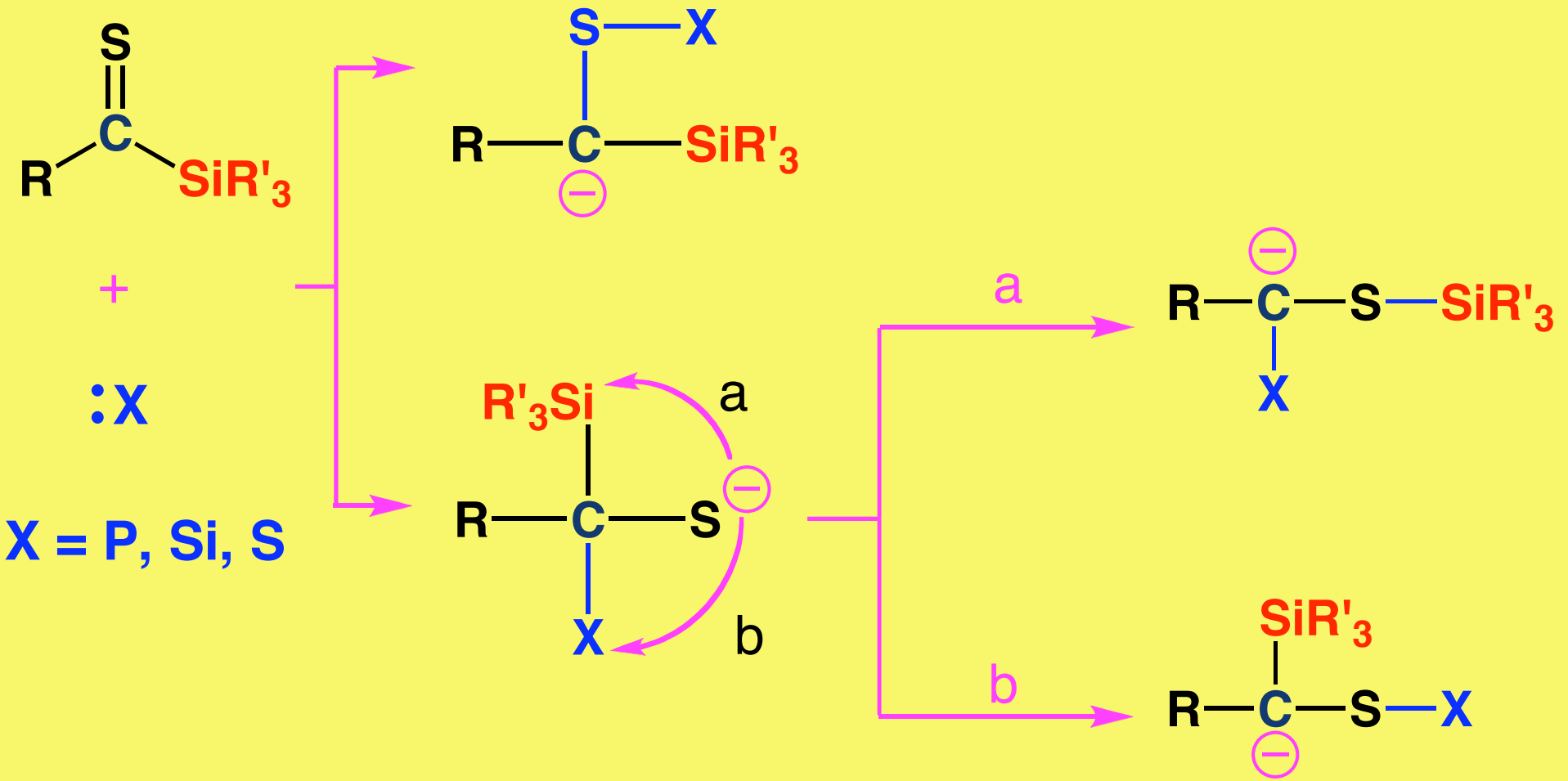
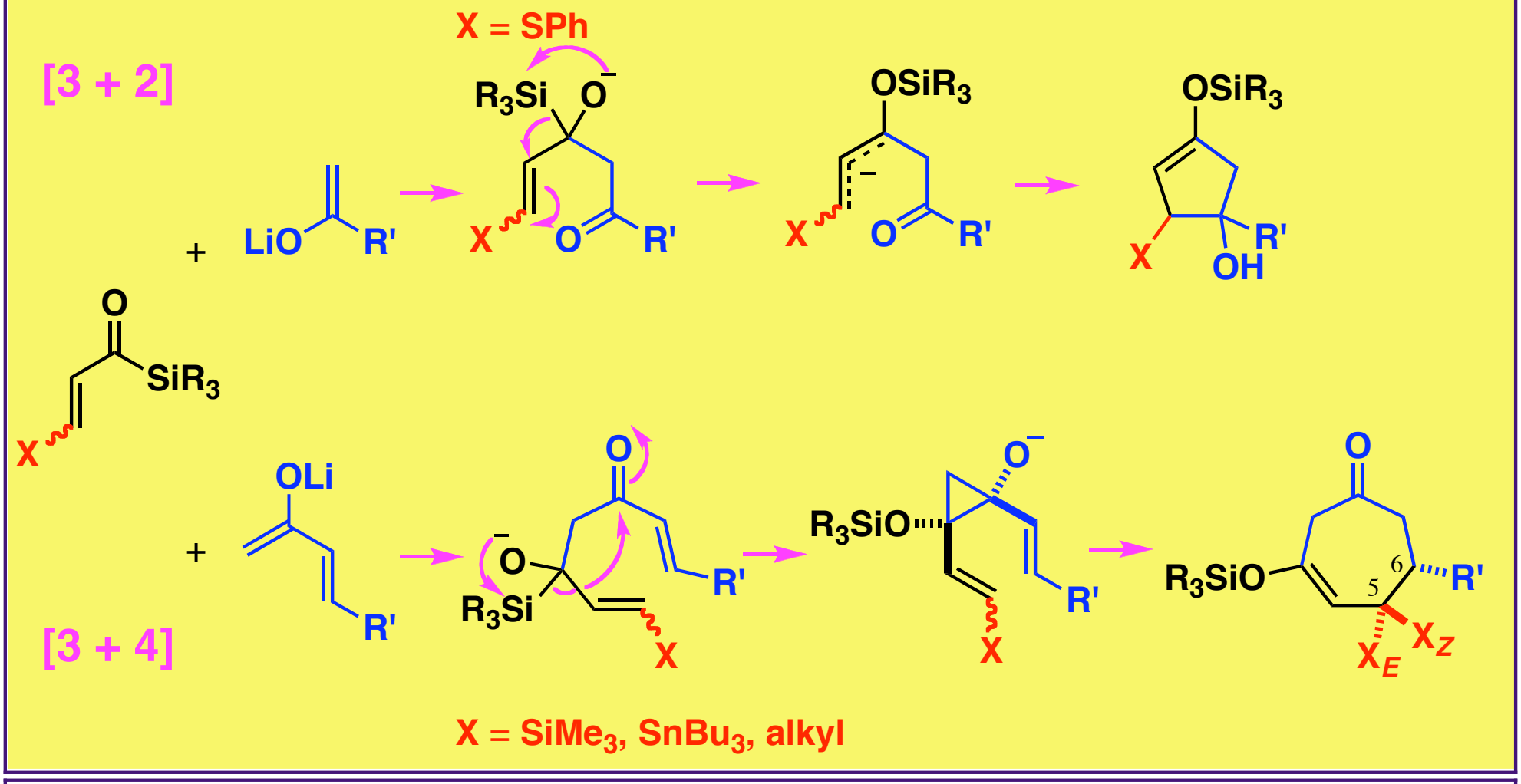
Formation of Interelement-Linkage in the Reaction of Silylthioketones with Nucleophiles



Brook Rearrangement-Mediated [3 + 2] and [3 + 4] Annulations



Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E.; Yamaguchi, K. *J. Am. Chem. Soc.* **1993**, *115*, 9351-9352.
Takeda, K.; Takeda, M.; Nakajima, A.; Yoshii, E. *J. Am. Chem. Soc.* **1995**, *117*, 6400-6401.
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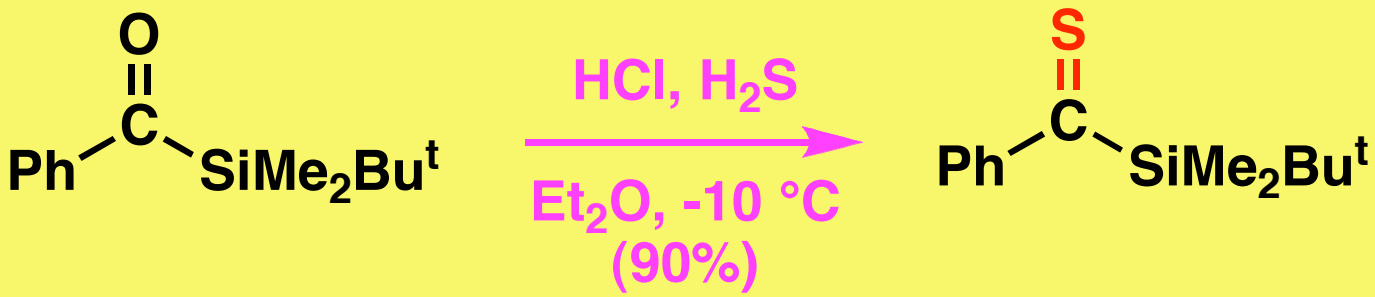
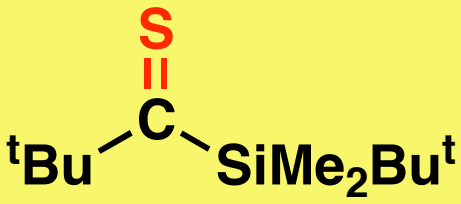
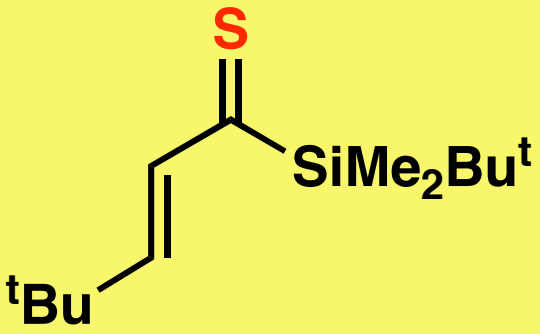
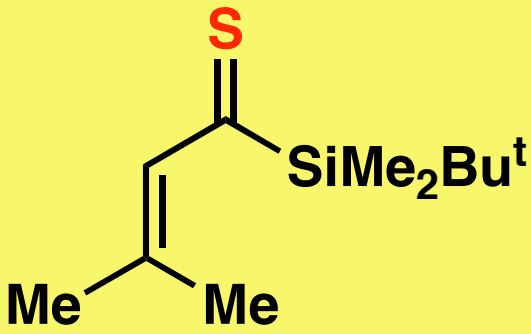
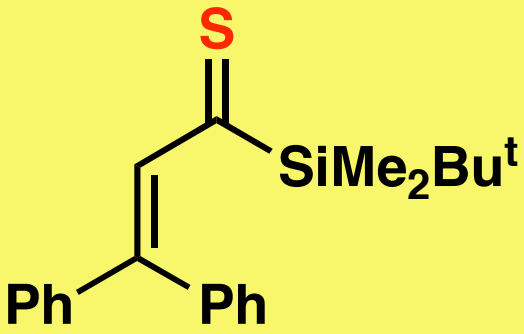
Preparation of Silylthioketones











Bonini, B. F. *Phosphorus, Sulfur, and Silicon* **1993**, *74*, 31-45.
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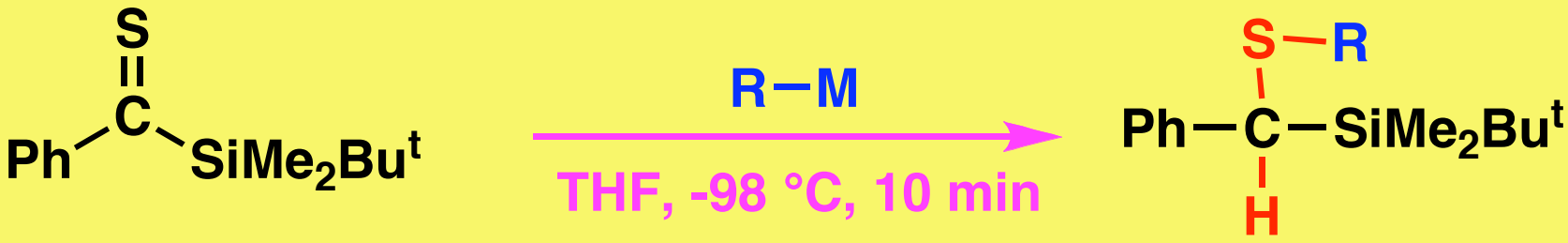
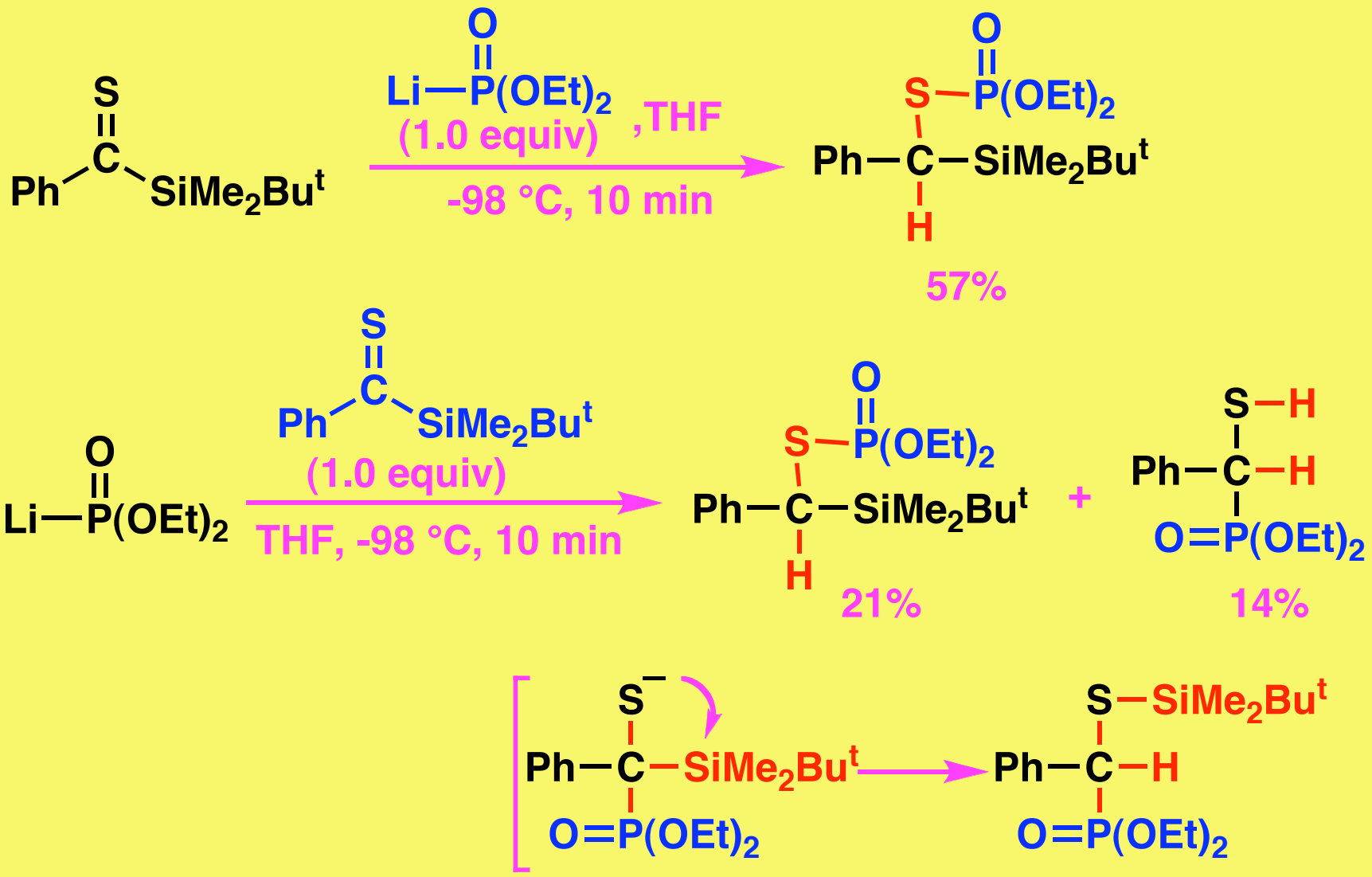
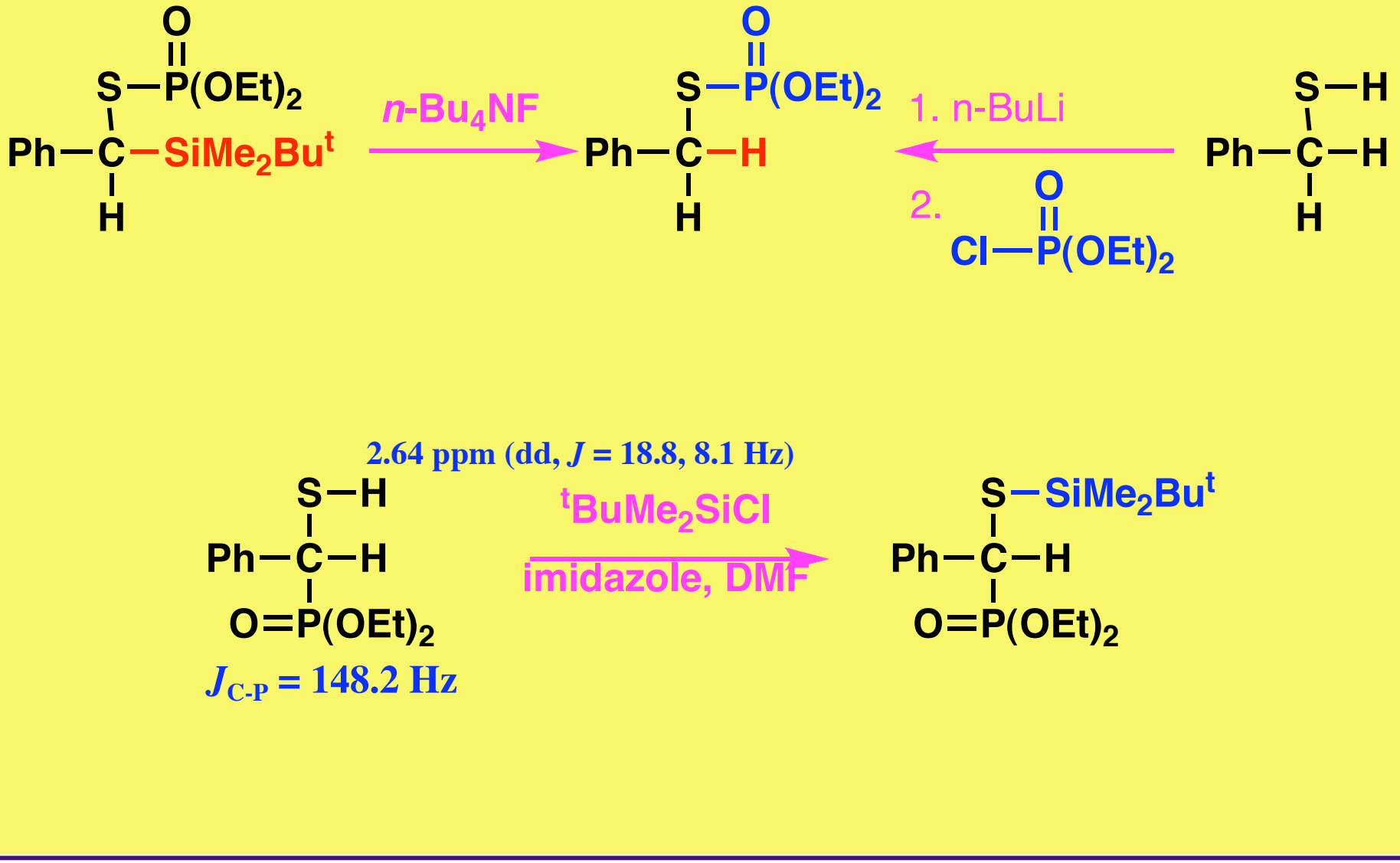
Reaction of Silylthioketone with Carbon Nucleophiles



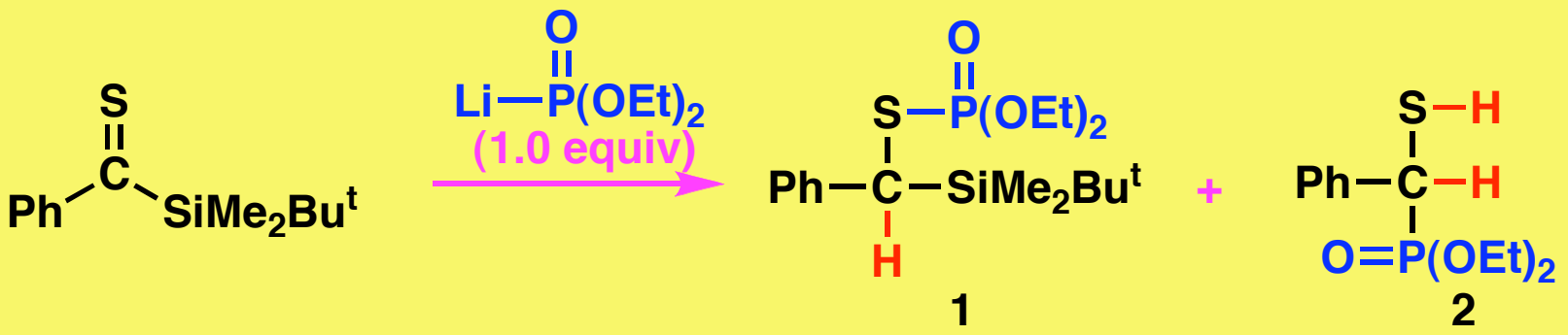
R-M	yield (%)
Me-Li	70
PhLi	63
MeMgBr	40

Reaction of Silylthioketone with Lithium Diethylphosphite (1)



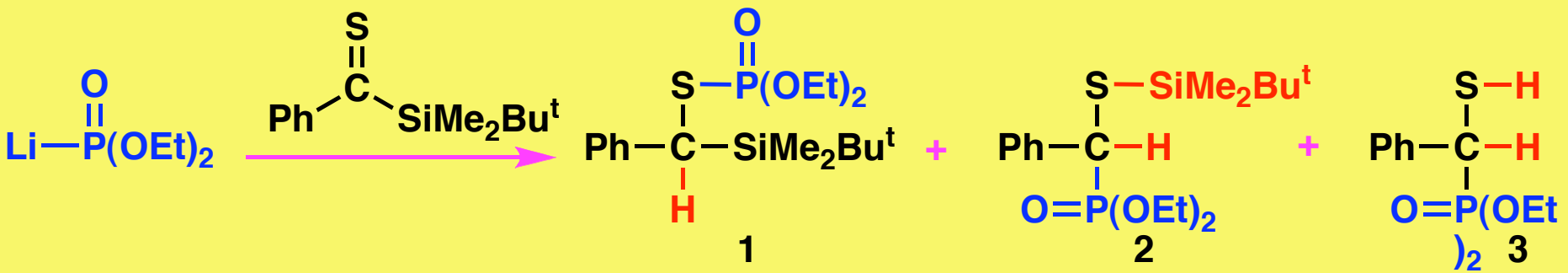

O
S—P(OEt)2
Ph—C—SiMe2But
H
n-Bu4NF
Ph—C—H
1. n-BuLi
2.
O
Cl—P(OEt)2
S—H
2.64 ppm (dd, J = 18.8, 8.1 Hz)
tBuMe2SiCl
imidazole, DMF
JC-P = 148.2 Hz

Reaction of Silylthioketone with Lithium Diethylphosphite (2)



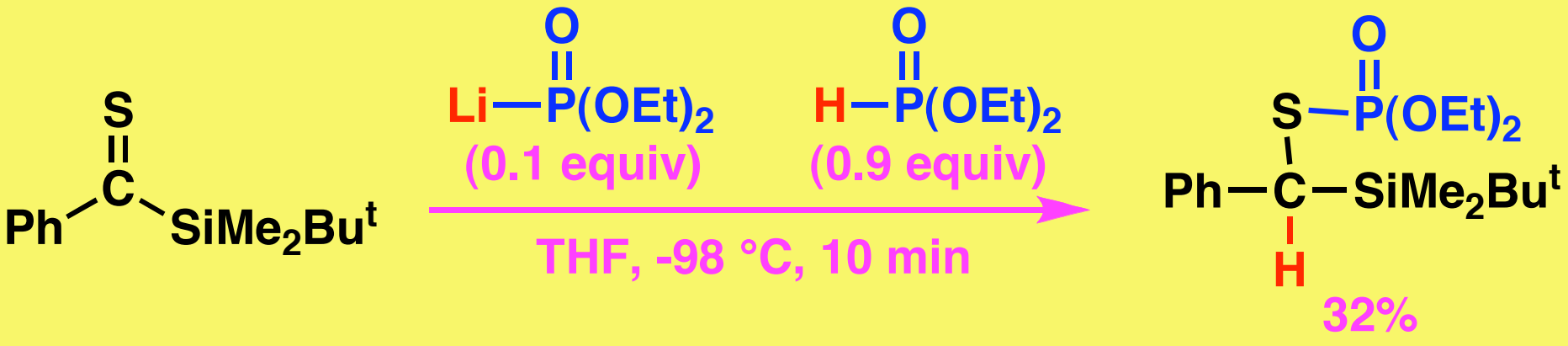
solvent	temperature (°C)	time (min)	yield (%) 1	2	HP(O)(OEt)$_2$
THF	-98 °C	10	57	-	10
THF	-98 °C	30	36	-	43
THF	-98 °C	60	25	8	22
toluene	-84 °C	10	58		5
toluene	-84 °C	30	53	-	-
THF-HMPA (9:1)	-98 °C	10	29	-	40
THF-HMPA (9:1)	-98 °C	30	27	-	30

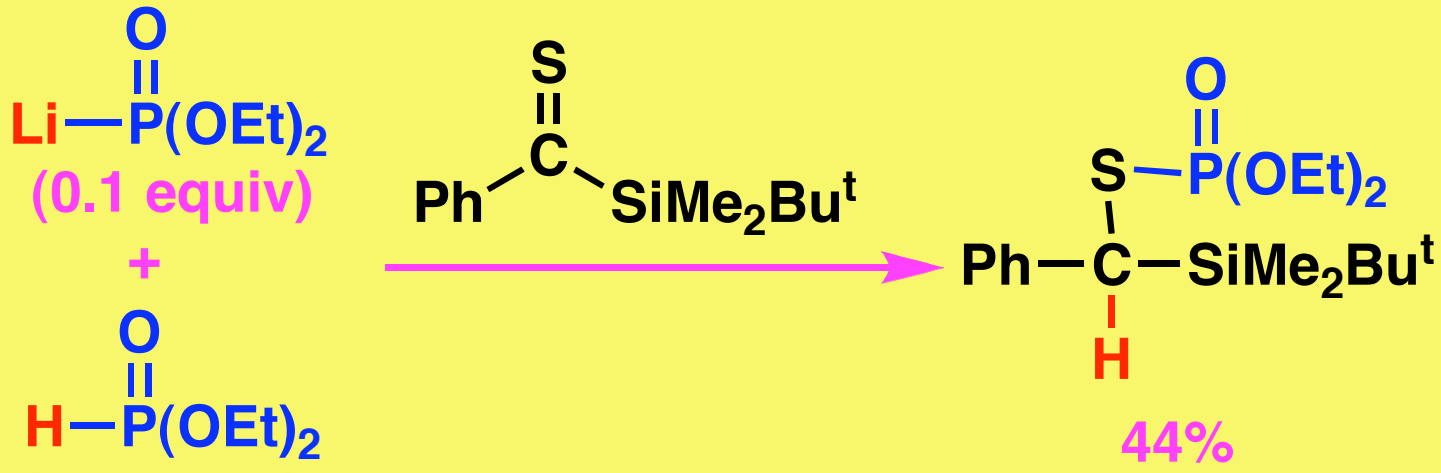
Reaction of Silylthioketone with Lithium Diethylphosphite (3)

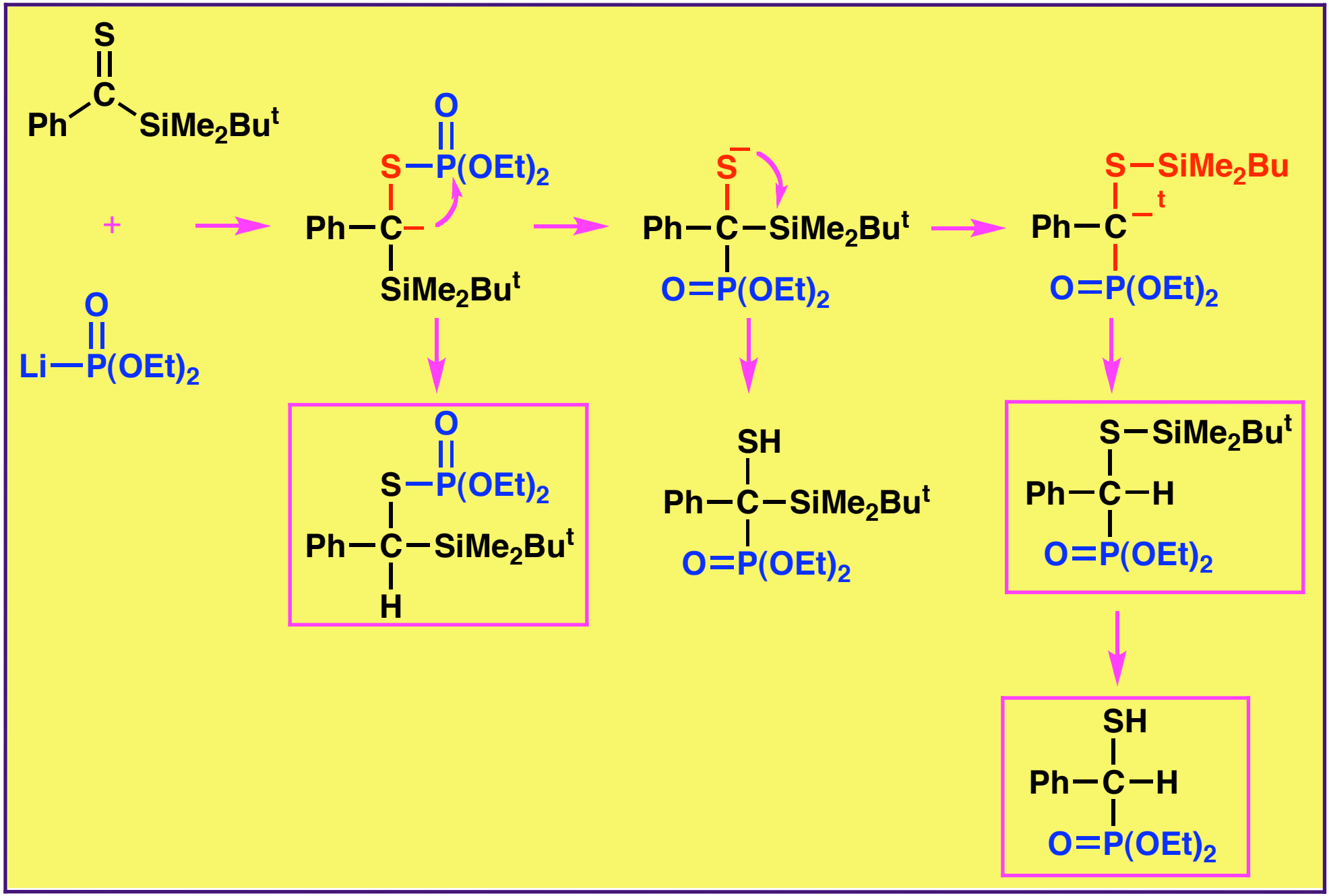


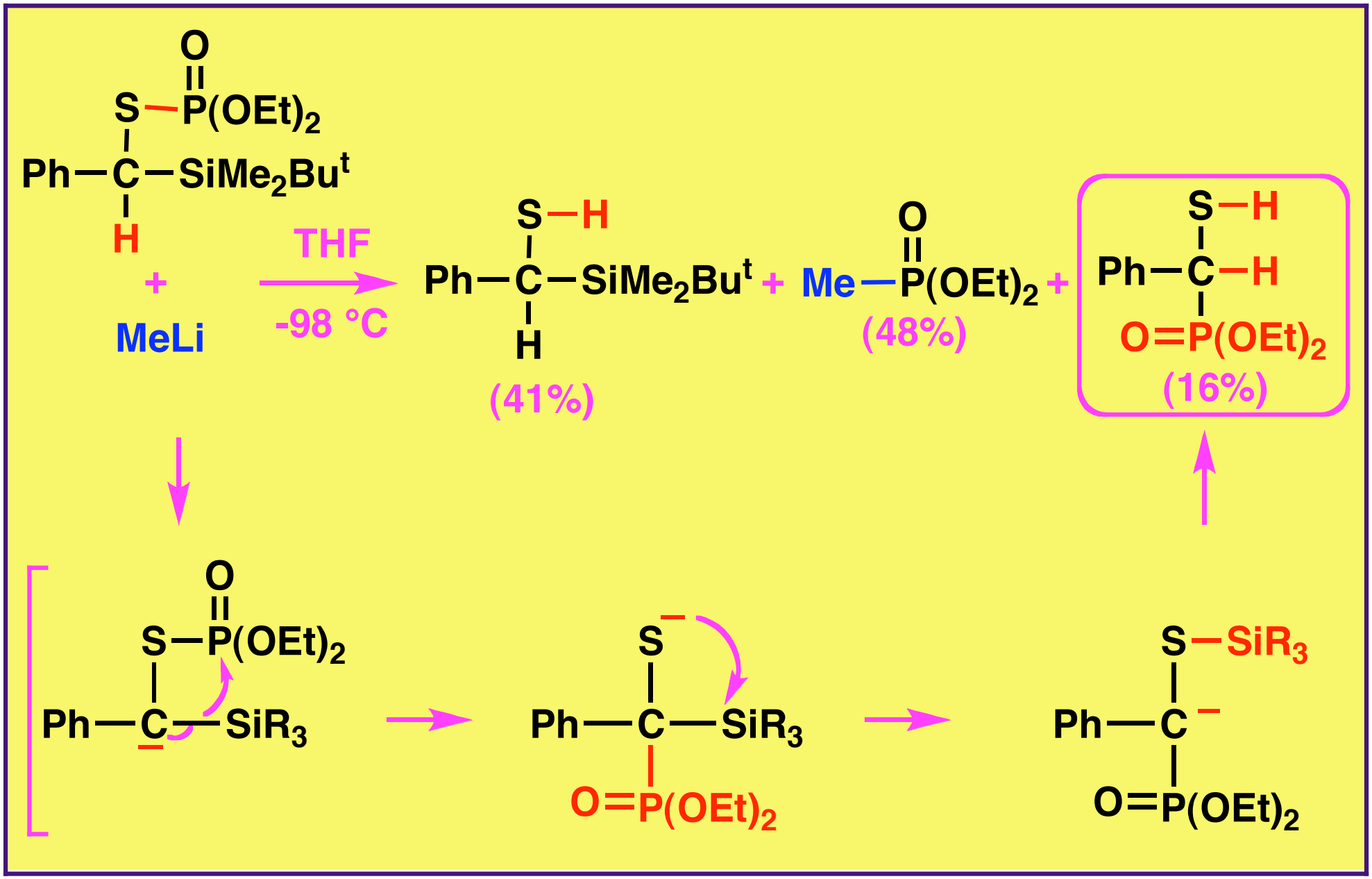
solvent	temperature (°C)	time (min)	yield (%)			
			1	2	3	$HP(O)(OEt)_2$
THF	-98 °C	10	21	-	14	16
THF	-98 °C	30	19	2	18	20
toluene	-84 °C	10	40	7	11	-
toluene	-84 °C	30	14	3	-	-
THF-HMPA (9:1)	-98 °C	10	29	-	-	40
THF-HMPA (9:1)	-98 °C	30	27	-	-	30

Reaction of Silylthioketone with Lithium Diethylphosphite (4)

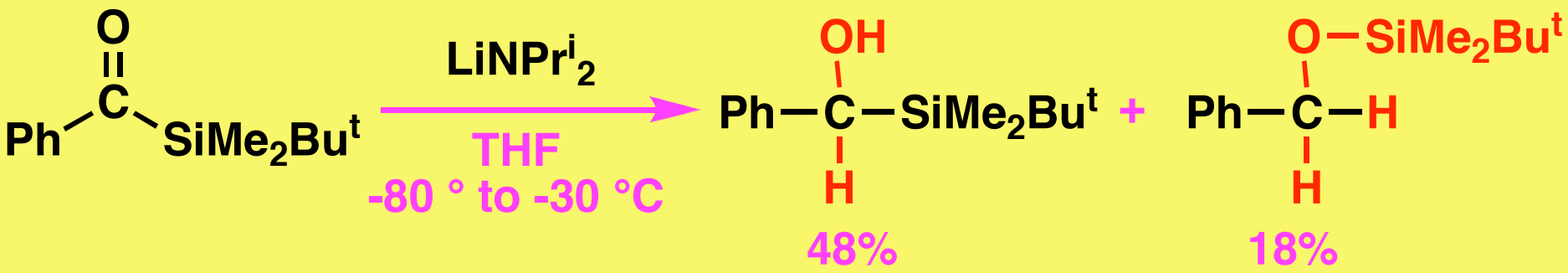


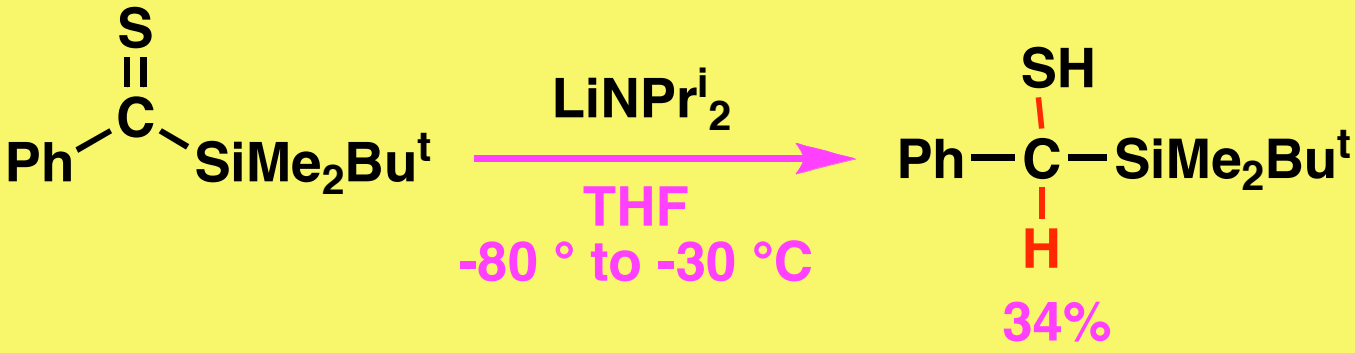



S
C
Ph
SiMe2But
+
O
Li—P(OEt)2
O
S—P(OEt)2
Ph—C—
SiMe2But
S—P(OEt)2
Ph—C—SiMe2But
H
S
Ph—C—SiMe2But
O=P(OEt)2
SH
Ph—C—SiMe2But
O=P(OEt)2
S—SiMe2Bu
t
Ph—C
O=P(OEt)2
S—SiMe2But
Ph—C—H
O=P(OEt)2
SH
Ph—C—H
O=P(OEt)2

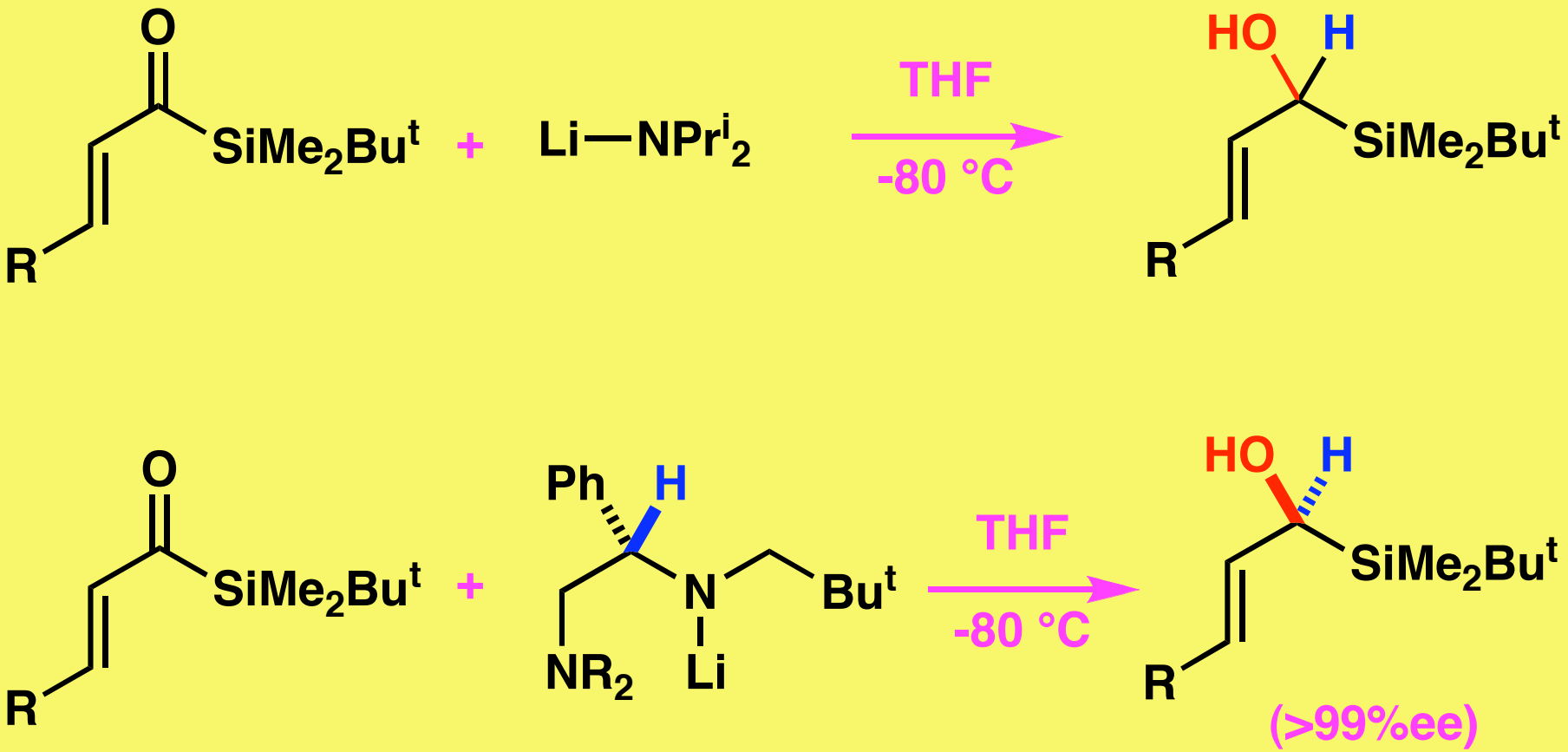

O
S—P(OEt)2
Ph—C—SiMe2But
H
+
MeLi
THF
-98 °C
S—H
Ph—C—SiMe2But
H
(41%)
+
O
Me—P(OEt)2
(48%)
+
S—H
Ph—C—H
O=P(OEt)2
(16%)
O
S—P(OEt)2
Ph—C—SiR3
S
Ph—C—SiR3
O=P(OEt)2
S—SiR3
Ph—C
O=P(OEt)2

Thia-Brook Rearrangement (1)



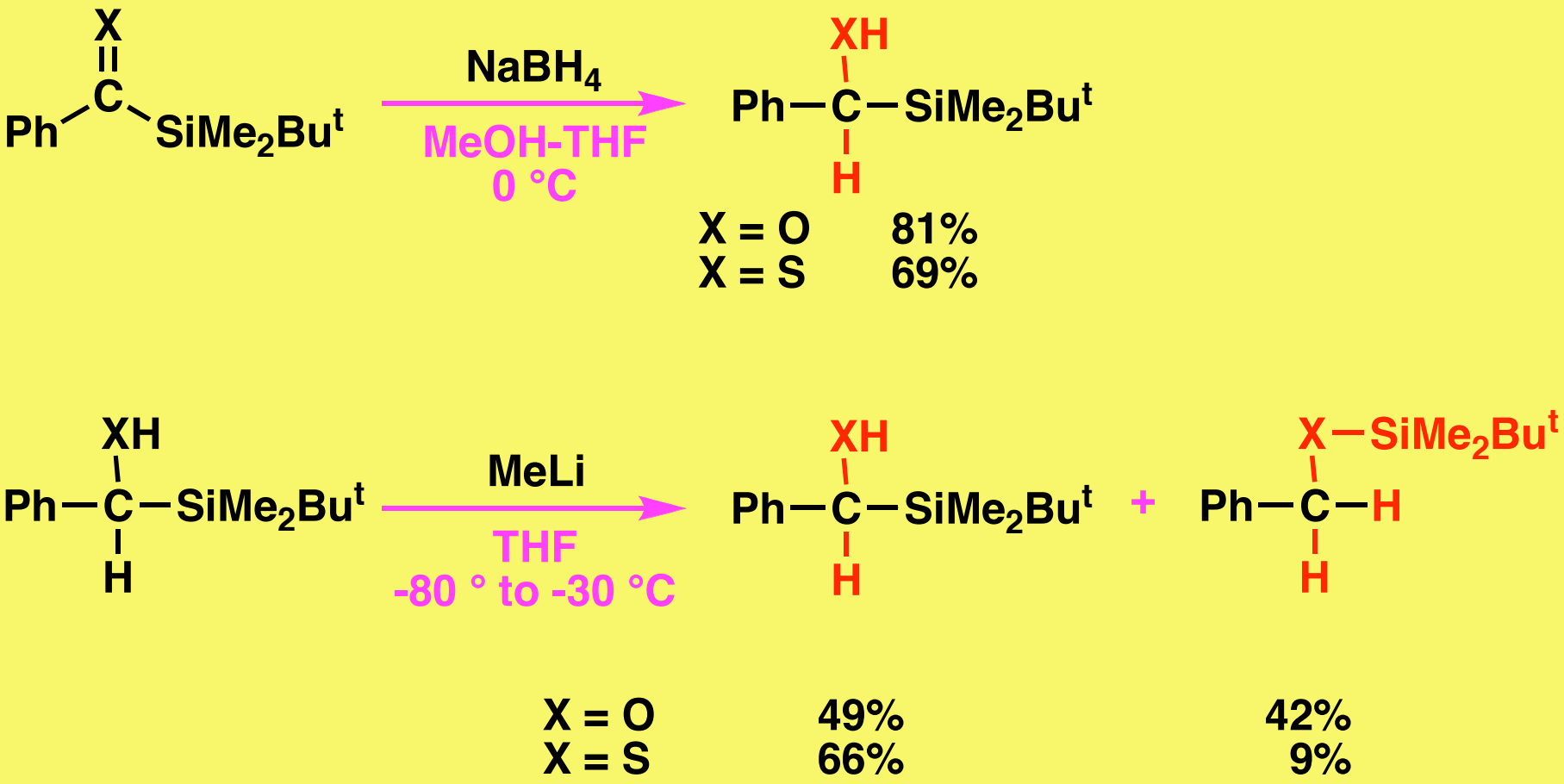


Enantioselective Reduction of Acylsilanes with Chiral Lithium Amides



Takeda, K.; Ohnishi, Y.; Koizumi, T. *Org. Lett.* **1999**, *1*, 237-239.

Thia-Brook Rearrangement (3)



Reaction of Benzoylsilane with Lithium Diethylphosphite