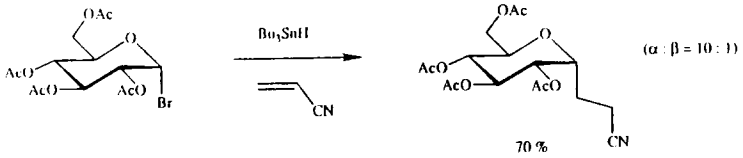
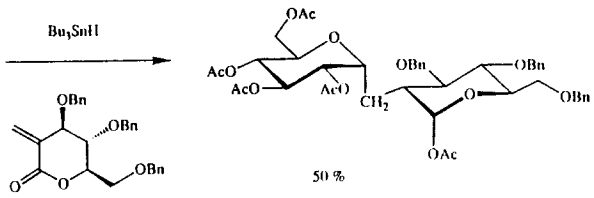
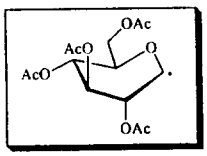


J. Dupuis, B. Giese *Angew Chem.* **1983**, *95*, 633.

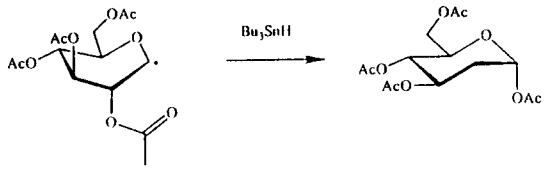


C. Lambert, B. Giese *Angew Chem.* **1986**, *98*, 459.

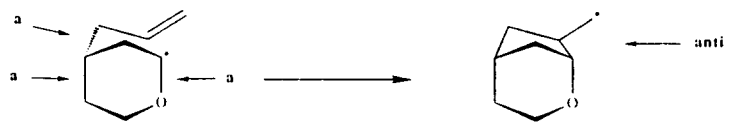


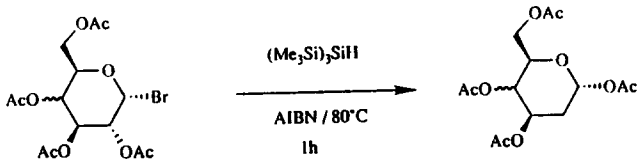
H. Fischer, B. Giese, R. Sustmann et al. *Angew Chem.* **1984**, *96*, 887.

K. Gröninger, K. Jäger, B. Giese *Liebigs Ann. Chem.* **1987**, 731.



K. Gröninger, T. Witzel, H.G. Korth, R. Sustmann, B. Giese *Angew Chem.* **1987**, *99*, 246.

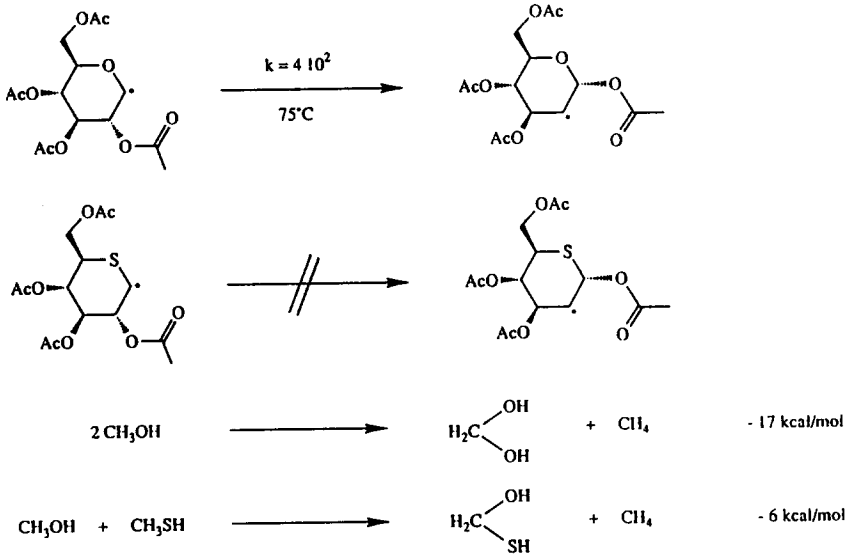




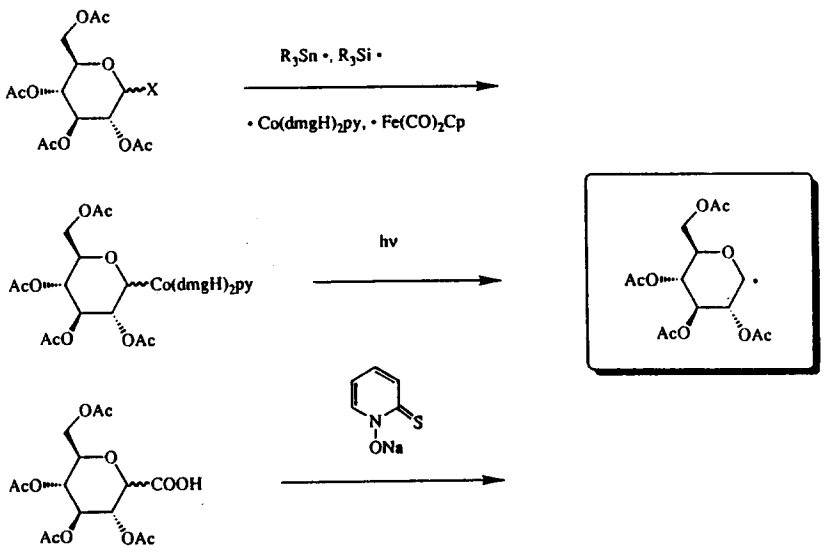
gluco : 71 %

galacto : 70 %

B. Giese, B. Kopping, C. Chatgilialoglu, *Tetrahedron Lett.* **1989**, *30*, 681



B. Giese, R. Sustmann, et al., *J.Org.Chem.* **1988**, *53*, 4364.



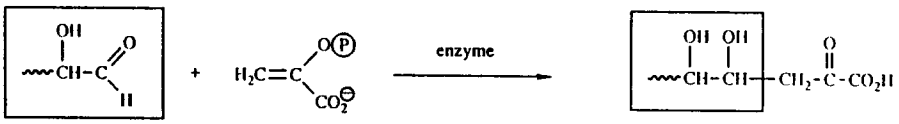
CARBOHYDRATE RADICALS

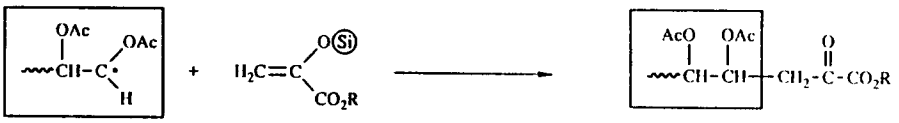
CC-Bond Formation

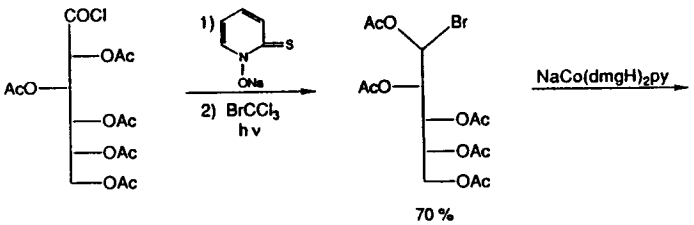
C-Glycosides
C-Disaccharides
Biomimetic Synthesis:
KDO
Neuraminic Acids

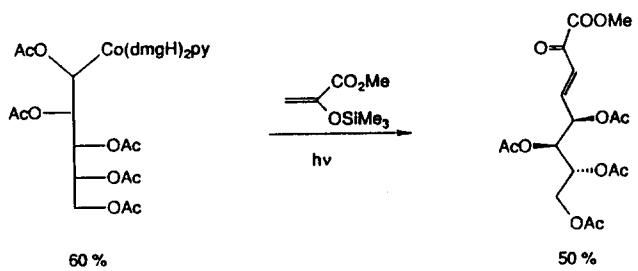
Rearrangement Reactions

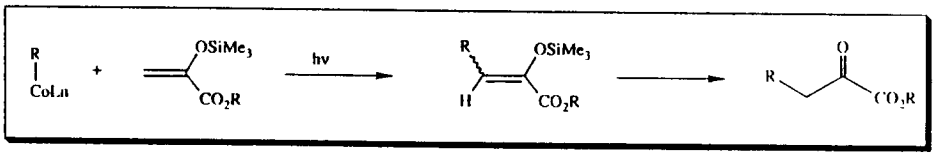
Deoxysugars
Nucleosides

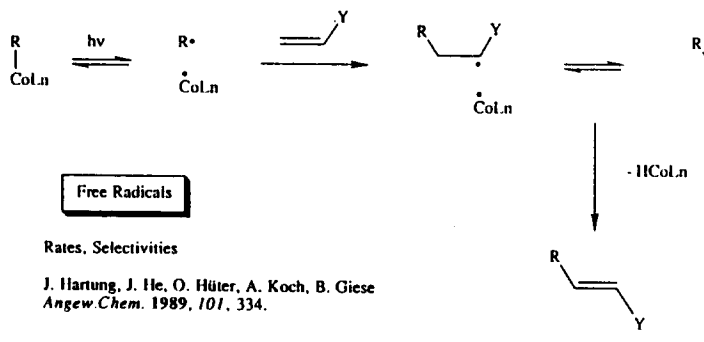










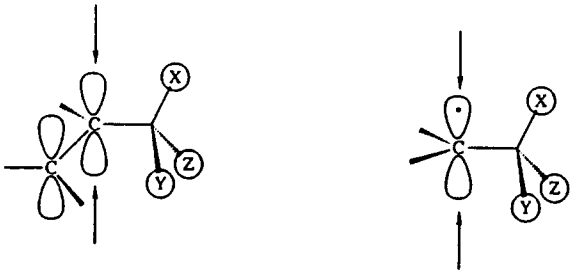


Free Radicals

Rates, Selectivities

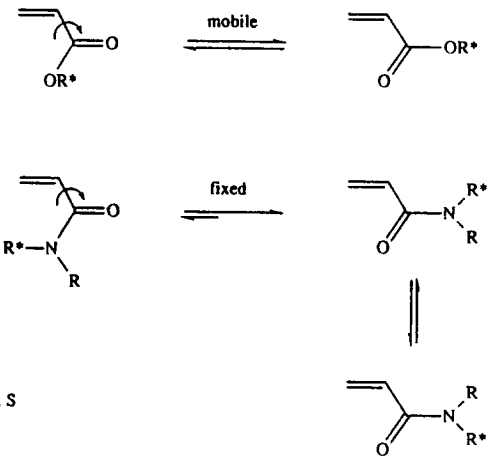
J. Hartung, J. He, O. Hüter, A. Koch, B. Giese
Angew.Chem. 1989, *101*, 334.

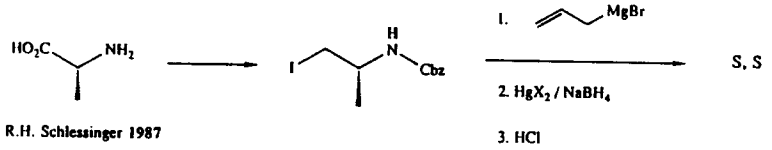
STEREOSELECTIVITY



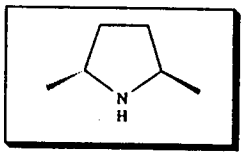
conformational effects

B. Giese, *Angew.Chem.* 1989, *101*, 993.

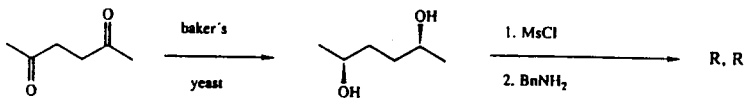




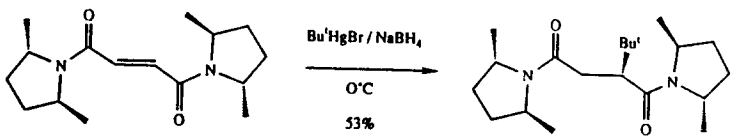
R.H. Schlessinger 1987



R, R

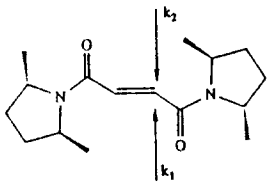


S.J. Masamune 1989



79 : 1

N.A. Porter, D.M. Scott, B. Lacher, H.G. Zeitz, H.J. Lindner, B. Giese, *J.Am.Chem.Soc.* 1989, *111*, 8311.



$(H_3C)_3C\cdot$

T (°C)	$k_1 : k_2$
110	16
65	22
20	40
0	79

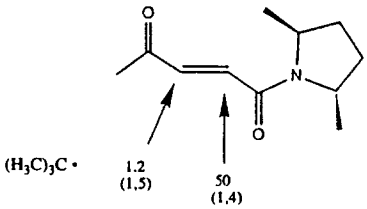
$\Delta\Delta H^{\neq}$ = 3.0 kcal/mol

$C_6H_{11}\cdot$

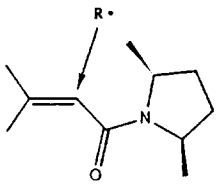
T (°C)	$k_1 : k_2$
110	13
60	16
20	35
0	50

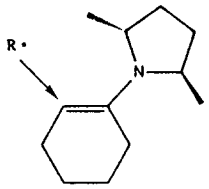
$\Delta\Delta H^{\neq}$ = 2.8 kcal/mol

1,n - INDUCTION



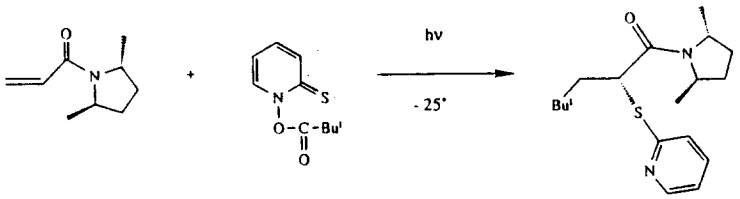
1,4 - INDUCTION

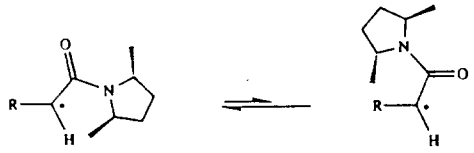




B. Giese, N. Porter et al. *J.Am.Chem.Soc.* 1989, *111*, 8311

P. Renaud et al. *Synlett* 1990

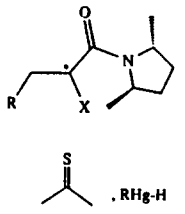


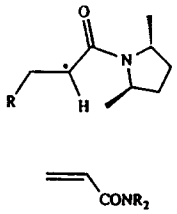


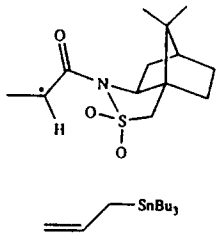
B. Giese, M. Zehnder, M. Roth, H.G. Zeitz, *J.Am.Chem.Soc.* 1990

R	selectivity (20°C)
$(H_3C)_3CCH_2$	9.5 : 1
$H_{11}C_6CH_2$	4.0 : 1
C_2H_5	2.1 : 1

1,4 - INDUCTION







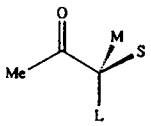
B. Giese, M. Roth
H.G. Zeitz
A. Veit

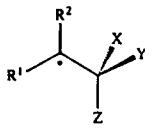
N. Porter et al.

D. Curran et al.

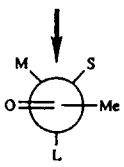
J.Am.Chem.Soc. **1990**, *112*

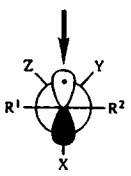
1,2 - INDUCTION

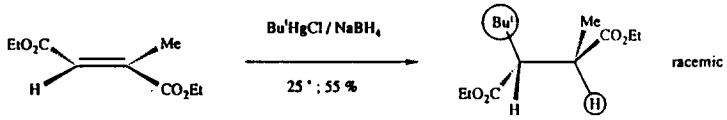




"Cram's Rule"

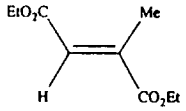


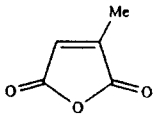


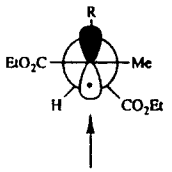


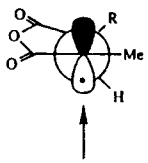
racemic

25 : 1





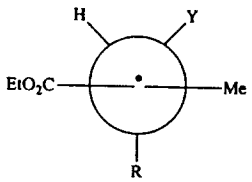




R	selectivity (20°C)
c-C_6H_{11}	12
t-C_4H_9	27

R	selectivity (20°C)
c-C_6H_{11}	8.1
t-C_4H_9	16

1,2 - INDUCTION



Y / CO_2R

high selectivity Y: CO_2R, OR, F

B. Giese et al. *J.Am.Chem.Soc.* 1990

Y. Guindon et al. *Tetrahedron Lett.* 1990