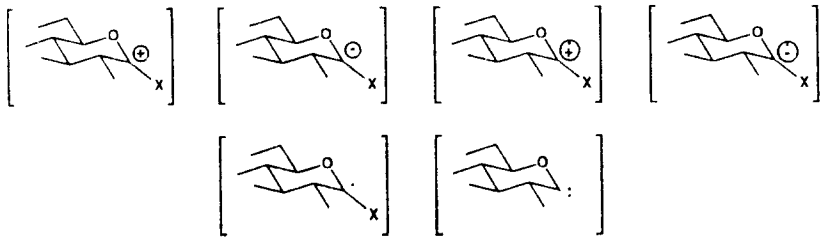
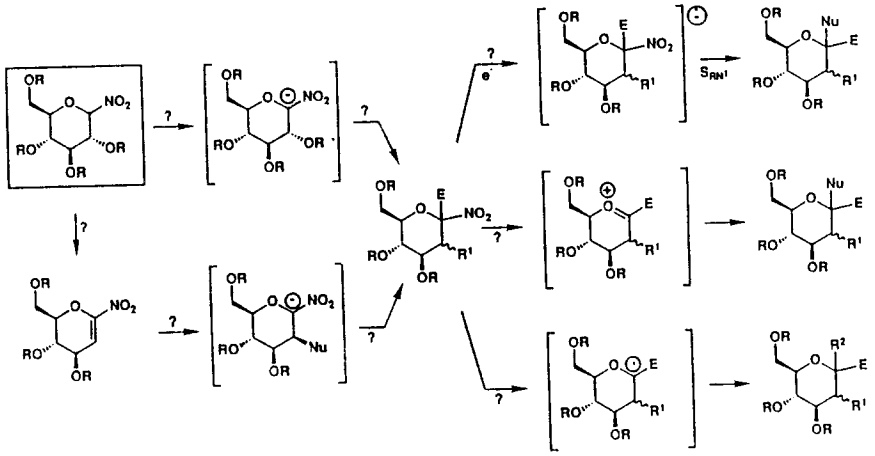
New Carbohydrate Derivatives and Intermediates

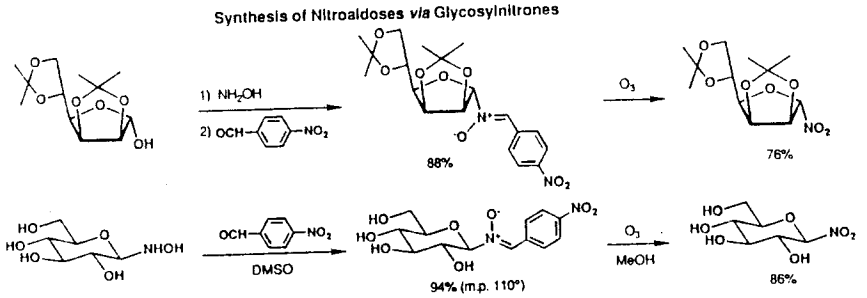
Intermediates



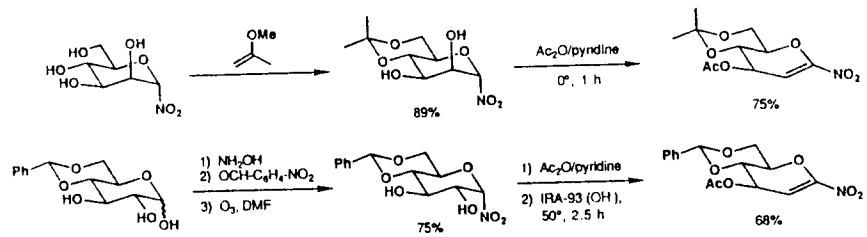
Derivatives



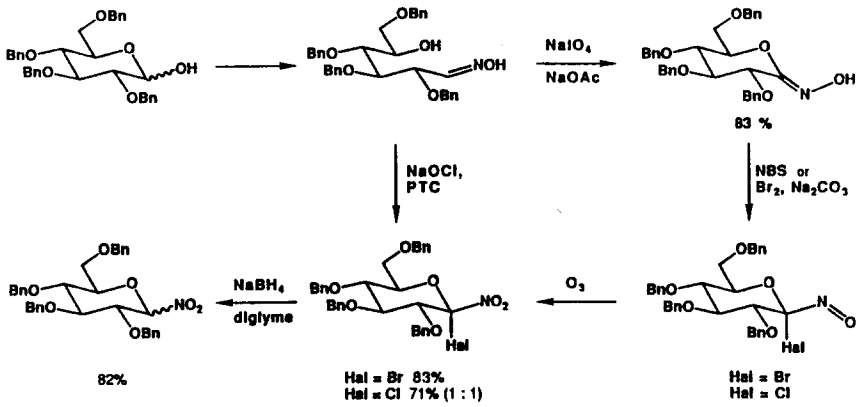
Synthesis of Nitroaldoses *via* Glycosylnitrones



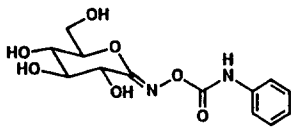
Partially Protected Nitroaldoses and Nitroglucals



Synthesis of Nitrosaldoses *via* Hydroximolactones, Halonitroso Ethers and Halonitro Ethers



Inhibition of Glycosidases and Glycogenphosphorylases

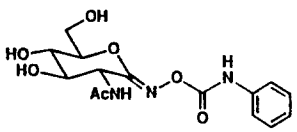


β-Glucosidases

Sweet almonds (emulsin) $K_i = 2.3 \cdot 10^{-6}$ M
$K_m/K_i = 1'220$

Glycogenphosphorylase b *)

Rabbit muscle $K_i = 4 \cdot 10^{-4}$ M



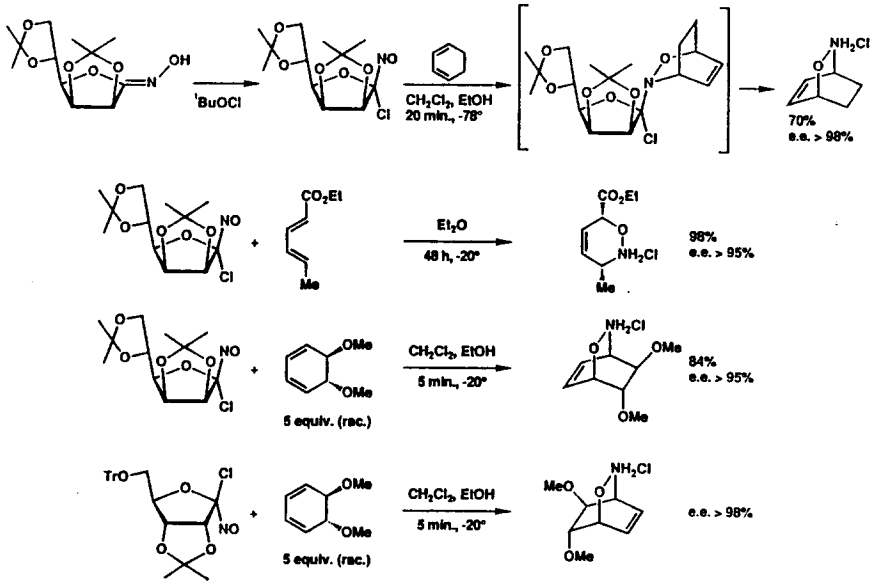
β-N-Acetylglucosaminidases

Bovine kidney $K_i = 11 \cdot 10^{-8}$ M
$K_m/K_i = 13'600$

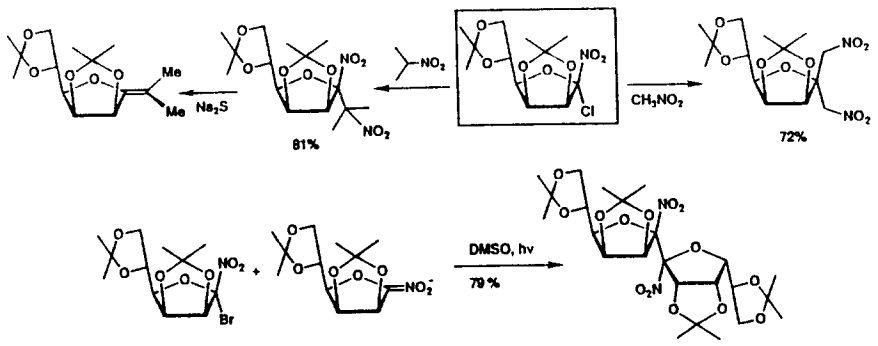
M. rouxii $K_i = 4 \cdot 10^{-8}$ M
$K_m/K_i = 3'200$

*) N. G. Oikonomakos, Athens
L. N. Johnson, Oxford

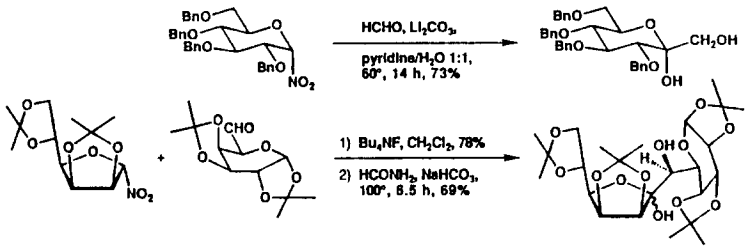
with M. Horsch, D. Rast, Zürich



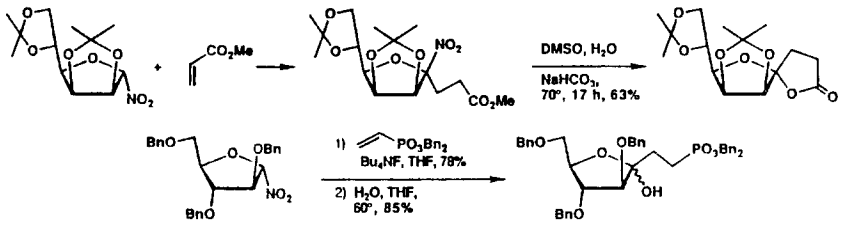
$S_{RN}1$ Reactions of Halonitro Ethers

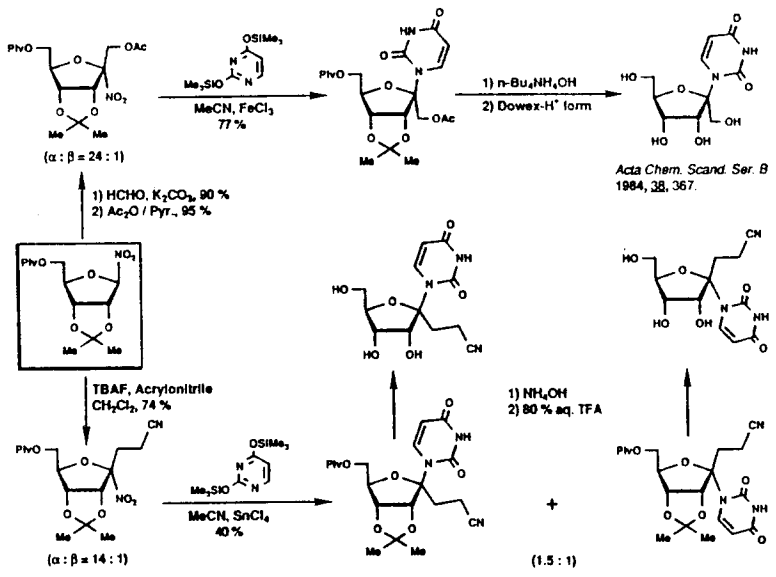


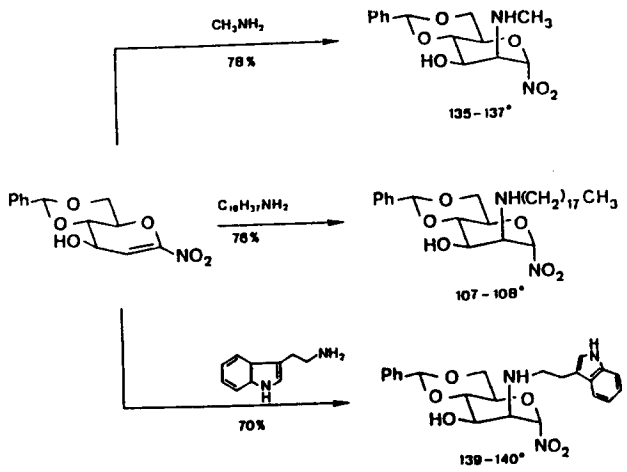
Henry Reaction and Solvolysis



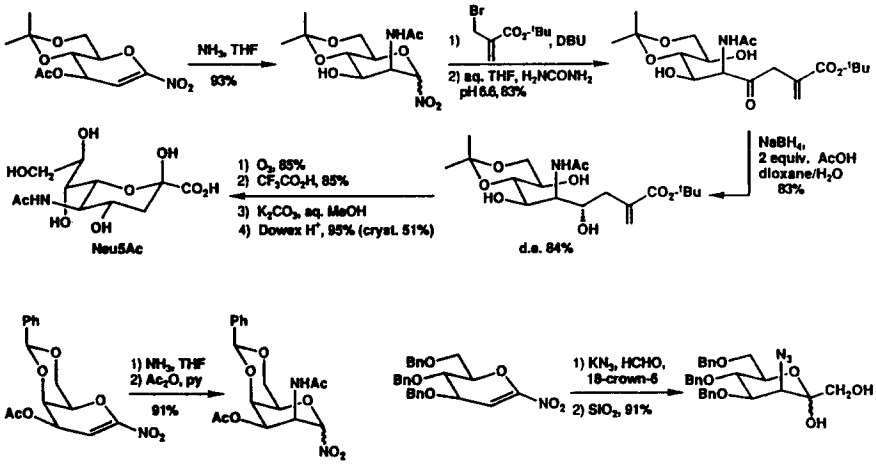
Michael Addition and Solvolysis



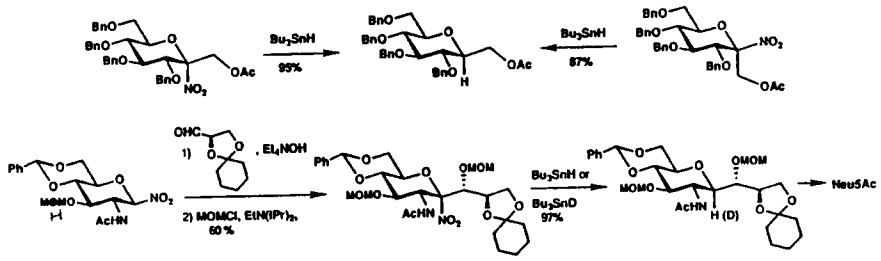




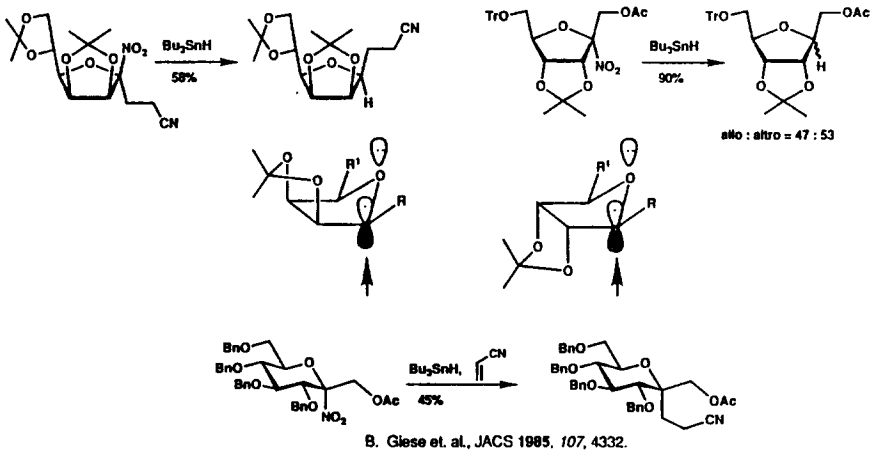
β-Addition, Michael Addition and Solvolysis



Glycosyl Radicals I

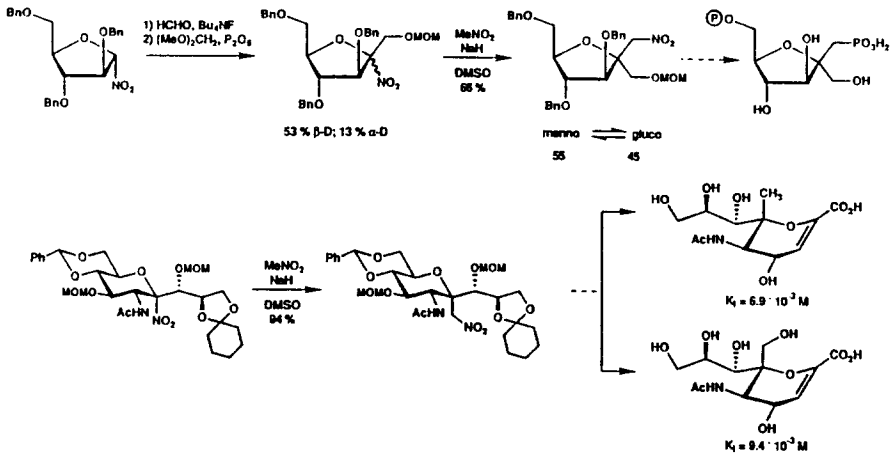


Glycosyl Radicals II



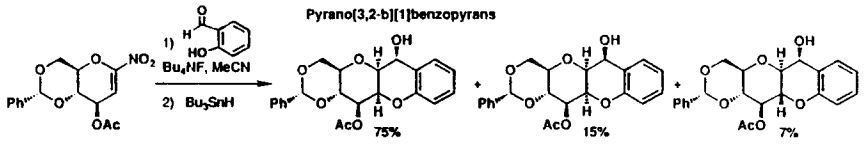
B. Giese et. al., JACS 1985, *107*, 4332.

Geminal Dialkylation

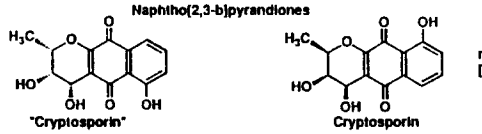


Annelation

Pyrano[3,2-b][1]benzopyrans



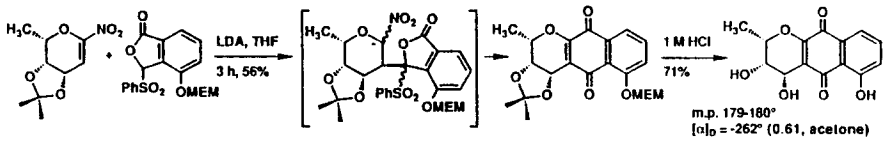
Naphtho[2,3-b]pyrandiones



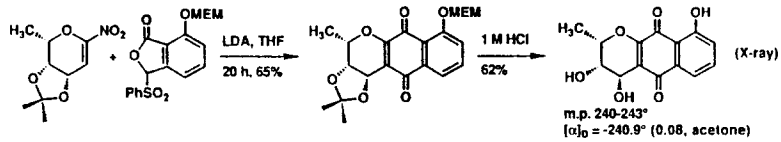
"Cryptosporin"
Helv. 1973, *56*, 619.

Cryptosporin

m.p. 244-250°
$[\alpha]_D$ = +238° (acetone)



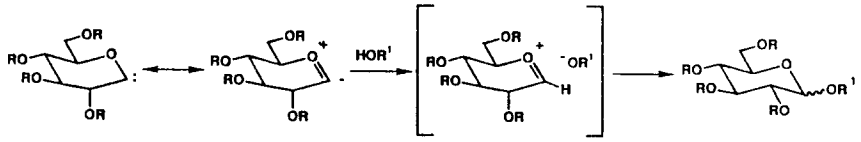
m.p. 179-180°
$[\alpha]_D$ = -262° (0.61, acetone)



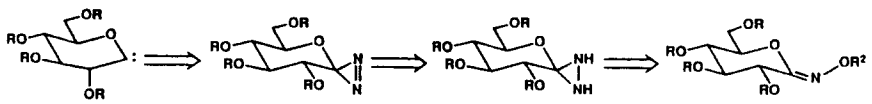
m.p. 240-243°
$[\alpha]_D$ = -240.9° (0.08, acetone)

Glycosidation without reagents ?

Glycosylidene Carbenes : Reactive Intermediates for Glycosidation

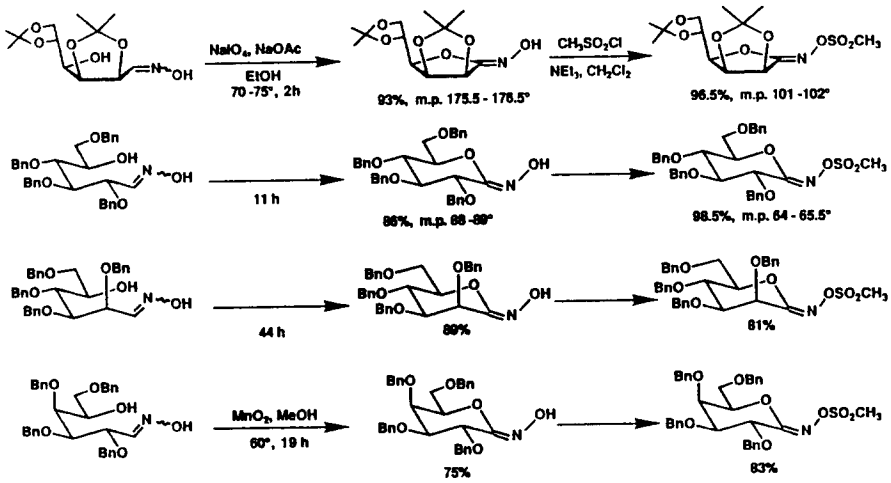


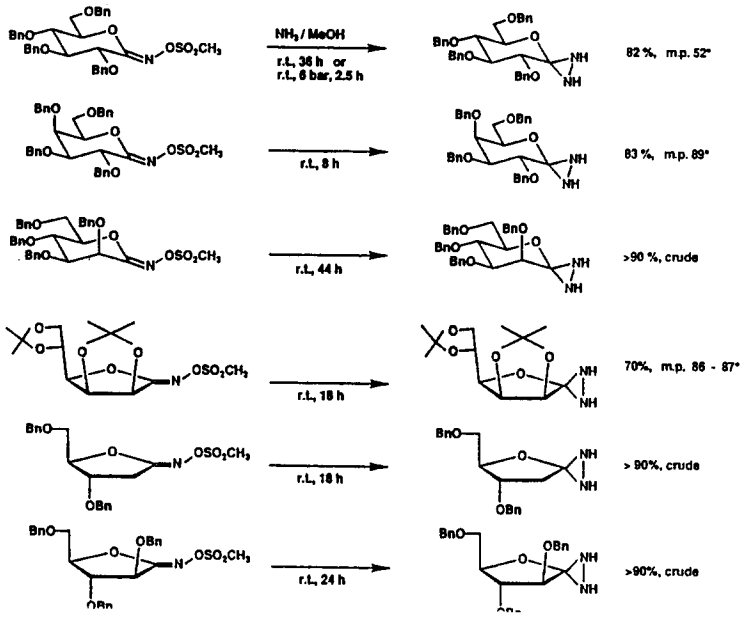
Glycosylidene-derived Diazirines : Ideal Precursors for Glycosylidene Carbenes ?



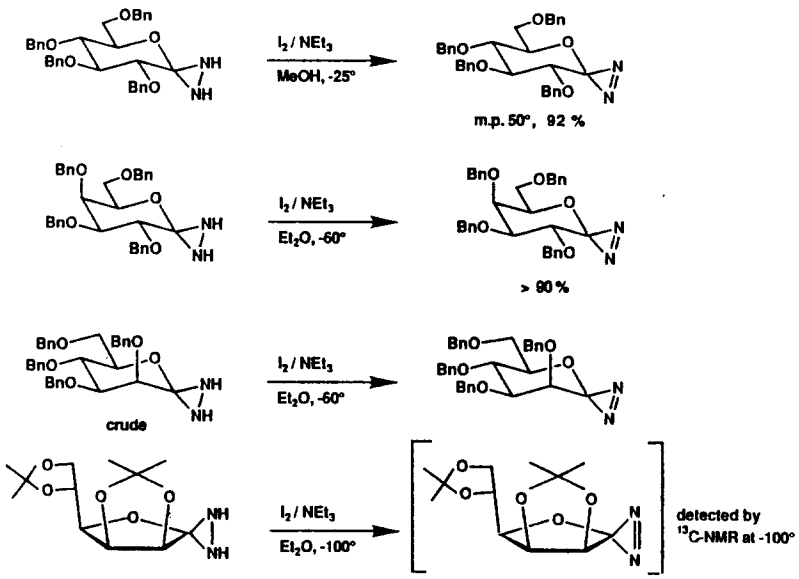
$R^2 = SO_2R^3 \Rightarrow R^2 = H$

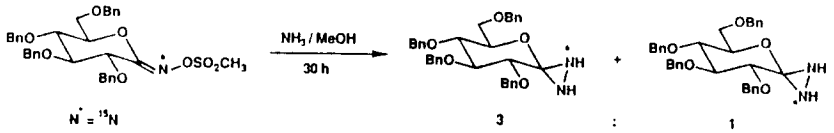
Preparation of Hydroximolactones and Their Mesylates

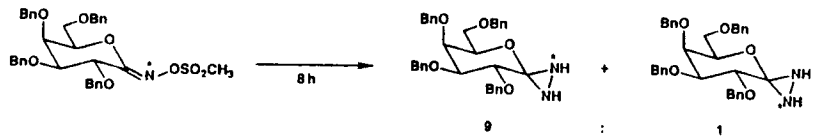


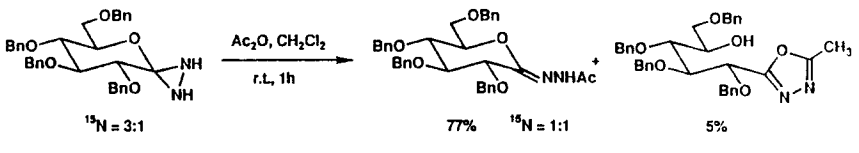


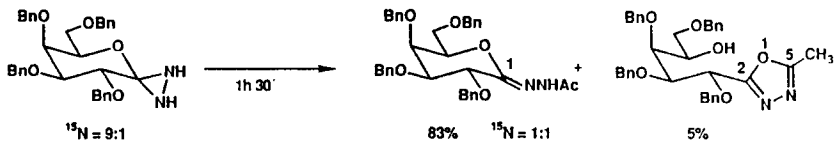
Glycosylidene Diazirines





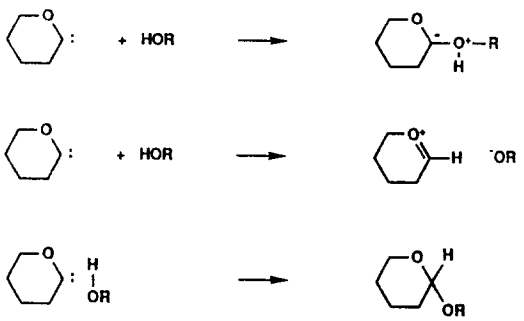






3:1 E/Z-mixture in $CDCl_3$

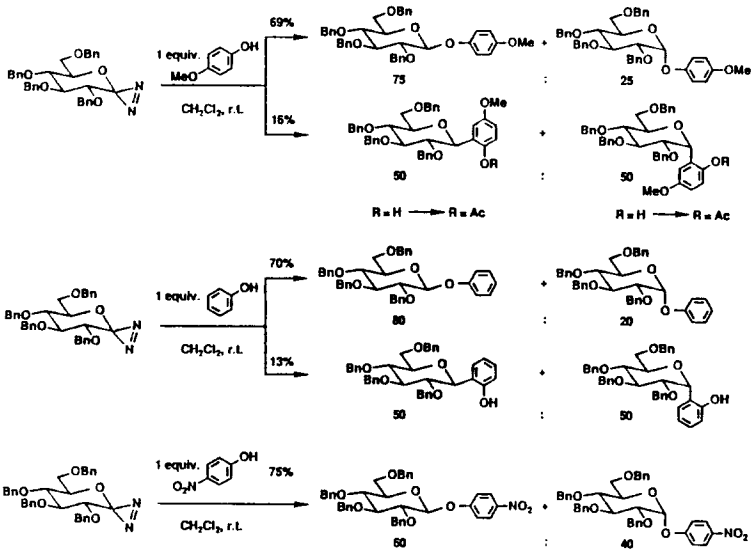
		major	minor		
^{1}H-NMR ($CDCl_3$):	N-H	8.77	9.09 s	O-H	2.61 d
	CH_3	2.29	1.91 s	CH_3	2.29 s
^{13}C-NMR ($CDCl_3$):	C=O	171.6	165.5 s	C(2)	164.5 s
	C(1)	144.4	146.5 s	C(5)	164.3 s
	CH_3	19.9	21.3 q	CH_3	10.7 q
IR ($CHCl_3$):	3360 w N-H			3560 w O-H	
	1665 s C=O			1660, 1590, 1560 w	



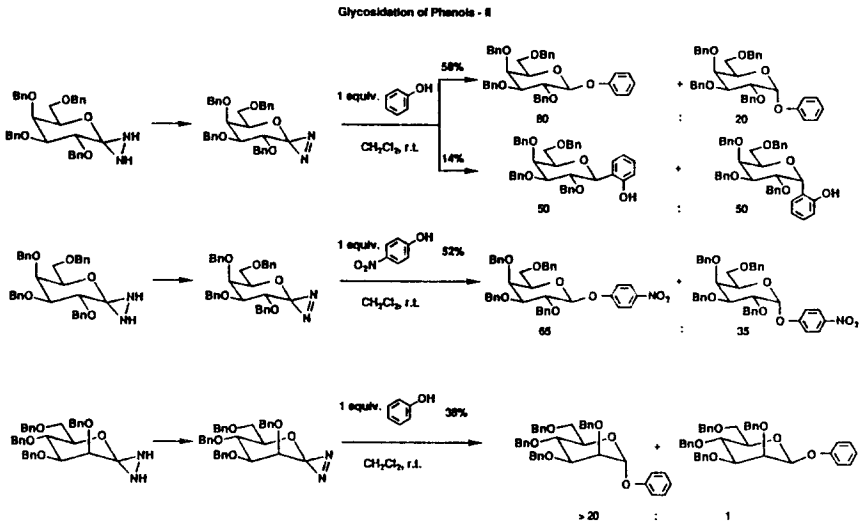
R. A. Moss et al., *Tetrahedron Lett.* 1988, 29, 6417:

KIE for  : + MeOH/MeOD = 3.3 ± 0.5

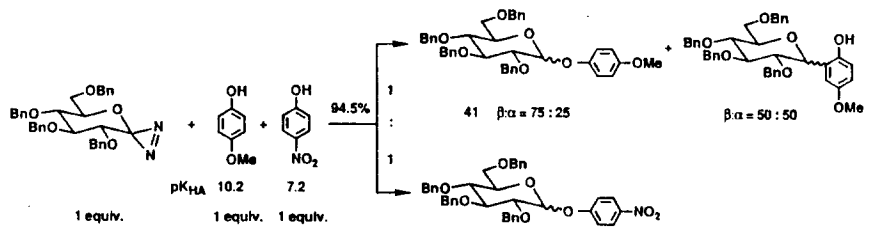
Glycosidation of Phenols - I



Glycosidation of Phenols - II



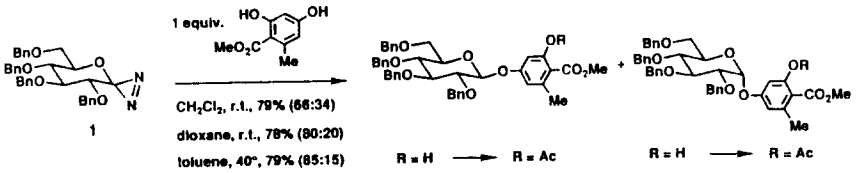
Competition Experiment
Dependence of Selectivity on Acidity ?

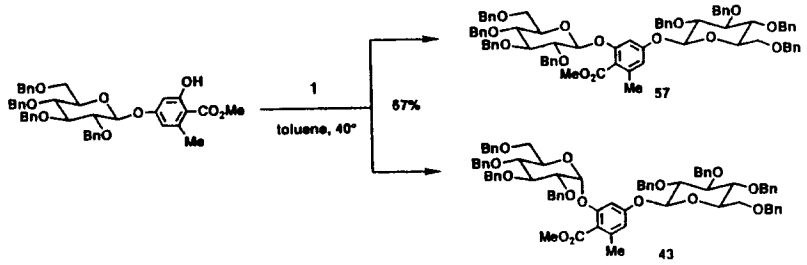


O-Glycosides
85

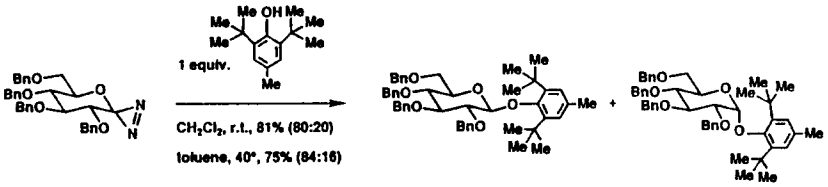
C-Glycosides
15

Kinetic Acidity and Regioselectivity

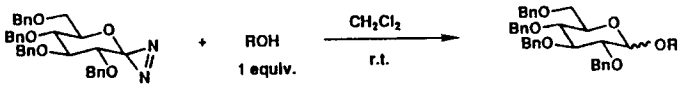




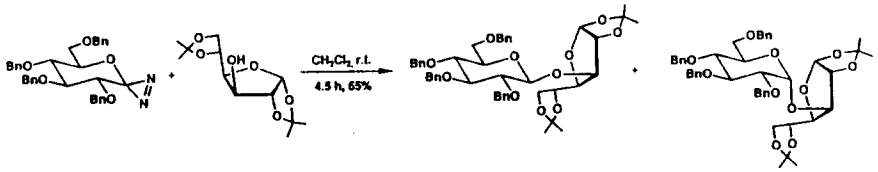
Influence of Steric Hindrance

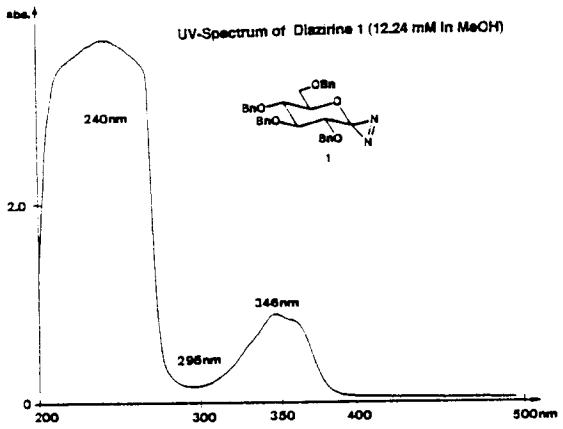


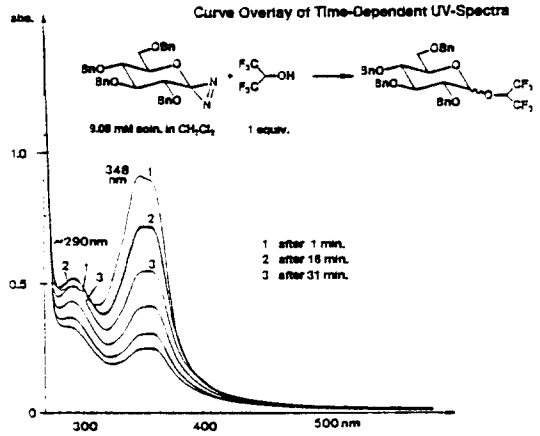
Glycosidation of Simple Alcohols



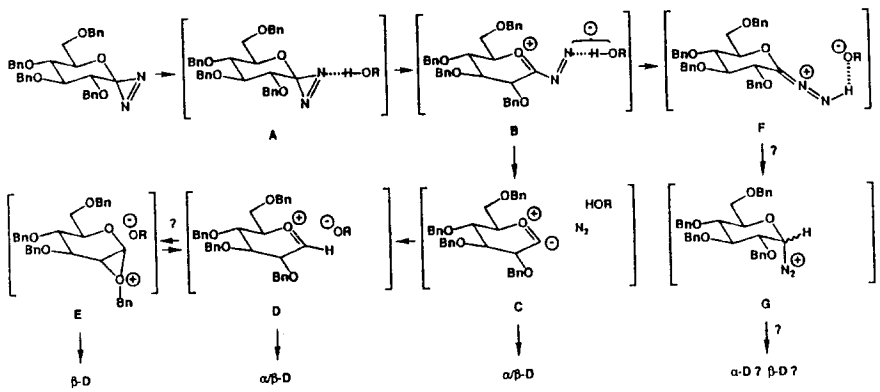
ROH	pK_{HA} (ROH)	% Glycosides	α : β
MeOH	17	60	50:50
EtOH	18	55	50:50
	18	39	50:50
	19	34	50:50
CF_3CH_2OH	12	70	35:65
	9	75	20:80



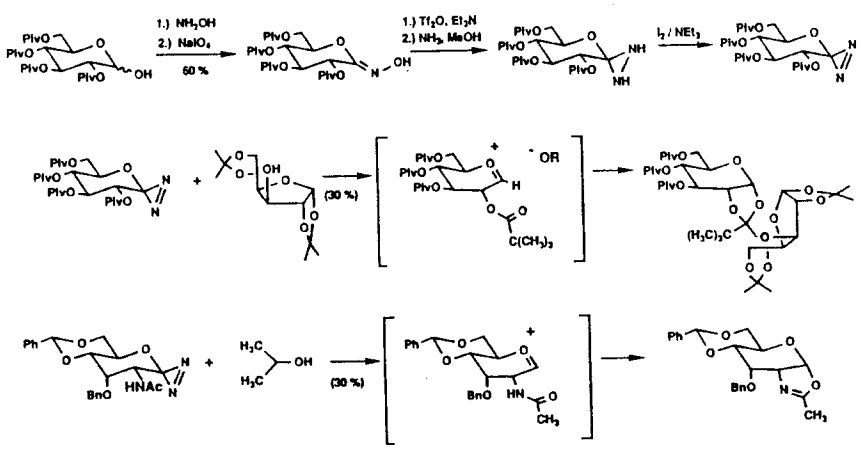


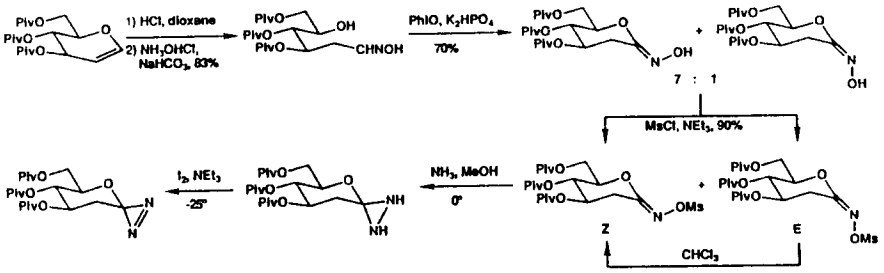


Working Hypothesis



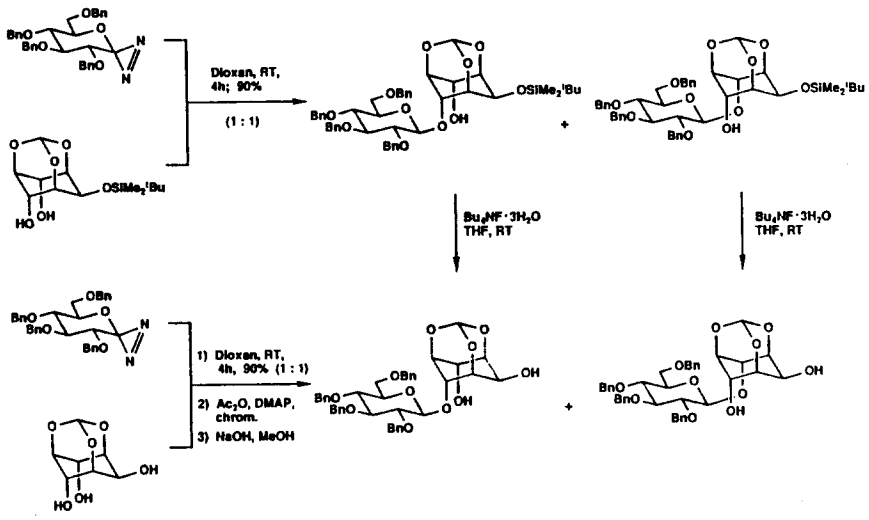
Carboxonium Ions as Intermediates



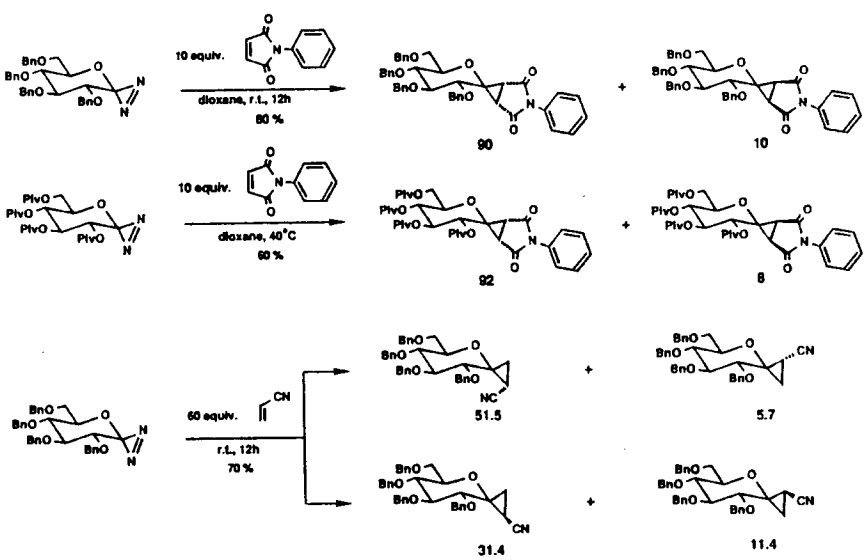


ROH	Solvent	% (from Z-mesylate)	α/β
	dioxane	48%	51 : 49
	toluene	40%	44 : 56
	dioxane	43%	59 : 41
	toluene	43%	52 : 48
MeOH	dioxane	28%	43 : 57
	toluene	32%	55 : 45
i-PrOH	toluene	26%	49 : 51

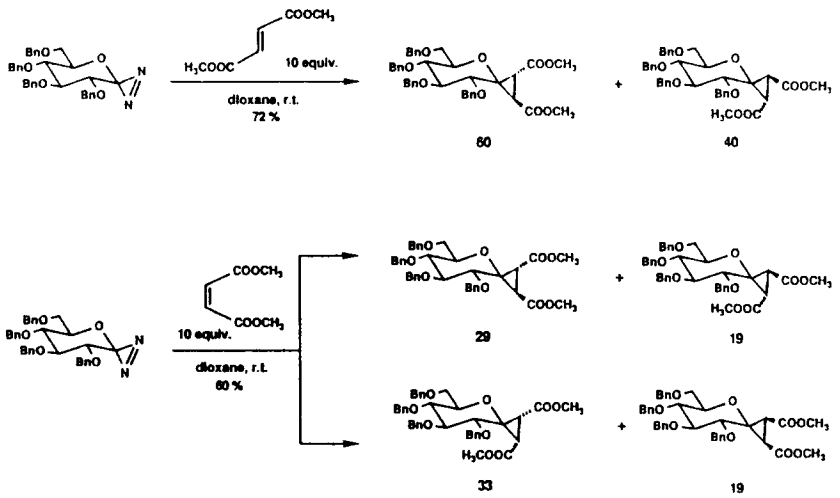
Regioselective Glycosidation

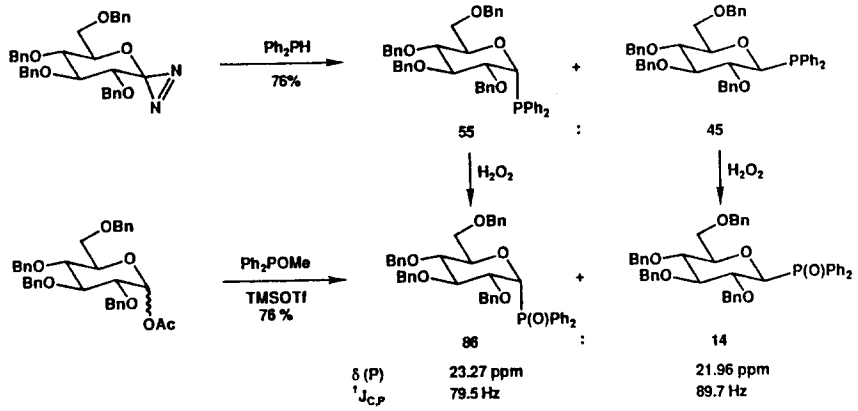


Spiro-Cyclopropanes



Cyclopropanation : Concertedness and Diastereoselectivity





Glycosyl-carbanions, Nitroaldoses and Related Compounds

Bernard Aebischer
Franz Baumberger
Dieter Beer
Dr. Bruno Bernet
Walter Brade
Kann Bnner
Dr. Laszlo Czollner
Helma Felber
Radomir Julina
Khalid Mahmood
Jean-Luc Maloisel
Roger Meuwly
René Wyler

Glycosylidene Carbenes and 1-Azi-1-deoxyglycoses

Kann Bnner
Dr. Luigi Panza
Dr. Thennati Rajamannar
Dr. Yoshikazu Takahashi
Peter Uhlmann
Christian Waldraff
Christian Witzig

Swiss National Science Foundation
F. Hoffmann La Roche & Co., Ltd., Basel
Sandoz, Inc., Basel