[2] H. Bock, S. Mohmand, T. Hirabayashi, G. Maier, H. P. Reisenauer, *Chem. Ber.* **1983**, *116*, 273 – 281.
[3] J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M.-H. Whangbo in *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory*, Prentice-Hall, New Jersey, **1992**, pp. 11 – 64.
[4] G. Märkl, R. Hennig, K. M. Raab, *Chem. Commun.* **1996**, 2057 – 2058.
[5] H. Kurata, T. Tanaka, T. Sauchi, T. Kawase, M. Oda, *Chem. Lett.* **1997**, 947 – 948.
[6] K. Ley, E. Müller, R. Mayer, K. Scheffler, *Chem. Ber.* **1958**, *91*, 2670 – 2681.
[7] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587 – 4589; M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1982**, *104*, 6167.
[8] E. Fluck, G. Heckmann in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: J. G. Verkade, L. D. Quin), VCH, New York, **1987**, pp. 61 – 113.
[9] R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. Scherer), Thieme, Stuttgart, **1990**, pp. 157 – 219.
[10] J. Zhou, A. Rieker, *J. Chem. Soc. Perkin Trans. 2* **1997**, 931 – 938.
[11] G. G. Aleksandrov, Y. T. Struchkov, D. I. Kalinin, M. G. Neigant, *Zh. Strukt. Khim.* **1973**, *14*, 852 – 858; R. West, J. A. Jorgenson, K. L. Stearley, J. C. Calabrese, *J. Chem. Soc. Chem. Commun.* **1991**, 1234 – 1235.
[12] J. Q. Chambers in *The Chemistry of the Quinoid Compounds*, *Part 2* (Ed.: S. Patai), Wiley, London, **1974**, pp. 737 – 791; J. Q. Chambers in *The Chemistry of the Quinoid Compounds*, *Vol. 2, Part 2* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1988**, pp. 719 – 758.
[13] M. Geoffroy, A. Jouaiti, G. Terron, M. Cattani-Lorente, Y. Ellinger, *J. Phys. Chem.* **1992**, *96*, 8241 – 8245.
[14] J. R. Morton, K. F. Preston, *J. Magn. Reson.* **1978**, *30*, 577 – 582.
[15] M. Culcasi, G. Gronchi, J. Escudié, C. Couret, L. Pujol, P. Tordo, *J. Am. Chem. Soc.* **1986**, *108*, 3130 – 3132; A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski, G. A. Heath, *J. Chem. Soc. Dalton Trans.* **1987**, 249 – 251; S. Shah, S. C. Burdette, S. Swavey, F. L. Urbach, J. D. Protasiewicz, *Organometallics* **1997**, *16*, 3395 – 3400.
[16] M. Geoffroy, E. A. C. Lucken, C. Mazeline, *Mol. Phys.* **1974**, *28*, 839 – 845; B. Çetinkaya, A. Hudson, M. F. Lappert, H. Goldwhite, *J. Chem. Soc. Chem. Commun.* **1982**, 609 – 610.
[17] A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[18] P. T. Beuskens, G. Admiraal, G. Beuskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.
[19] Crystal Structure Analysis Package, Molecular Structure Corporation, **1985** and **1992**.

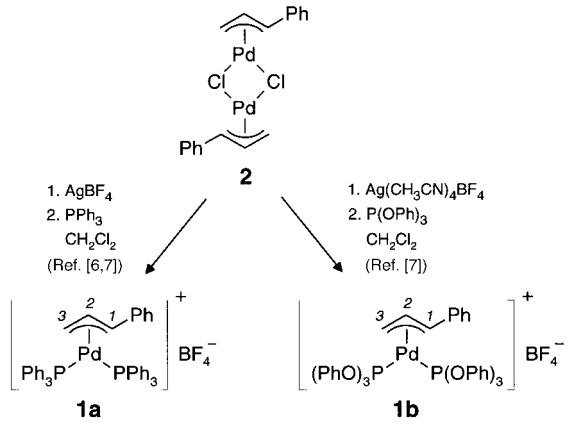
Kinetics and Mechanisms of the Reactions of π-Allylpalladium Complexes with Nucleophiles**

Oliver Kuhn and Herbert Mayr*

Dedicated to Professor Wolfgang Steglich on the occasion of his 65th birthday

Palladium(0)-catalyzed allylations of nucleophiles proceed under mild conditions, often with high regio- and stereoselectivity.[1] Detailed mechanistic investigations revealed that these reactions generally involve the intermediacy of cationic allylpalladium complexes which have been isolated and characterized by X-ray crystallography.[2] In the course of our program to quanitify the reactivities of cationic electrophiles[3] we have now turned to palladium-stabilized allyl cations. Herein we report on the kinetics of the reactions of the allylpalladium complexes **1a** and **1b** with noncharged nucleophiles, and we demonstrate how to employ the electrophilicity parameters derived therefrom for analyzing the reactivities of these cationic complexes.

The allylpalladium complexes **1a**, **b**[4] were synthesized from **2**[5] using known procedures[6, 7] (Scheme 1). The reaction products **4a – f** were obtained from the nucleophiles **3a – f** and



Scheme 1. Synthesis of the complexes **1a**-BF_4 and **1b**-BF_4 from **2**.

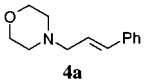
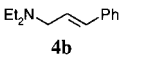
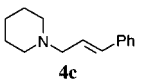
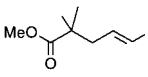
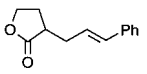
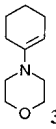
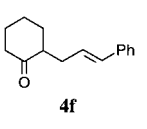
the allyl complexes **1a** and **1b**, either by employing stoichiometric quantities of the allylpalladium tetrafluoroborates **1a**-BF_4 or **1b**-BF_4 or by generating **1a** and **1b** in situ in the presence of the nucleophiles **3** from $[Pd(PPh_3)_4]$ or $[Pd_2(dba)_3 \cdot CHCl_3]/P(OPh)_3$ (10 mol%) and 3-phenylallyl acetate, as specified in Table 1 (Scheme 2; dba = dibenzylideneacetone).

To determine the reaction kinetics, the allyl complexes **1a**-BF_4 and **1b**-BF_4 were prepared and combined with 10 – 50 equivalents of the nucleophiles **3a – f**, and the decay of the

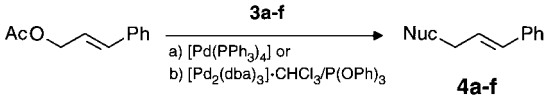
[*] Prof. Dr. H. Mayr, Dr. O. Kuhn
Institut für Organische Chemie der Universität
Karlstrasse 23, D-80333 München (Germany)
Fax: (+49) 89-5902-254
E-mail: hmy@cup.uni-muenchen.de

[**] We thank C. Schlierf for experimental contributions as well as the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Table 1. Products and rate constants (20 °C, CH_2Cl_2) of the reactions of **1a** and **1b** with the nucleophiles **3a–f**.

Nucleophile	Product	Yield [%]	Pd complex	k [L mol^{-1} s^{-1}] (number of experiments)
 **3a**	 **4a**	61[a]	**1a**-BF_4	4.49 ± 0.30 (3)
Et_2NH **3b**	 **4b**	67[a]	**1a**-BF_4	7.53 ± 0.18 (4)
			1a-PF_6	7.03 ± 0.40 (2)
			1a-BF_4[h]	7.30
			1a-BF_4[i]	6.49
			average value	7.25 ± 0.42 (8)
		80[b]	**1b**-BF_4	2410 ± 735[c] (6)
 **3c**	 **4c**	61[a]	**1a**-BF_4	29.9 ± 1.2 (6)
			1a-PF_6	36.8
			average value	30.9 ± 2.8 (7)
		93[b]	**1b**-BF_4	5227 ± 970[d] (6)
 **3d**	 **4d**	70[e]	**1a**-BF_4	
		69[b]	**1b**-BF_4	0.35 ± 0.03[f] (4)
 **3e**	 **4e**	52[b]	**1b**-BF_4	4.49 ± 0.23 (3)
 **3f**	 **4f**	55[g]	**1b**-BF_4	17.5 ± 2.1 (4)

[a] Reaction of 3-phenylallyl acetate with **3** in the presence of $[Pd(PPh_3)_4]$ (10 mol %). [b] Dropwise addition of 3-phenylallyl acetate and **3** to a solution of $[Pd_2(dba)_3 \cdot CHCl_3]$ (10 mol %) and $P(OPh)_3$. [c] Calculated from $\Delta H^{\neq} = (32.74 \pm 2.05)$ kJ mol^{-1} and $\Delta S^{\neq} = (-68.35 \pm 9.49)$ J mol^{-1} K^{-1} (six experiments in the range between −72 and −31 °C). [d] Calculated from $\Delta H^{\neq} = (26.18 \pm 1.53)$ kJ mol^{-1} and $\Delta S^{\neq} = (-84.29 \pm 6.99)$ J mol^{-1} K^{-1} (six experiments in the range between −72 and −30 °C). [e] Reaction of **3d** with stoichiometric amounts of **1a**-BF_4. [f] The ^{1}H NMR spectroscopic investigation in $CDCl_3$ yielded $k = 0.2$ L mol^{-1} s^{-1}. [g] Reaction of **3f** with stoichiometric amounts of **1b**-BF_4. [h] Under addition of 3 equivalents of tolane. [i] Under addition of 5 equivalents of fumaronitrile.



Scheme 2. Palladium-catalyzed synthesis of **4a–f**.

absorbance at 350 nm (**1a**) or 330 nm (**1b**) was determined by using an immersion probe and fiber optics.[8] The pseudo first-order rate constants were found to depend linearly on the concentrations of the nucleophiles, indicating a second-order rate law. The observation of isosbestic points (Figure 1) rules out the appearance of long-lived intermediates.

Neither the replacement of BF_4^- by PF_6^- nor the addition of tolane or fumaronitrile (additives for trapping PdL_2 fragments[9]) affected the reaction rates noticeably (Table 1).

In accord with these findings we suggest the mechanism outlined in Scheme 3.[10] While the initial attack of the nucleophiles at the metal centers of **1a** and **1b** cannot be excluded by the kinetic data, the direct nucleophilic attack at the allyl ligand, as depicted in Scheme 3, is highly probable in

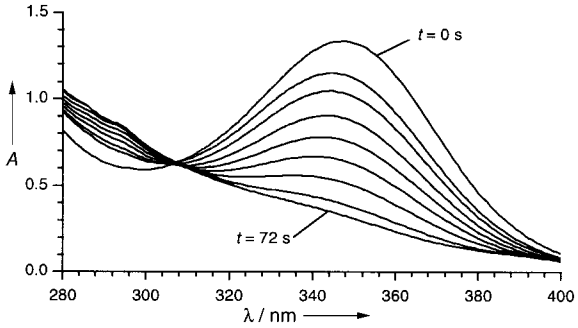
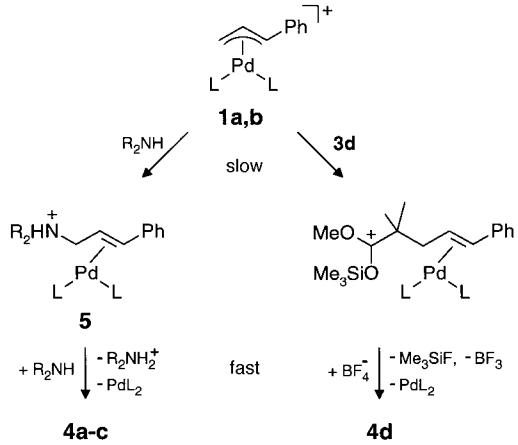


Figure 1. UV spectra during the reaction of the complex **1a**-BF_4 with diethylamine **3b** (CH_2Cl_2, 20 °C).



Scheme 3. Proposed mechanism of the synthesis of **4a–d**, which proceeds via **1a**, **b**.

view of the stereoselectivities of the reactions of related allylpalladium complexes with amines[11] and silylated ketene acetals.[12] Identical rates for the disappearance of the reactants and the appearance of **4d** were found when the reaction of **1b**-BF_4 with **3d** was monitored by ^{1}H NMR spectroscopy, in accord with the mechanism in Scheme 3. The rate constant determined from NMR spectra in $CDCl_3$ is 35 % smaller than that determined from UV spectra in CH_2Cl_2,[13] corroborating the internal consistency of these kinetic data.

In previous work we have shown that the reactions of cationic metal π complexes[14] with noncharged nucleophiles follow the same linear free enthalpy relationship [Eq. (1);

$$\lg k = s(E + N) \quad (1)$$

E = electrophilicity parameter, N = nucleophilicity parameter, s = nucleophile-specific slope parameter] as the corresponding reactions of ordinary carbocations.[3] It seemed probable, therefore, that the rate constants summarized in Table 1 could be reproduced by Equation (1). However, since reliable reactivity parameters for the amines **3a–c** are not available at present, only the E parameter of **1b** can be determined by substituting the lg k value and the N and s parameters of **3d–f** into Equation (1).

In spite of its relatively large error limit, the electrophilicity parameter $E(\mathbf{1b}) = -10.1 \pm 0.8$ (Table 2) provides a semiquantitative characterization of the electrophilic reactivity of **1b**, since the E value is based on reactions with nucleophiles

  1433-7851/99/3803-0344 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1999**, *38*, No. 3

Table 2. Determination of the electrophilicity parameter E for the allylpalladium complex **1b**.

Nucleophile	N	s	$\lg k$[a]	E
3d	9.49[b]	0.93[b]	– 0.45	– 10.0
3e	11.7[b]	0.93[b]	0.65	– 11.0
3f	10.5[c]	1	1.24	– 9.3

[a] From Table 1 of this work. [b] Ref. 15. [c] H. Mayr, A. R. Ofial, K.-H. Müller, N. Hering, unpublished results.

of large structural variety (Table 2). The relative reactivities of the complexes **1a** and **1b** towards diethylamine and piperidine (Table 1) yield E(**1a**) ≈ -12.5. Because of the higher electron-donating ability of $P(Ph)_3$ compared to $P(OPh)_3$, **1a** is two orders of magnitude less electrophilic than **1b**.

The E parameters thus derived now allow one to compare the reactivities of **1a** and **1b** with those of other electrophiles. As shown in Figure 2, the palladium complexes **1a** and **1b** are

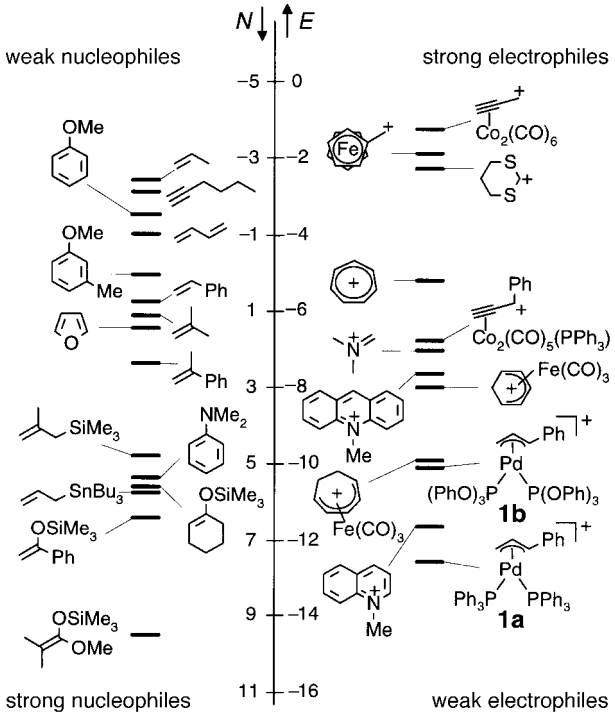
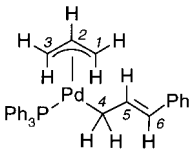


Figure 2. Combination of the electrophilicity and the nucleophilicity scale.

considerably weaker electrophiles than dicobalt-coordinated propargyl cations,[14c] the tropylium ion,[3a] or iminium ions.[16] By using the respective electrophilicities as criteria, **1b** corresponds to the tricarbonylironcycloheptadienylium ion,[14a] while **1a** corresponds to the *N*-methylquinolinium ion.

The approximation $s \approx 1$, which holds for most nucleophiles, implies the rule of thumb that electrophiles and nucleophiles which are located on an equal level in Figure 2 ($N + E = -5$) will combine slowly at room temperature, whereas electrophiles will not react with nucleophiles which are located above them.[3] The applicability of this rule to reactions of allylpalladium complexes is limited, however: Because of the ambident electrophilic character of **1**, reactions with nucleophiles may either occur at the allyl ligand or at the metal center. The latter reaction is not covered by Equation (1).

This is exemplified by the fact that the reaction of **1a** with allyltributylstannane, which does not follow clear-cut second-order kinetics, is approximately 10^4 times faster than predicted by Equation (1). The NMR spectroscopic monitoring of this reaction showed the formation of the bisallyl complex **6**,[17] indicating the attack of allylstannane at the palladium center, in accord with literature reports.[18]



6

Equation (1) and Figure 2, therefore, allow one to predict that only nucleophiles with $N > 6-7$ may attack directly at the allylic ligand of **1a** and **1b**. If reactions with weaker nucleophiles take place, they must proceed by initial attack at the metal center, which has consequences for the regio- and stereoselectivities.

Received: August 7, 1998 [Z12264IE]
German version: *Angew. Chem.* **1999**, *111*, 356 – 358

Keywords: allyl complexes · carbocations · kinetics · palladium · reaction mechanisms

[1] a) B. M. Trost, T. R. Verhoeven in *Comprehensive Organometallic Chemistry*, *Vol. 8* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**, pp. 799 – 938; b) S. Godleski in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming, M. F. Semmelhack), Pergamon, Oxford, **1991**, pp. 585 – 659; c) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395 – 422; d) P. von Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rüegger, P. S. Pregosin, *Helv. Chim. Acta* **1995**, *78*, 265 – 284; e) J. Sprinz, M. Kiefer, G. Helmchen, M. Reggelin, G. Huttner, O. Walter, L. Zsolnai, *Tetrahedron Lett.* **1994**, *35*, 1523 – 1526; f) A. Stolle, J. Ollivier, P. P. Piras, J. Salaün, A. de Meijere, *J. Am. Chem. Soc.* **1992**, *114*, 4051 – 4067.

[2] a) P. S. Manchand, H. S. Wong, J. F. Blount, *J. Org. Chem.* **1978**, *43*, 4769 – 4774; b) N. W. Murall, A. J. Welch, *J. Organomet. Chem.* **1986**, *301*, 109 – 130; c) D. P. Grant, N. W. Murall, A. J. Welch, *J. Organomet. Chem.* **1987**, *333*, 403 – 414.

[3] a) H. Mayr, M. Patz, *Angew. Chem.* **1994**, *106*, 990 – 1010; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 938 – 957; b) H. Mayr, O. Kuhn, M. F. Gotta, M. Patz, *J. Phys. Org. Chem.* **1998**, *11*, 642 – 654.

[4] Physical properties: O. Kuhn, Dissertation, Universität München, **1998**.

[5] P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2033 – 2046.

[6] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 3089 – 3091.

[7] B. Åkermark, B. Krakenberger, S. Hansson, A. Vitagliano, *Organometallics* **1987**, *6*, 620 – 628.

[8] H. Mayr, R. Schneider, C. Schade, J. Bartl, R. Bederke, *J. Am. Chem. Soc.* **1990**, *112*, 4446 – 4454.

[9] a) B. Crociani, S. Antonaroli, F. Di Bianca, L. Canovese, F. Visentin, P. Uguagliati, *J. Chem. Soc. Dalton Trans.* **1994**, 1145 – 1151; b) P. B. Mackenzie, J. Whelan, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2046 – 2054.

[10] In contrast, the first step of the aminations of allylpalladium complexes containing stronger donor ligands (chloride, amines) is reversible, and the deprotonation of the allylammonium ions (e.g. **5**) becomes rate-determining, resulting in a second-order dependence of the rates on amine concentration: A. Vitagliano, B. Åkermark, *J. Organomet. Chem.* **1988**, *349*, C22 – C26.

[11] A ratio of 93:7 to 86:14 for *trans*:*cis* attack was observed for the additions of secondary amines to (4-methoxy-1,2,3-η^3-cyclohexenyl)-palladium tetrafluoroborates: J.-E. Bäckvall, R. E. Nordberg, K. Zetterberg, B. Åkermark, *Organometallics* **1983**, *2*, 1625 – 1629.

[12] C. Carfagna, L. Mariani, A. Musco, G. Sallese, R. Santi, *J. Org. Chem.* **1991**, *56*, 3924 – 3927.

  1433-7851/99/3803-0345 $ 17.50+.50/0

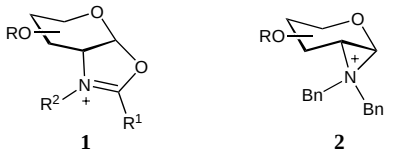
[13] The solvent dependence of the reactions of cationic electrophiles with neutral nucleophiles was shown in Table 1 of ref. [3a].
[14] a) Tricarbonyldienyliron cations: H. Mayr, K.-H. Müller, D. Rau, *Angew. Chem.* **1993**, *105*, 1732 – 1734; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1630 – 1632; b) ferrocenylmethylium ions: H. Mayr, D. Rau, *Chem. Ber.* **1994**, *127*, 2493 – 2498; c) hexacarbonylpropargyldicobalt cations: O. Kuhn, D. Rau, H. Mayr, *J. Am. Chem. Soc.* **1998**, *120*, 900 – 907.
[15] J. Burfeindt, M. Patz, M. Müller, H. Mayr, *J. Am. Chem. Soc.* **1998**, *120*, 3629 – 3634.
[16] H. Mayr, A. R. Ofial, *Tetrahedron Lett.* **1997**, *38*, 3503 – 3506.
[17] ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 1.98$ (d, $J = 7.3$ Hz, 2H, 4-H), 3.14 – 3.47 (m, 2H, 1-H-*anti*, 3-H-*anti*), 4.02 (d, $J = 6.8$ Hz, 2H, 1-H-*syn*, 3-H-*syn*), 5.33 – 5.46 (m, 1H, 2-H), 6.21 (d, $J = 15.7$ Hz, 1H, 6-H), 6.41 – 6.52 (m, 1H, 5-H), 7.11 – 7.45 (m, Ph).
[18] a) A. Goliaszewski, J. Schwartz, *Organometallics* **1985**, *4*, 417 – 419; b) A. Goliaszewski, J. Schwartz, *Tetrahedron* **1985**, *24*, 5779 – 5789; see also: B. Henc, P. W. Jolly, R. Salz, S. Stobbe, G. Wilke, R. Benn, R. Mynott, K. Seevogel, R. Goddard, C. Krüger, *J. Organomet. Chem.* **1980**, *191*, 449 – 475.

The 2-*N,N*-Dibenzylamino Group as a Participating Group in the Synthesis of β-Glycosides**

Hailong Jiao and Ole Hindsgaul*

2-Amino-2-deoxyglycopyranosides are important constituents of proteoglycans, glycoproteins, peptidoglycans, and glycolipids, which are widely distributed in living organisms or plants.[1, 2] Most are N-acetylated and are present in 1,2-*trans*-glycosidic linkages. Numerous synthetic approaches to this class of glycosidic linkage have been developed. Because of its nucleophilicity, the amino functionality is always protected during the glycosylation reaction to avoid N-glycosylation, and the choice of protecting group can provide control of stereoselectivity. The most commonly used method for the construction of 1,2-*trans*-glycosidic linkages employs 2-amino sugar donors that contain a participating group as the amino-protecting functionality. The ideal amino protecting group should be stable and impart sufficient reactivity, stereoselectivity, and high yield in glycosylation reactions. Moreover, the protecting group should be readily removed under mild conditions and in high yield.

Many amino protecting groups have been developed for the 1,2-*trans*-glycosylation of 2-amino sugars. The *N*-phthalimido (NPhth)[3] group is most widely used for this purpose. The *N*-acetamido (NHAc) group has also been used,[2] but the oxazolinium intermediate **1** (Figure 1), which is presumed to be formed in the glycosylation reaction, is rather stable and makes this donor unreactive. Generation of a free amine from either NPhth or NHAc requires strongly basic conditions that often cause partial decomposition of the product.[4] A number of alternative amino protecting groups have therefore been developed. These include *N*-4,5-dichlorophthaloyl (NDCPhth),[5a] *N*-tetrachlorophthaloyl (NTCPhth),[5b, c] *N*-2,2,2-trichloroethoxycarbonyl (NTroc),[5d] *N*-trichloroacetyl ($NCOCl_3$),[5e] *N*-dichloroacetyl ($NCOCHCl_2$),[5f] *N*-monochloroacetyl ($NCOCH_2Cl$),[5g] *N*-trifluoroacetyl ($NCOCF_3$),[5h] *N*-sulfonyl (NSO_2-Ph),[5i] *N,N*-diacetyl (NAc_2),[5j] *N*-acetyl-*N*-2,2,2-trichloroethoxycarbonyl (NAcTroc),[5k] and *N*-*p*-nitrobenzyloxycarbonyl (PNZ).[5l] These protecting groups have proven very useful.



1 **2**

Figure 1. Postulated intermediates in glycosylation reactions. R = Bn, R^1 = Me, R^2 = Ph; Bn = benzyl.

In the course of a program on the preparation of N-linked oligosaccharide analogues, we found that attempted synthesis of the β-GalNPhth(1 $\rightarrow$2)α-Man linkage resulted in an unusually high proportion of α-linked disaccharide, despite the expected participation of the NPhth group. A similar situation had been previously encountered.[6] A β:α mixture (3:1, 75% yield) was formed on glycosylation of acceptor **7** with the tri-*O*-benzyl-NPhth-thioglycoside donor **8** (see Scheme 1). This was presumably due to a "mismatch"[7] in the donor – acceptor pair, and we therefore sought out an alternative donor that would not result in an intermediate similar to the oxazolinium ion **1**. In the search for such a donor, we also recognized that the final deprotection step in almost all synthetic schemes for oligosaccharides involves the removal of persistent O-benzyl ether groups by hydrogenolysis. We therefore elected to examine the *N,N*-dibenzylthioglycoside donor **6** as a potential glycosylation agent. 2-Amino sugars bearing N-alkyl groups have not previously been used as glycosylation donors, presumably because of the expected problematic N-glycosylation.

The donors **6** and **8** were prepared as shown in Scheme 1. Removal of the phthalimido group in **4** followed by O- and N-benzylation with BnBr and NaH in DMF provided **6** in 85% overall yield. Treatment of **4**, which is obtained from **3**,[8] with BnBr and NaH in the presence of Bu_4NI in DMF gave **8** in high yield (88%).

To evaluate **6** as a glycosyl donor for the synthesis of the 2-amino-2-deoxy-β-D-galactopyranosyl-(1 $\rightarrow$2)-α-D-mannopyranoside sequence, we condensed it with octyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**7**)[9] in the presence of the neutral promoter dimethyl(methylthio)sulfonium tetrafluoroborate ($DMTSBF_4$)[10] (Scheme 1). The glycosylation with **6** resulted in excellent β-selectivity (β:$\alpha \geq$ 13:1) and high yield (86%). One-step deprotection of **10** by hydrogenolysis gave the free amine **11** in 94% yield.

We then investigated the behavior of **6** with the partially protected galactopyranosides **12** – **15**,[9] which represent a

[*] Prof. O. Hindsgaul, H. Jiao
Department of Chemistry
University of Alberta
Edmonton, Alberta, T6G 2G2 (Canada)
Fax: (+1) 403-492-7705
E-mail: ole.hindsgaul@ualberta.ca

[**] We thank Dr. A. Morales-Isquierdo for measuring the high-resolution mass spectra (ES) on a Macromass ZabSpec Hybrid Sector-TOF, and Dr. A. Otter for recording the NMR spectra on a Varian-INOVA 600 spectrometer. This work was supported by PENCE and NSERC of Canada.

  1433-7851/99/3803-0346 $ 17.50+.50/0