

Activation of selenoglycosides by photoinduced electron transfer

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The activation of selenoglycosides is achieved by photo-induced electron transfer between aromatic compounds and the phenylselenyl group, while cleavage of the C–Se bond of the resulting radical cation generates a glycosyl cation that reacts with various alcohols to give the *O*-glycosides.

The generation of reactive intermediates, such as carbocations and carbanions, *via* cleavage of radical cations (or anions) generated by photochemical electron transfer (ET) processes is an interesting alternative to organometal-based procedures because the former would proceed under neutral conditions.¹ To demonstrate the ability of the photochemical ET method, we report herein the photochemical generation of a glycosyl cation from selenoglycoside and subsequent *O*-glycoside synthesis. Many methods have been reported involving *O*-glycoside synthesis,² however, until now only one example has been reported for the glycosylation reaction using a photochemical ET process.³ Noyori and co-workers reported the generation of the glycosyl cation from *O*-aryl glycoside *via* a photochemical ET process, and the *O*-glycosylation reaction using a 2-deoxy sugar as the glycosyl donor and octan-1-ol as the glycosyl acceptor.⁴ We chose the selenoglycosides as a glycosyl donor. The generation of simple carbocations from alkyl selenides using a photochemical ET method has been reported by Pandey and co-workers.⁵ The oxidation potential of alkyl selenides is lower than alkyl ethers and the bond dissociation energy of the C–Se bond is lower than that of the C–O bond; therefore, it is anticipated that the electron transfer of selenoglycosides is easier than that of their oxygen counterparts. In addition, selenoglycosides are stable under various protection–deprotection conditions.

Thus, we examined a permethylated glucose derivative as the glycosyl donor and simple alcohols as the glycosyl acceptors in the presence of aromatics, which act as good electron acceptors in their excited states. Irradiation (using a 100 W high pressure mercury lamp through a Pyrex filter) of the acetonitrile solution (0.1 mol dm^{−3}) of 2,3,4,6-tetra-*O*-methyl-1-phenylseleno-β-D-glucopyranoside **1**, cyclohexanol (20 equiv.) and an aromatic compound (1 equiv.) produced cyclohexylglucoside **2** and 1-hydroxy-2,3,4,6-tetra-*O*-methyl-D-glucopyranose **3**. The results of the irradiation reactions are presented in Table 1. The use of 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) as a sensitizer gave a 75% isolated yield of the desired glucoside **2** as a stereoisomeric mixture (α/β = 25/75) and hydrolysed product **3** (25%, α/β = 75/25) (entry 1). This result indicated that photosensitized oxidation of the selenoglycoside could be successfully achieved in order to quantitatively generate the glycosyl cation and produce *O*-glycoside. The use of 1,4-dicyanobenzene (DCB), 9,10-dicyanoanthracene (DCA) and

1,2,4,5-tetracyanobenzene (TCB) was also effective but required a prolonged reaction time (13.5 h for DCB, 12.5 h for DCA and 26 h for TCB, entries 2–4).

The reactions of **1** and other alcohols in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) are presented in Table 2. Not only simple alcohols (isopropanol and octanol) but also a sugar derivative are used as glycosyl acceptors. This is the first example of a photochemical disaccharide synthesis. The observed β selectivity of the products is identical with that of the Lewis acid promoted reaction of various glycosyl donors in acetonitrile.

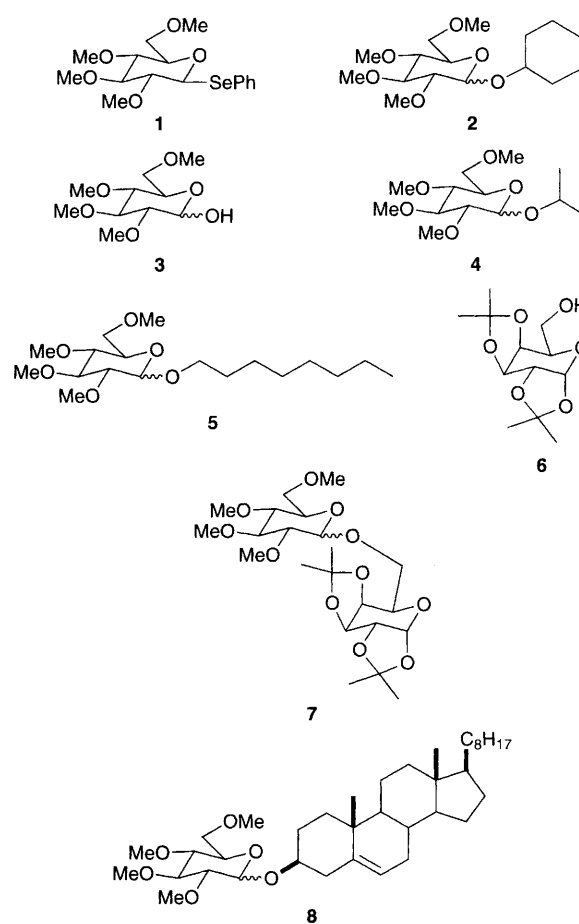


Table 1 Photochemical glycosylation of **1** with cyclohexanol as the glycosyl acceptor

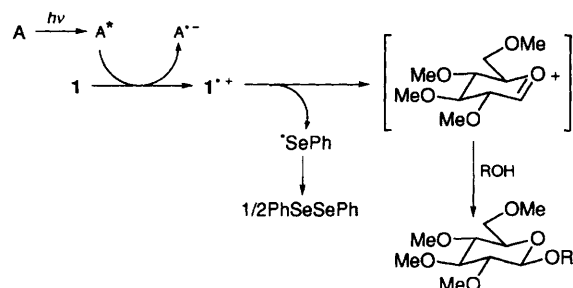
Entry	Sensitizer	$E_{\text{red}}/\text{V}^a$	E_{ox}/V^a	ΔG_{ET}	t/h	Product, yield (%) (α:β)
1	TPT	−0.29	2.82	−23	4	2 , 75 (25:75) 3 , 25 (75:25)
2	DCB	−1.60	4.27	−26	13.5	2 , 70 (26:74) 3 , 30 (75:25)
3	DCA	−0.89	2.86	−10	12.5	2 , 68 (26:74) 3 , 32 (76:24)
4	TCB	−0.66	4.10	−44	26	2 , 55 (28:72) 3 , 41 (69:31)

^a Data from ref 1(b).

Table 2 Photochemical glycosylation of **1** with various glycosyl acceptors

Entry	Glycosyl acceptor (equiv.)	Sensitizer (equiv.)	t/h	Glycoside	Isolated yield (%)	$\alpha : \beta^a$
1	cyclohexanol (20)	TPT (1)	4	2	75	25 : 75
2	isopropanol (20)	TPT (1)	6.5	4	71	30 : 70
3	octan-1-ol (12)	TPT (1)	3	5	68	30 : 70
4	6 (2)	TPT (0.35)	13	7	59	14 : 86
5	cholesterol (2)	TPT (0.1)	20	8	8	0 : 100

^a Determined by integration of the H-1 proton in the ¹H NMR spectra of the crude mixtures.

**Scheme 1** Proposed mechanism for the glycosylation reaction

The photoinduced electron transfer between selenoglycoside and the excited TPT is expected because the fluorescence quenching of TPT ($\lambda_{\text{ex}} = 369 \text{ nm}$) by **1** has been observed at a rate ($k_q = 1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) close to the diffusion controlled limit ($k_{\text{diff}} = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for acetonitrile). The oxidation potential of **1** was measured ($E_{1/2}^{\text{ox}} = 1.48 \text{ V}$) by cyclic voltammetry† and the existence of the photochemical SET process is further supported by the estimated ΔG_{ET} value ($-23 \text{ kcal mol}^{-1}$; see Table 1, entry 1) ($1 \text{ cal} = 4.184 \text{ J}$) according to the Rehm–Weller equation.⁶ The proposed mechanism of the glycosylation reaction is outlined in Scheme 1. After the excitation of TPT [or other aromatics (A)], the electron transfer might occur and generate the radical cation of **1**. Heterolytic cleavage of the C–Se bond generates a glycosyl cation which is allowed to react with various glycosyl acceptors (and water for the production of **3**).

The yields are not yet optimized, but from the present study, we have demonstrated a new method for the glycosylation reaction under neutral conditions using phenylselenoglycoside as the glycosyl donor. The possibility of the selective activation of the selenoglycoside over other acid-labile glycosides and the scope and limitations of this reaction are currently under investigation.

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Footnote

† Referenced to Ag/AgCl electrode using tetrabutylammonium perchlorate as the supporting electrolyte in dry acetonitrile.

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