Microreactors

DOI: 10.1002/anie.201100854

Indirect Cation-Flow Method: Flash Generation of Alkoxycarbenium Ions and Studies on the Stability of Glycosyl Cations**

*Kodai Saito, Koji Ueoka, Kouichi Matsumoto, Seiji Suga, Toshiki Nokami, and Jun-ichi Yoshida**

Organic cations such as alkoxycarbenium ions and N-acyliminium ions are believed to be unstable and transient in common organic solvents and are usually generated in the presence of nucleophiles.[1] In 1999, we developed a method for the generation and accumulation of highly reactive carbocations in solution in the absence of a nucleophile, based on low-temperature electrochemical oxidation.[2] This method is called the cation-pool method.[3]

Because electrochemical reactions take place only on the surface of the electrode, the accumulation of a cation usually takes several hours in the cation-pool method. Therefore, the method is not applicable to highly unstable cations. We have already reported two solutions to this problem. The first one is the cation-flow method using an electrochemical flow microreactor system.[4] Unstable cations are generated and quickly transferred to another location to be used in the next reaction before they decompose. Another solution is the indirect cation-pool method,[5] which involves electrochemical generation of $[ArS(ArSSAr)]^+$[6] and its reaction with a precursor to generate a desired unstable organic cation. Because the cation generation takes place in a homogeneous solution, it is complete within approximately one minute at −78 °C.

However, there is still a strong need for a new method that is applicable to more unstable organic cations such as glycosyl cations.[7] Glycosyl cations are considered to play key roles in glycosylation reactions. However, they have not yet been characterized spectroscopically and their stability and reactivity remain relatively poorly understood, although they are believed to be definitely more reactive and less stable than simple alkoxycarbenium ions. Herein, we report proof-of-principle studies of the indirect cation-flow method, which involves flash generation of highly unstable organic cations using electrochemically generated $[ArS(ArSSAr)]^+$ in the absence of nucleophiles, and their reactions with nucleophiles in a flow microreactor system.[8] We also report the application of the method to studies on the stability of glycosyl cations and glycosylation reactions.

At first we examined the generation of a simple alkoxycarbenium ion **3** by treatment of thioacetal **1a** ($R = C_8H_{17}$, $R' = CH_3$, $Ar' = Ph$) with electrogenerated $[ArS(ArSSAr)]^+BF_4^-$ ($Ar = p\text{-}FC_6H_4$; **2**) using a flow microreactor system consisting of three micromixers (M1, M2, and M3) and two microtube reactors (R1 and R2; Figure 1). Thus, the

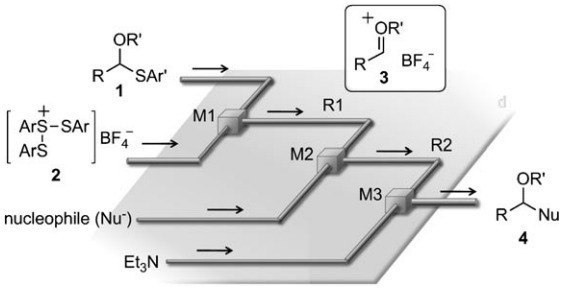


Figure 1. Integrated flow microreactor system for the generation and reactions of alkoxycarbenium ions.

electrochemical oxidation of ArSSAr ($Ar = p\text{-}FC_6H_4$) was carried out in nBu_4NBF_4/CH_2Cl_2 at −78 °C (0.67 F mol^{-1}) to generate **2**.[9] A CH_2Cl_2 solution of **1** was mixed with **2** at M1 to generate **3**, which was reacted with allyltrimethylsilane as a nucleophile (M2 and R2). Triethylamine was added at M3 to quench the reaction to give the desired product **4**.

The reactions were carried out at several temperatures (T) and with a variety of the residence times in R1 (t^R), which were altered by varying the length of R1 (Table 1). At −78 °C, a significant amount of **1a** remained unchanged when the residence time was short (Table 1, entries 1–3). However, an increase in t^R caused an increase in the conversion of **1a**, thus giving **4a** in quantitative yield at a t^R of 1.20 seconds (entry 4). At −28 °C, **4a** was obtained quantitatively at a t^R of 0.17 seconds (Table 1, entry 5). However, an increase in t^R at −28 °C caused a decrease in the yield presumably because of the decomposition of **3** (Table 1, entries 6–8). At 0 °C the yield was low even with short residence times (entry 9). These results indicate that electrogenerated $[ArS(ArSSAr)]^+$ is highly effective for the rapid generation of alkoxycarbenium ions from the corresponding thioacetals in the flow microreactor system. Notably, the reaction can be performed at

[*] Dr. K. Saito, K. Ueoka, Dr. K. Matsumoto,[++] Prof. S. Suga,[+] Dr. T. Nokami, Prof. J. Yoshida
Department of Synthetic and Biological Chemistry
Graduate School of Engineering, Kyoto University
Nishikyo-ku, Kyoto, 615-8510 (Japan)
Fax: (+81) 75-383-2727
E-mail: yoshida@sbchem.kyoto-u.ac.jp
Homepage: http://www.sbchem.kyoto-u.ac.jp/yoshida-lab/index.html

[+] Present address: Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University Tsushima-naka, Kita-ku, Okayama, 700-8530 (Japan)

[++] Present address: Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka, 577-8502 (Japan)

[**] We thank a grant-in-aid for scientific research for partial support of this work. We are also grateful to Nippon Shokubai Co. and Nippoh Chemicals Co. for providing $NaB(C_6F_5)_4$.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100854.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1: Effect of the residence time in R1 (t^R) on the reaction of **1a** (R = C_8H_{17}, R′ = CH_3, Ar′ = Ph) and **2** in the flow microreactor system.

Entry	T [°C]	l [cm][a]	t^R [s]	Yield of **4a** [%][b]	RSM [%][b,c]
1	−78	3.5	0.17	27	65
2	−78	6.0	0.29	68	31
3	−78	12.5	0.60	88	11
4	−78	25.0	1.20	quant.	0
5	−28	3.5	0.17	quant.	0
6	−28	6.0	0.29	97	0
7	−28	12.5	0.60	93	0
8	−28	25.0	1.20	89	0
9	0	3.5	0.17	45	0

[a] Length of the microtube reactor R1. [b] Determined by GC analysis using hexadodecane as an internal standard. [c] RSM = recovered starting material.

−28 °C, although much lower temperatures, such as −78 °C, are required for larger batch reactions.

The reactions of various carbon nucleophiles were examined (Table 2). Allyltrimethylsilanes, enol silyl ethers, ketene silyl acetals, and enol acetate were effective to give the corresponding C–C bond-formation products (**4a**, **4b**, **4c**, **4d**, and **4e**, respectively). Other thioacetals (**1b** and **1c**) could also be used as precursors of the alkoxycarbenium ions, and the corresponding products were obtained in good yields. In particular, cyclic thioacetals having five- (**1d**) and six-membered ring structures (**1e** and **1f**), which serve as models for thioglycosides, were effective as substrates.

Having demonstrated the successful generation of the alkoxycarbenium ions and their reactions using the indirect cation-flow method, we examined glycosylation reactions,[10,11] which involve glycosyl cations. The reaction of thioglycoside **5a** with $[ArS(ArSSAr)]^+BF_4^-$ (Ar = p-FC_6H_4; **2**) to generate glycosyl cation **6** (or its equivalent) followed by the reaction with MeOH was carried out using the flow microreactor system shown in Figure 2. However, the desired glycosylation product **7a** was not obtained at all, instead glycosyl fluoride **8** was obtained in 74% yield ($t^R = 0.17$ s, −48 °C). This result is consistent with our previous observation that the direct electrochemical oxidation of thioglycosides in the presence of BF_4^- leads to glycosyl fluorides.[12] Therefore, we chose to use $B(C_6F_5)_4^-$ as a counter anion to $[ArS(ArSSAr)]^+$ to avoid the attack on the glycosyl cation **6** by the fluoride derived from BF_4^-. Thus, $[ArS(ArSSAr)]^+$ $[B(C_6F_5)_4]^-$ (**9**) was generated by the electrochemical oxidation of ArSSAr using nBu$_4$N$^+$[B(C$_6$F$_5$)$_4$]$^-$ and was used as a reagent for cation generation.

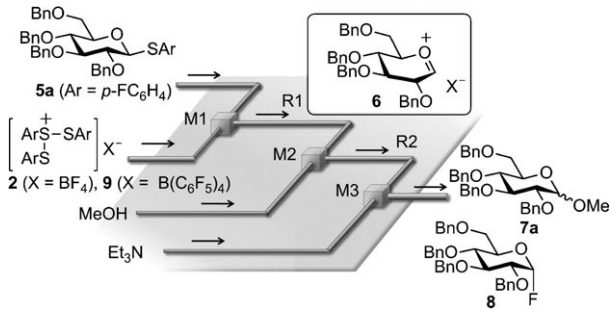
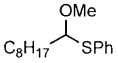
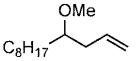
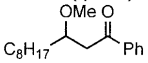
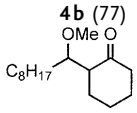
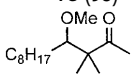
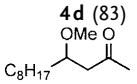
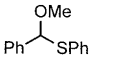
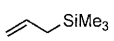
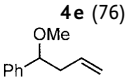
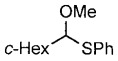
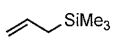
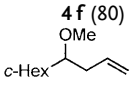
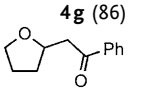
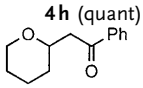


Figure 2. Integrated flow microreactor system for the glycosylation reaction of **5a** with MeOH. Bn = benzyl.

Table 2: The reaction of alkoxycarbenium ions with various carbon nucleophiles using the flow microreactor.

Thioacetal	Nucleophile[a]	Product (yield[b] [%])
 **1a**		 **4a** (quant)[c]
1a		 **4b** (77)
1a		 **4c** (98)[d]
1a		 **4d** (83)
1a		 **4e** (76)
 **1b**		 **4f** (80)
 **1c**		 **4g** (86)
 **1d**		 **4h** (quant)
 **1e**		 **4i** (82)
1f		**4j** (92)

[a] 3.0 equiv of nucleophile was used (0.35 M in CH_2Cl_2, flow rate 2 mL min^{-1}). [b] Yields are of the isolated product unless otherwise stated. [c] The yield was determined by GC analysis using hexadodecane as an internal standard. [d] Diastereomer ratio = 62:38.

The flow reactions were carried out at a variety of temperatures (T) and a range of residence times in R1 (t^R). The results are summarized in Figure 3, in which the yield of **7a** is plotted against T and t^R as a contour map with a scattered overlay.

As shown in Figure 3, the yield of **7a** strongly depends on the residence time and the temperature. At higher temperatures with longer residence times the yield was low presumably because of decomposition of **6**. Because it was technically difficult to operate the reaction at shorter residence times we chose $T = -48$ °C and $t^R = 0.17$ seconds as the optimized conditions, under which **7a** was obtained in 84% yield ($\alpha/\beta = 15{:}85$).

Notably, the stability of glycosyl cation **6** is shown by the data in Figure 3, although it is reasonable to consider that the

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

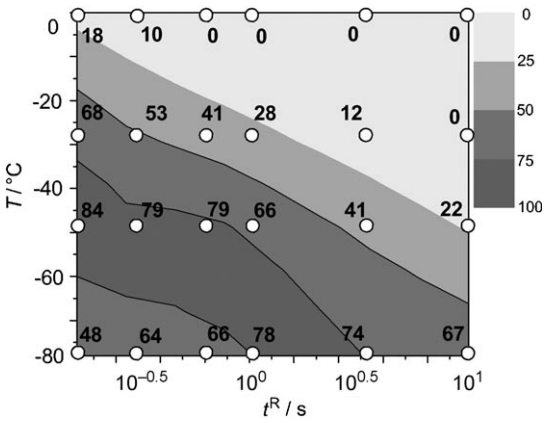


Figure 3. Effects of temperature (T) and residence time in R1 (t^R) on the yield (%) of **7a**.

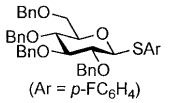
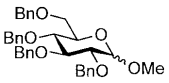
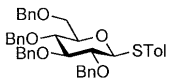
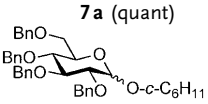
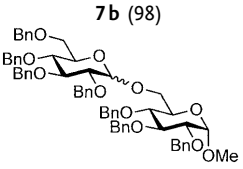
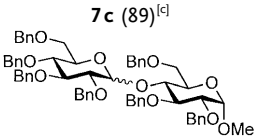
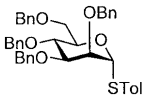
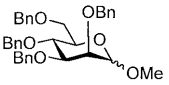
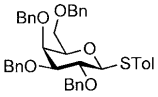
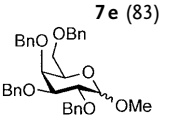
real intermediate is not a naked glycosyl cation but a glycosyl cation somewhat stabilized by the coordination of ArSSAr, which is inevitably produced by the reaction of **5a** and **9**. The data in Figure 3 indicates that the lifetime of the intermediate strongly depends upon the temperature, and that the lifetime is on the order of a second even at −78 °C.

Such information also indicates that a larger batch reaction is practically impossible. To confirm this, we examined the reaction of thioglycoside **5a** with $[ArS(ArSSAr)]^+[B(C_6F_5)_4]^-$ (**9**; 1.3 equiv) in a 20 mL flask. After they had reacted at −78 °C for 5 minutes, MeOH was added and the mixture was stirred for 5 minutes at the same temperature before quenching with triethylamine. A complex mixture was obtained presumably because of the decompositon of glycosyl cation intermediate **6**. A decrease in the reaction time to 1 minute gave the desired methyl glycoside **7a**, but the yield was very low (23 %).

Under the optimized reaction conditions, reactions of several thioglycosides (glycosyl donors) and glycosyl acceptors were examined using the flow microreactor system. As summarized in Table 3, *p*-tolyl thioglycoside (**5b**) was also effective as a glycosyl donor, and various acceptors could be used for the method. The thiomannoside (**5c**) and the thiogalactoside (**5d**) also reacted under similar reaction conditions to give the corresponding products in good yields.

In conclusion, we have developed the indirect cation-flow method, in which highly reactive organic cations are rapidly generated in the absence of nucleophiles and subsequently reacted with nucleophiles before they decompose using the integrated flow microreactor system. The method is quite effective for the generation and reactions of alkoxycarbenium ions. The method is also effective for glycosylation reactions involving the glycosyl cation intermediate or its equivalent. The residence time–temperature map provides information on the stability of the glycosyl cation intermediate. The results shown here add a new dimension to the chemistry of organic cations and flow microreactor chemistry. Detailed mechanistic studies involving characterization of glycosyl cation intermediates, or their equivalents, and applications to other organic cations are in progress.

Table 3: Generality of glycosylation reaction using flow microreactor.

Glycosyl donor	Products[a] (Yield[b] [%])	α/β
		
5a	**7a** (82)	15:85
		
5b	**7a** (quant)	18:82
		
5b	**7b** (98)	15:85
		
5b	**7c** (89)[c]	32:68
		
5b	**7d** (67)[c]	42:58
		
5c	**7e** (83)	54:46
		
5d	**7f** (76)	38:62

[a] 5.0 equiv of acceptor was used unless otherwise stated (0.58 M in CH_2Cl_2, flow rate 2 mL min^{-1}). [b] Yield of the isolated product. [c] 2.5 equiv of acceptor was used (0.29 M in CH_2Cl_2, flow rate 2 mL min^{-1}). Tol = *para*-methylphenyl.

Experimental Section

General procedure: A flow microreactor system consisting of three T-shaped micromixers (M1, M2, and M3), and four microtube reactors [R1 (inner diameter $\phi = 1000$ μm, length $l = 100$ cm), R2 ($\phi = 1000$ μm, length $l = 50$ cm), R3 ($\phi = 1000$ μm, length $l = 100$ cm), and R4 ($\phi = 1000$ μm, length $l = 50$ cm)] were used. A solution of $[ArS(ArSSAr)]^+BF_4^-$ (**2**) or $[ArS(ArSSAr)]^+[B(C_6F_5)_4]^-$ (**9**; Ar = *p*-FC_6H_4, ca. 0.038 M in CH_2Cl_2, flow rate: 7.8 mL min^{-1}) and a solution of a thioacetal or a thioglycoside (0.115 M in CH_2Cl_2, flow rate: 2.0 mL min^{-1}) were introduced into M1 ($\phi = 500$ μm) by syringe pumps. The resulting solution was passed through R1 and was mixed with a solution of a nucleophile (0.360 M, in CH_2Cl_2, flow rate: 2.0 mL min^{-1}) in M2 ($\phi = 500$ μm). The resulting solution was passed through R2 ($\phi = 1000$ μm, $l = 100$ cm) and was mixed with Et_3N (flow rate: 1 mL min^{-1}) in M3 ($\phi = 500$ μm). The resulting solution was passed through R3 ($\phi = 1000$ μm, $l = 50$ cm). After a steady state was reached, the product solution was collected for 30 s. Volatile materials were removed under reduced pressure. The residue was diluted with a small amount of CH_2Cl_2 and the solution was passed through a short-pad silica gel column using Et_2O as eluent to remove the supporting electrolyte. Solvents were removed under reduced pressure and the crude product either was analyzed by GC and NMR spectroscopy or purified by flash column chromatography on silica gel.

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Received: February 2, 2011
Published online: April 20, 2011

Keywords: carbohydrates · cations · electrochemistry · microreactors · sulfur

[1] a) G. K. S. Prakash, P. V. R. Schleyer, *Stable Carbocation Chemistry*, Wiley, New York, **1997**; b) G. A. Olah, K. K. Laali, Q. Wang, G. K. S. Prakash, *Onium Ions*, Wiley, New York, **1998**.

[2] a) K. D. Moeller, *Tetrahedron* **2000**, *56*, 9527 – 9554; b) J. B. Sperry, D. L. Wright, *Chem. Soc. Rev.* **2006**, *35*, 605 – 621; c) J. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, *Chem. Rev.* **2008**, *108*, 2265 – 2299; d) J. Yoshida, *Interface* **2009**, Summer, 40 – 45.

[3] Recent reports of the cation-pool method: a) T. Maruyama, Y. Mizuno, I. Shimizu, S. Suga, J. Yoshida, *J. Am. Chem. Soc.* **2007**, *129*, 1902 – 1903; b) S. Suga, I. Shimizu, Y. Ashikari, Y. Mizuno, T. Maruyama, J. Yoshida, *Chem. Lett.* **2008**, *37*, 1008 – 1009; c) T. Nokami, K. Ohata, M. Inoue, H. Tsuyama, A. Shibuya, K. Soga, M. Okajima, S. Suga, J. Yoshida, *J. Am. Chem. Soc.* **2008**, *130*, 10864 – 10865; d) M. Okajima, K. Soga, T. Watanabe, K. Terao, T. Nokami, S. Suga, J. Yoshida, *Bull. Chem. Soc. Jpn.* **2009**, *82*, 594 – 599; e) S. Suga, D. Yamada, J. Yoshida, *Chem. Lett.* **2010**, *39*, 404 – 406; f) K. Terao, T. Watanabe, T. Suehiro, T. Nokami, J. Yoshida, *Tetrahedron Lett.* **2010**, *51*, 4107 – 4109.

[4] a) S. Suga, M. Okajima, K. Fujiwara, J. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 7941 – 7942; b) J. Yoshida, S. Suga, *Chem. Eur. J.* **2002**, *8*, 2650 – 2658; c) S. Suga, M. Okajima, K. Fujiwara, J. Yoshida, *QSAR Comb. Sci.* **2005**, *24*, 728 – 741.

[5] Indirect cation-pool method: a) S. Suga, K. Matsumoto, K. Ueoka, J. Yoshida, *J. Am. Chem. Soc.* **2006**, *128*, 7710 – 7711; b) K. Matsumoto, K. Ueoka, S. Suzuki, S. Suga, J. Yoshida, *Tetrahedron* **2009**, *65*, 10901 – 10907; c) K. Matsumoto, K. Ueoka, S. Fujie, S. Suga, J. Yoshida, *Heterocycles* **2008**, *76*, 1103 – 1119; d) K. Matsumoto, S. Fujie, K. Ueoka, S. Suga, J. Yoshida, *Angew. Chem.* **2008**, *120*, 2540 – 2542; *Angew. Chem. Int. Ed.* **2008**, *47*, 2506 – 2508; e) K. Matsumoto, S. Fujie, S. Suga, T. Nokami, J. Yoshida, *Chem. Commun.* **2009**, 5448 – 5450; f) S. Fujie, K. Matsumoto, S. Suga, J. Yoshida, *Chem. Lett.* **2009**, *38*, 1186 – 1187; g) S. Fujie, K. Matsumoto, S. Suga, T. Nokami, J. Yoshida, *Tetrahedron* **2010**, *66*, 2823 – 2829.

[6] Examples of organic synthesis using $[ArS(ArSSAr)]^+$: a) A. S. Gybin, W. A. Smit, V. S. Bogdanov, M. Z. Krimer, J. B. Kalyan, *Tetrahedron Lett.* **1980**, *21*, 383 – 386; b) V. S. Bogdanov, A. S. Gybin, E. G. Cherepanova, W. A. Smith, *Izv. Akad. Nauk SSSR Ser. Khim.* **1981**, 2681 – 2693.

[7] Recent reports of alkoxycarbenium ions (oxocarbenium ions) including glycosyl cations: a) S. Chamberland, J. W. Ziller, K. A. Woerpel, *J. Am. Chem. Soc.* **2005**, *127*, 5322 – 5323; b) M. T. Yang, K. A. Woerpel, *J. Org. Chem.* **2009**, *74*, 545 – 553; c) D. M. Smith, K. A. Woerpel, *Org. Biomol. Chem.* **2006**, *4*, 1195 – 1201; d) J. R. Krumper, W. A. Salamant, K. A. Woerpel, *Org. Lett.* **2008**, *10*, 4907 – 4910; e) D. L. Zechel, S. G. Withers, *Acc. Chem. Res.* **2000**, *33*, 11 – 18; f) D. Crich, N. S. Chandrasekera, *Angew. Chem.* **2004**, *116*, 5500 – 5503; *Angew. Chem. Int. Ed.* **2004**, *43*, 5386 – 5389; for background on the glycosyl cation chemistry, see: g) L. Bohé, D. Crich, *C. R. Chim.* **2011**, *14*, 3 – 16, and references therein.

[8] Reviews on microreactor synthesis: a) K. Jähnisch, V. Hessel, H. Löwe, M. Baerns, *Angew. Chem.* **2004**, *116*, 410 – 451; *Angew. Chem. Int. Ed.* **2004**, *43*, 406 – 446; b) G. N. Doku, W. Verboom, D. N. Reinhoudt, A. van den Berg, *Tetrahedron* **2005**, *61*, 2733 – 2742; c) P. Watts, S. J. Haswell, *Chem. Soc. Rev.* **2005**, *34*, 235 – 246; d) K. Geyer, J. D. C. Codee, P. H. Seeberger, *Chem. Eur. J.* **2006**, *12*, 8434 – 8442; e) A. J. deMello, *Nature* **2006**, *442*, 394 – 402; f) H. Song, D. L. Chen, R. F. Ismagilov, *Angew. Chem.* **2006**, *118*, 7494 – 7516; *Angew. Chem. Int. Ed.* **2006**, *45*, 7336 – 7356; g) J. Kobayashi, Y. Mori, S. Kobayashi, *Chem. Asian J.* **2006**, *1*, 22 – 35; h) M. Brivio, W. Verboom, D. N. Reinhoudt, *Lab Chip* **2006**, *6*, 329 – 344; i) B. P. Mason, K. E. Price, J. L. Steinbacher, A. R. Bogdan, D. T. McQuade, *Chem. Rev.* **2007**, *107*, 2300 – 2318; j) B. Ahmed-Omer, J. C. Brandt, T. Wirth, *Org. Biomol. Chem.* **2007**, *5*, 733 – 740; k) P. Watts, C. Wiles, *Chem. Commun.* **2007**, 443 – 467; l) T. Fukuyama, M. T. Rahman, M. Sato, I. Ryu, *Synlett* **2008**, 151 – 163; m) J. Yoshida, A. Nagaki, T. Yamada, *Chem. Eur. J.* **2008**, *14*, 7450 – 7459; n) J. Yoshida, *Flash Chemistry. Fast Organic Synthesis in Microsystems*, Wiley-Blackwell, **2008**; o) W.-Y. Lin, Y. Wang, S. Wang, H.-R. Tseng, *Nano Today* **2009**, *4*, 470 – 481; p) *Micro Process Engineering* (Eds.: V. Hessel, A. Renken, J. C. Schouten, J. Yoshida), Wiley-VCH, Weinheim, **2009**; q) J. P. McMullen, K. F. Jensen, *Annu. Rev. Anal. Chem.* **2010**, *3*, 19 – 42; r) K. Tanaka, *J. Synth. Org. Chem. Jpn.* **2010**, *68*, 124 – 135; s) D. Webb, T. F. Jamison, *Chem. Sci.* **2010**, *1*, 675 – 680; t) J. Yoshida, *Chem. Rec.* **2010**, *10*, 332 – 341.

[9] The theoretical amount of electricity to convert ArSSAr into $[ArS(ArSSAr)]^+$.

[10] Reviews on glycosylation reactions: a) K. Toshima, K. Tatsuta, *Chem. Rev.* **1993**, *93*, 1503 – 1531; b) G. J. Boons, *Tetrahedron* **1996**, *52*, 1095 – 1121; c) S. J. Danishefsky, M. T. Bilodeau, *Angew. Chem.* **1996**, *108*, 1482 – 1522; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1380 – 1419; d) P. H. Seeberger, W.-C. Haase, *Chem. Rev.* **2000**, *100*, 4349 – 4393; e) J. D. C. Codée, R. E. J. N. Litjens, L. J. van den Bos, H. S. Overkleeft, G. A. van der Marel, *Chem. Soc. Rev.* **2005**, *34*, 769 – 782; f) P. H. Seeberger, D. B. Werz, *Nature* **2007**, *446*, 1046 – 1051; g) Y. Wang, X.-S. Ye, L.-H. Zhang, *Org. Biomol. Chem.* **2007**, *5*, 2189 – 2200; h) P. H. Seeberger, *Chem. Soc. Rev.* **2008**, *37*, 19 – 28; i) L. K. Mydock, A. V. Demchenko, *Org. Biomol. Chem.* **2010**, *8*, 497 – 510; j) D. Crich, *Acc. Chem. Res.* **2010**, *43*, 1144 – 1153.

[11] Examples of glycosylations using a flow microreactor system: a) D. M. Ratner, E. R. Murphy, M. Jhunjhunwala, D. A. Snyder, K. F. Jensen, P. H. Seeberger, *Chem. Commun.* **2005**, 578 – 580; b) K. Tanaka, T. Miyagawa, K. Fukase, *Synlett* **2009**, 1571 – 1574; c) K. Tanaka, Y. Fujii, H. Tokimoto, Y. Mori, S.-i. Tanaka, G.-m. Bao, E. R. O. Siwu, A. Nakayabu, K. Fukase, *Chem. Asian J.* **2009**, *4*, 574 – 580; d) H. Kawakami, K. Goto, M. Mizuno, *Chem. Lett.* **2009**, *38*, 906 – 907; e) K. Geyer, P. H. Seeberger, *Helv. Chim. Acta* **2007**, *90*, 395 – 403; f) K. Tanaka, K. Fukase, *Beilstein J. Org. Chem.* **2009**, *5*, 40; g) K. Geyer, T. Gustafsson, P. H. Seeberger, *Synlett* **2009**, 2382 – 2391; h) S. Tanaka, T. Goi, K. Tanaka, K. Fukase, *J. Carbohydr. Chem.* **2007**, *26*, 369 – 394; i) K. Tanaka, Y. Mori, K. Fukase, *J. Carbohydr. Chem.* **2009**, *28*, 1 – 11; j) F. R. Carrel, K. Geyer, J. D. C. Codée, *Org. Lett.* **2007**, *9*, 2285 – 2288; k) K. Tanaka, T. Miyagawa, K. Fukase, *Org. Process Res. Dev.* **2009**, *13*, 983 – 990; l) K. Fukase, M. Takashima, Y. Hori, D. Tanaka, K. Tanaka, S. Kusumoto, *Synlett* **2005**, 2342 – 2346.

[12] S. Suzuki, K. Matsumoto, K. Kawamura, S. Suga, J. Yoshida, *Org. Lett.* **2004**, *6*, 3755 – 3758.

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim