

Cover Page



Universiteit Leiden



The handle <http://hdl.handle.net/1887/31437> holds various files of this Leiden University dissertation

Author: Rijssel, Erwin Roelof van

Title: Stereoelectronic and conformational effects in carbohydrate derived oxocarbenium, iminium and ammonium ions

Issue Date: 2015-01-14

**Stereoelectronic and conformational effects in
carbohydrate derived oxocarbenium, iminium and
ammonium ions**

PROEFSCHRIFT

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden,
op gezag van Rector Magnificus prof. mr. C. J. J. M. Stolker,
volgens besluit van het College voor promoties
te verdedigen op woensdag 14 januari 2015
klokke 16:15 uur

door

Erwin Roelof van Rijssel

Geboren te Haarlemmermeer in 1987

Promotiecommissie

Promotor: Prof. dr. G. A. van der Marel

Co-promotor: Dr. J. D. C. Codée

Overige leden: Prof. dr. H. S. Overkleeft
Prof. dr. K. A. Woerpel
Prof. dr. F. M. Bickelhaupt
Prof. dr. J. Brouwer
Prof. dr. J. Lugtenburg

ISBN/EAN: 978-94-6108-878-9

Geprint door: Gildeprint

Table of Contents

List of Abbreviations	6
Chapter 1 General Introduction	9
Chapter 2 Furanosyl Oxocarbenium Ion Stability and Stereoselectivity	33
Chapter 3 Stereoselectivity in the Lewis acid mediated reduction of ketofuranosides	61
Chapter 4 Chiral Pyrroline-Based Ugi-Three-Component Reactions are under Kinetic Control	81
Chapter 5 A library of lipophilic iminosugars based on all eight stereoisomeric pentofuranosyl iminosugars	121
Chapter 6 Stereolectronic substituent effects determine the conformational preferences of mannuronic acid based iminosugar cations	151

Chapter 7	167
Summary and future prospects	
Samenvatting	179
List of publications	182
Curriculum Vitae	185
Appendix	187

List of Abbreviations

Ac	acetyl	DMAP	4-dimethylaminopyridine
AMP	5-(adamantane-1-yl-methoxy)pentyl	DMF	dimethylformamide
aq.	aqueous	DMJ	deoxymannojirimycin
Ar	aromatic	DMSO	dimethyl sulfoxide
B3LYP	Becke 3-Parameter, Lee, Yang and Parr	DTBMP	2,6-di- <i>tert</i> -butyl-4-methylpyridine
Bn	benzyl	eq.	molar equivalents
Bu	butyl	E	energy
C	chair	<i>E</i>	envelope
cal	calorie	Et	ethyl
calc.	calculated	FES	Free Energy Surface
cat.	catalytic	<i>g</i>	<i>gauche</i>
COSY	correlation spectroscopy	<i>H</i>	half-chair
C _q	quaternary carbon atom	HR-MS	high-resolution mass spectroscopy
Cy	cyclohexane	HMBC	Heteronuclear multiple-bond correlation spectroscopy
δ	chemical shift (ppm)	HSQC	Heteronuclear Single Quantum Coherence
d	doublet	Hz	Herz
DCM	dichloromethane	IR	infrared
DFT	density function theory	<i>J</i>	coupling constant
DiBAL-H	di-isobutylaluminiumhydride		
DiPEA	<i>N,N</i> -diisopropylethylamine		

m	multiplet	sat.	saturated
M	molar	t	triplet
Me	methyl	<i>t</i>	<i>trans</i>
Ms	methanesulfonyl	<i>T</i>	twist
NIS	<i>N</i> -iodosuccinimide	τ_m	amplitude
NMR	Nuclear Magnet Resonance	TBAI	tetrabutylammonium iodide
NOESY	Nuclear Overhauser effect spectroscopy	<i>t</i> Bu	<i>tert</i> -butyl
Nu	nucleophile	TES	triethylsilane
nPP	5-neopentoxypentyl	Tf	triflyl
obs.	observed	TFA	trifluoromethanesulfonic acid
P	pseudorotational phase angle	THF	tetrahydrofuran
PBP	5-(<i>p</i> -phenylbenzyloxy)pentyl	TLC	thin layer chromatography
PCM	polarizable continuum model	TMS	trimethylsilane
PE	petroleum ether (40-60)	Tol	tolyl
PES	Potential Energy Surface	Tr	trityl
Ph	phenyl	Triflate	trifluoromethanesulfonyl
ppm	parts per million	TS	transition state
q	quartet	TTBP	2,4,6-tri- <i>tert</i> -butylpyrimidine
R_f	retention factor	UV	ultraviolet
s	singlet	ZPE	zero-point energy
S	skew-boat		

