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Facile Synthesis of α- and β-*O*-Glycosyl Imidates; Preparation of Glycosides and Disaccharides[**]

By *Richard R. Schmidt* and *Josef Michel*[*]

Glycosides and saccharides are largely synthesized *via* haloses and their activation by heavy metal salts—especially silver salts[1,2]. The disadvantages of this method are self-evident. Simplification of this approach should come from the synthesis of sterically pure, readily isolable intermediates with other leaving groups not requiring activation by heavy metal salts[2,3]. Suitable candidates would seem to be, *e.g.*, α- and β-glycosyl imidates, since β-glycosyl imidates—prepared from α-haloses with silver salts—undergo acid-catalyzed reaction to give good chemical and stereochemical yields of α-glycosides and α-saccharides[4]. Thus a facile synthesis of α- and β-glycosyl imidates is called for[5].

Ketenimines and nitriles containing electron-withdrawing substituents are known to afford imidates directly on reaction with alcohols[6]. We shall now demonstrate for the case of the C-1-unprotected glucopyranose *(1)* that this reaction can be applied to cyclic hemiacetals. Use of sodium hydride as base and aryl-substituted ketenimines gave exclusively the β-imidates *(2)*—*(5)* whereas the same reaction both with benzyl- and with acetyl-protected glucopyranose *(1)* and trichloroacetonitrile led diastereospecifically to the α-imidates *(6)* and *(7)* (Table 1). Both the β-imidates and the α-imidates, now prepared for the first time, could be conveniently isolated.

Table 1. *O*-Glycosyl imidates *(2)*—*(7)* prepared [a].

	Yield [%] [b]	^{1}H-NMR [c] H-1	H^A	$J_{1,2}$	IR [d] $\nu_{C=N}$	$[\alpha]_{578}^{20}$	*c* [e]
(2)	84	6.11	5.22	7.0	1670	+ 33.0	2.0
(3)	83	6.11	5.22	7.0	1650	+ 33.0	1.75
(4)	93	6.05	5.04	7.2	1670	+ 34.5	1.88
(5)	38	6.11	5.30	7.5	1670	+ 68.7	1.6
(6)	96	6.56	8.60	3.5	1670 (ν_{NH}: 3320)	+ 61.5	1.0
(7)	85	6.60	8.77	3.5	1680 (ν_{NH}: 3330) (ν_{CO}: 1755)	+103.0	1.2

[a] Abbreviations: Ac = acetyl; Bn = benzyl. All compounds gave correct elemental analyses. [b] Isolated yields. [c] 80 MHz spectra in $CDCl_3$ with tetramethylsilane as internal standard; δ values, coupling constants in Hz. [d] [cm^{-1}], film between NaCl plates. [e] In $CHCl_3$.

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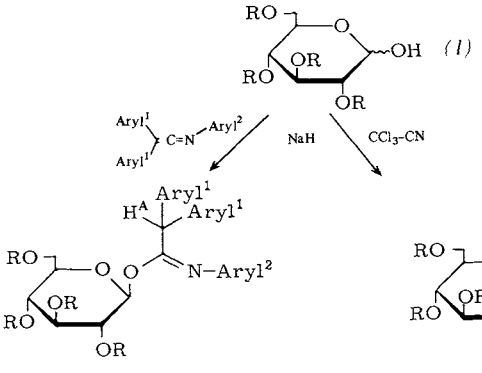
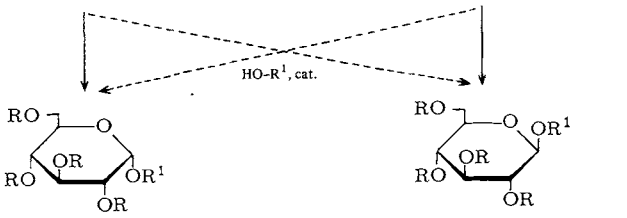


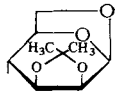
(2): R = Bn, $Aryl^1 = C_6H_5$, $Aryl^2 = p\text{-}CH_3\text{-}C_6H_4$ *(6)*: R = Bn
(3): R = Bn, $Aryl^1 = Aryl^2 = C_6H_5$ *(7)*: R = Ac
(4): R = Bn, $Aryl^1 = Aryl^2 = p\text{-}Cl\text{-}C_6H_4$
(5): R = Bn, $Aryl^1 = C_6H_5$, $Aryl^2 = p\text{-}(CH_3)_2N\text{-}C_6H_4$



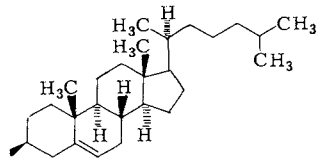
(8a)–(8e), *(8h)*: R = Bn

(a): $R^1 = -CO-CH_3$
(b): $R^1 = p\text{-}C_6H_4\text{-}CH_3$

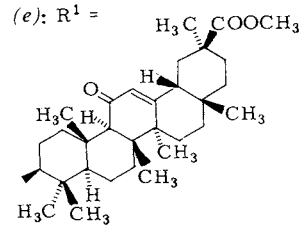
(c): R^1 =



(d): R^1 =

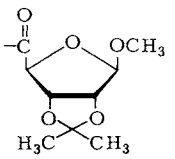


(e): R^1 =

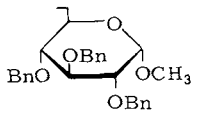


(9c)–(9h): R = Bn
(9i)–(9k): R = Ac

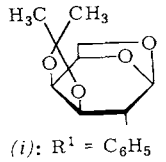
(f): R^1 =



(g), *(k)*: R^1 =

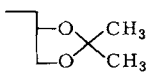


(h): R^1 =



(i): $R^1 = C_6H_5$

(j): R^1 =



As expected, the benzyl-protected β-imidates *(2)*—*(5)* undergo acid-catalyzed reaction with hydroxy components in dichloromethane to form mainly or exclusively the α-linkage product *(8)* while the α-imidate *(6)* correspondingly affords the β-linkage product *(9)* (see Table 2). The use of carboxylic acids [→*(8a)*, *(9f)*], *p*-cresol [→*(8b)*], steroid alcohols [→*(8d)*, *(9d)*; *(8e)*, *(9e)*], and carbohydrates [→*(8c)*, *(9c)*; *(9g)*; *(8h)*, *(9h)*] demonstrates the considerable scope of this simple method of glycosidation; however, the stereochemical result has not yet been optimized in all cases. The particularly readily accessible acetyl-protected α-imidate *(7)* reacts on ca-

Table 2. Reactants, reaction conditions, and products of glycoside and disaccharide synthesis. Dichloromethane as solvent [a].

Reactant	Cat.	Ratio [Reactant]:[HO—R¹]:[Cat.]	Conditions T [°C]	t [h]	Yield (8)+(9) [%] [b]	(8):(9)		Physical data of products ¹H-NMR [c] H-1	$J_{1,2}$	m.p. [°C]	$[\alpha]_{578}^{20}$	c [d]
(2)	—	1 :4 —	20	6	87	>19:1 [d]	*(8a)* [e]	6.36 (d)	3.5	oil	—	
(2)	TsOH	1.2:1:1	20	6	83	5:1	*(8b)*	5.43 (d)	3.5	oil	+ 63.7	1.5 [f]
(4)	TsOH	1.4:1:1	20	18	58	3:1	*(8c)*	4.86 (d)	3.5	oil	+ 21.0	1.3
							(9c)	[g]			− 16.3	1.0
(5)	TsOH	1.5:1:1	20	96	84	3:1	*(8d)* [e]	[g]		140—142	+ 47.3	1.5
							(9d) [e]	[g]		102—103	+ 0.6	1.6
(5)	TsOH	1.3:1:1	20	96	76	5:1	*(8e)*	5.02 (d)	3.5	oil	+126.0	1.15
							(9e)	4.45 (d)	7.5	oil	+ 98.2	1.0
(6)	—	1 :1 —	20	4	66	< 1:19 [d]	*(9f)* [e]:	5.63 (d)	7.0	oil	− 9.2	1.5
(6)	$BF_3 \cdot Et_2O$	1.3:1:1.3	−20	2	90	< 1:19 [d]	*(9g)* [e]	[g]		133—134	+ 17.9	1.0
(6)	TsOH	1.1:1:0.2	20	96	66	1:2	*(8h)*	[g]		oil	+ 29.0	1.52
							(9h)	[g]		oil	− 7.4	1.7
(7)	$BF_3 \cdot Et_2O$	1 :1:2.4	20	24	75	< 1:19 [d]	*(9i)* [e]	[g]		123—125	− 24.0	1.0
(7)	$BF_3 \cdot Et_2O$	1 :1:0.25	20	1	58	< 1:19 [d]	*(9j)* [e]	4.61 [d]	7.5	115—117	− 18.8	1.0
(7)	$BF_3 \cdot Et_2O$	1 :1:1	20	1.5	44	< 1:19 [d]	*(9k)*	[g]		61—64 [h]	+ 3.6	1.1

[a] Abbreviations: Bn = benzyl, TsOH = *p*-toluenesulfonic acid. All compounds gave correct elemental analyses. [b] Isolated yields based on the limiting reactant. [c] 80 MHz spectra in $CDCl_3$ with tetramethylsilane as internal standard; δ values, multiplicity in parentheses; H-1 of the glucopyranosyl group, coupling constants in Hz. [d] Only *(8a), (9f), (9g), (9i), (9j), (9k)* could be detected by chromatography; detection limit < 1:19. [e] The data of compounds reported in the literature are in agreement with those given; *(8a): P. W. Austin, F. E. Hardy, J. G. Buchanan, J. Baddiley,* J. Chem. Soc. *1964*, 2128; *(8d), (9d): G. Wulff, U. Schröder, J. Wichelhaus,* Carbohydr. Res. *72*, 280 (1979); *(9f): J. Michel,* Diplomarbeit, Universität Konstanz 1978; *(9g):* see [3]; *(9i): I. Karasawa, R. Onishi,* Nippon Nogei Kagaku Kaishi, *35* (8), 707 (1971); Chem. Abstr. *63*, 5729e (1965); *(9j): T. Ogawa, K. Katano, M. Matsui,* Carbohydr. Res. *70*, 37 (1979). [f] Rotation of the 5:1 mixture. [g] Cannot be determined from the ¹H-NMR spectrum. [h] Amorphous product.

talysis by boron trifluoride-ether to give exclusively the β-glycosides and β-disaccharides *(9i)—(9k)*. Thus a facile method is now also available for the synthesis of β-glucopyranosides.

Procedure

(2)—(7): Ketenimine (10 mmol) and sodium hydride (0.1–0.2 mol), or trichloroacetonitrile (3.5 ml) and sodium hydride (10 mmol), are added to a solution of *(1)* (10 mmol) in dichloromethane (50 ml) at room temperature. After some time [*(2)*, 35 h; *(3)*, 24 h; *(4)*, 5 h; *(5)*, 3 d; *(6)*, 2 h; *(7)*, 20 min] the mixture is filtered, concentrated, and filtered over a short column [*(2)—(5)*, basic alumina (activity grade I), eluant, dichloromethane/ether 1:1; *(6)*, silica gel, light petroleum (low boiling)/ether 3:2; *(7)*, silica gel, ether]. Compound *(5)* is also purified by column chromatography on silica gel (light petroleum (low boiling)/ether = 3:2).

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CAS Registry numbers:
(1) (R = Bn), 38768-81-9; *(1)* (R = Ac), 40437-08-9; *(2)*, 74808-05-2; *(3)*, 74808-06-3; *(4)*, 74808-07-4; *(5)*, 74808-08-5; *(6)*, 74808-09-6; *(7)*, 74808-10-9; *(8a)*, 56822-49-2; *(8b)*, 74808-11-0; *(8c)*, 74808-12-1; *(8d)*, 41736-89-4; *(8e)*, 74808-13-2; *(8h)*, 74824-34-3; *(9c)*, 74808-14-3; *(9d)*, 70753-59-2; *(9e)*, 74824-28-5; *(9f)*, 74808-15-4; *(9g)*, 56632-57-6; *(9h)*, 74808-16-5; *(9i)*, 4468-72-8; *(9j)*, 34382-09-7; *(9k)*, 74808-17-6

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N-Sulfinylnonafluorobutanesulfonamide—A Supernucleophile[**]

By *Reinhard Bussas* and *Günter Kresze*[*]

A few years ago we had found that sulfinyl-*p*-toluenesulfonamide *(2)* is a very reactive enophile[1]. In the meantime

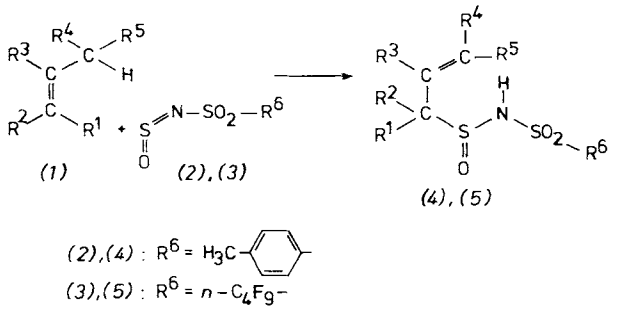

Table 1. Comparison of the ¹H-NMR spectroscopically determined half-lives ($\tau_{1/2}$) [a] in the ene-reaction of alkenes *(1a—g)* with *N*-sulfinylnonafluorobutanesulfonamide *(3)* and with *N*-sulfinyl-*p*-toluenesulfonamide *(2)*.

(1)	R^1	R^4	R^2	R^3	R^5	$\tau_{1/2}$ [min] (3)	(2)
(a)	—$(CH_2)_3$—		H	H	H	1	600
(b)	—$(CH_2)_4$—		H	H	H	1	600
(c)	—$(CH_2)_5$—		H	H	H	1	600
(d)	Cl	H	H	CH_3	H	1	≫6000
(e)	H	H	H	Cl	H	5	12000
(f)	H	H	H	Br	H	5	12000
(g)	H	CH_2OCOCH_3	H	H	H	5	15000

[a] In each case determined in a 3 M $CDCl_3$ solution of *(1)* and *(3)* or *(2)* at 20 °C.

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