Chemoselective Catalysis

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Organocatalytic Chemoselective Monoacylation of 1,*n*-Linear Diols**

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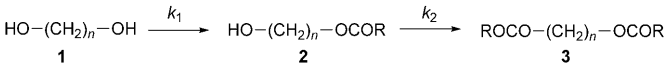
Selective monoacylation of 1,*n*-linear diols seems to be a simple molecular transformation, however, it is still a challenging subject in current organic synthesis because overacylation is usually unavoidable. High reactivity of primary hydroxy groups at the both ends of the linear diols makes selective monoacylation difficult. Since the steric environments of the free OH groups in diol **1** are similar to those of a free OH in **2** (Scheme 1), the strategy for

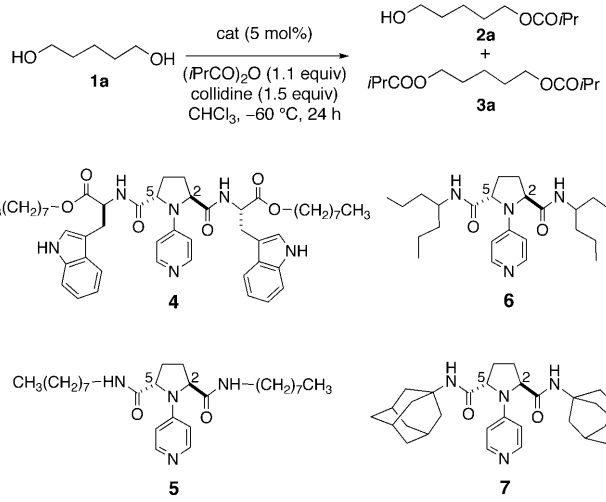


Scheme 1. Acylation of 1,*n*-primary diols.

monoacylation based on conventional steric repulsive interaction is not effective, especially in the cases of long-chain diols. In contrast, chemoselective acylation by discriminating between **1** and **2** through molecular recognition appears to be effective to achieve a high k_1/k_2 ratio. Enzymatic acylation has been frequently used for chemoselective acylation of various polyols.[1] Lipase-catalyzed acylation of 1,*n*-linear diols has been reported to give monoacylates highly selectively, however, overacylation is again unavoidable.[2] To avoid overacylation, excess amounts of diol substrates have been often employed.[3] Alternatively, highly selective monoacylation of linear diols have been achieved by the use of solid-supported reagents.[4] Organometallic catalysts have been developed for selective acylation of various diols.[5] To the best of our knowledge, however, highly selective homogeneous catalysts for monoacylation of linear diols have never been developed. Herein we report highly selective monoacylation of 1,*n*-linear diols ($n = 2$–5) through substrate recognition by organocatalysts. The relative rate (k_1/k_2) for acylation of **1** and **2** ($n = 5$) was estimated to be greater than 100 in the presence of the catalyst.

We chose 1,5-pentanediol (**1a**) as a standard linear diol for investigating the reaction conditions towards selective monoacylation (Table 1). Treatment of **1a** with 1.1 equivalents of isobutyric anhydride in the presence of 5 mol% of 4-dimethylaminopyridine (DMAP) in $CHCl_3$ at −60 °C gave

Table 1: Effects of catalysts on chemoselectivity of acylation of 1,5-pentandiol.[a]



Entry	Cat.	**2a** [%]	**3a** [%]	**2a**/**3a**	Recovery of **1a** [%]
1	DMAP	45	26	1.7	23
2	**4**	92	3	31	3
3	**5**	76	5	15	16
4	**6**	74	6	15	15
5	**7**	67	7	9.6	23

[a] Reactions were run at the substrate concentration of 0.07 M.

monoacylate **2a** and diacylate **3a** in 45% and 26% yield, respectively, in addition to 23% recovery of **1a** (monoacylate/diacylate: **2a**/**3a** = 1.7; entry 1). We examined catalyst **4**, which was shown to be effective for chemo- and regioselective acylation of glycopyranoses[6] and a glycoside.[7] In the presence of **4**, **1a** underwent selective monoacylation to give **2a** and **3a** in 92% and 3% yield, respectively (**2a**/**3a** = 31, entry 2). We further examined catalysts **5**, **6**, and **7**, each possessing side chains with various degrees of steric bulk, thereby examining whether catalysts with bulky side chains are effective for selective monoacylation by using steric interaction to prevent the second acylation. Selectivities (**2a**/**3a** = 9.6–15) for the monoacylation of **1a** in the presence of catalysts **5**–**7** were obtained, with the lowest selectivity (**2a**/**3a** = 9.6) being for the acylation promoted by **7**, which possesses the most-bulky side chains. These results indicate that steric effects are not the key factors to promoting selective monoacylation.

We next investigated the solvent effects on the ratio of mono- and diacylation using 1.03 equivalents of isobutyric anhydride and a substrate concentration of 0.03 M (Table 2, entries 1–3). The mono/diacylation selectivity (**2a**/**3a**) in the presence of catalyst **4** was strongly dependent on the solvent. The selectivity increases as follows: DMF (**2a**/**3a** = 1.7)

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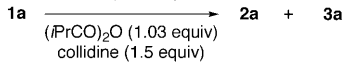
Table 2: Effects of solvents and temperature upon the selective monoacylation of 1,5-pentandiol catalyzed by either **4** or DMAP.[a]



Entry	Cat.	Solvent	T [°C]	t [h]	**2a** [%]	**3a** [%]	**2a**/**3a**	Recovery of **1a** [%]
1	**4**	DMF	−60	24	48	29	1.7	23
2	**4**	toluene	−60	24	74	9	8.2	15
3	**4**	$CHCl_3$	−60	24	71	≤1	≥71	23
4[b]	**4**	$CHCl_3$	−60	24	86	≤1	≥86	13
5	**4**	$CHCl_3$	20	18	75	13	5.8	10
6	**4**	$CHCl_3$	−20	18	79	9	8.7	10
7	**4**	$CHCl_3$	−60	36	82	3	27	11
8	DMAP	$CHCl_3$	20	12	49	14	3.5	37
9	DMAP	$CHCl_3$	−20	12	47	14	3.4	39
10	DMAP	$CHCl_3$	−60	12	45	16	2.8	38

[a] Reactions of entries 1–4 and 5–10 were run at the substrate concentration of 0.03 M and 0.07 M, respectively. [b] 10 mol% of catalyst **4** was used.

< toluene (**2a**/**3a** = 8.2) < $CHCl_3$ (**2a**/**3a** ≥ 71). The observed solvent effects indicate that hydrogen-bonding interactions between the catalyst and the substrate would be responsible for the selective monoacylation.[6,8,9] Effects of the temperature upon the selectivity for monoacylation were also examined in the acylation catalyzed by **4**, as well as DMAP, at the substrate concentration of 0.07 M (entries 5–10). The selectivity (**2a**/**3a**) of the acylation catalyzed by **4** depended strongly upon temperature (5.8–27; entries 5–7), whereas the temperature effects on the selectivity for the DMAP-catalyzed acylation were negligible (2.8–3.5; entries 8–10). These contrasting results indicate a significant contribution of the entropy term to the acylation process catalyzed by **4**, thus indicating the importance of hydrogen-bonding interactions. Finally, the highest selectivity (**2a**/**3a** ≥ 86) was obtained by increasing the catalyst loading to 10 mol% at a substrate concentration of 0.03 M (entry 4).

The acylation of various 1,*n*-linear diols were examined under the optimized conditions for monoacylation (see Table 2, entry 4), with the exception that a slightly larger amount (1.7 equiv) of collidine was used. The results are shown in Figure 1a. For comparison, DMAP-catalyzed acylation (Figure 1b) was also run under reaction conditions identical to those used for the experiments shown in Figure 1a. In the presence of **4**, monoacylation took place exclusively in the acylation of HO-$(CH_2)_n$-OH (n = 2, 3, and 5) and HO-$(CH_2)_2$O-$(CH_2)_2$-OH using 1.03 equivalents of isobutyric anhydride to give 66–86% conversion without overacylation (Figure 1a). 1,4-Butanediol was exceptional, thus giving both the mono- and diacylate in 77% and 4% yield, respectively, (monoacylate/diacylate = 19) together with 15% of the recovered starting material (for the recovery% in each column, see the Supporting information). Significant amounts of diacylates (11–15%) were obtained in the acylation of HO-$(CH_2)_n$-OH when $n \geq 6$, even in the presence of **4** (monoacylate/diacylate < 7). Thus, the highly selective monoacylation catalyzed by **4** is limited to linear diols whose chain length is equal to or shorter than five carbon atoms.[1] In sharp contrast to the acylation catalyzed by **4**, random acylation of linear diols was observed in DMAP-catalyzed acylation, independent of the chain length of diols (monoacylate/diacylate = 0.6–3.1, Figure 1b). Diacylates were the major products in the acylation of 1,4-butanediol and 1,7-heptanediol even in the presence of the recovered diols (32–34%; for the details see the Supporting Information). The ratios of monoacylate/diacylate observed in the DMAP-catalyzed acylation is assumed to result from the relative intrinsic reactivities of the linear diol and the corresponding monool generated in the reaction medium, whereas those in the acylation catalyzed by **4** appear to be controlled by the catalyst independently from their intrinsic reactivities of substrates. Acetylation of **1a** with acetic anhydride under the conditions similar to those in Figure 1a, but using acetic anhydride instead of isobutyric anhydride, gave the mono- and diacylate in 89% and 5% yield, respectively, together with 3% recovery of the starting material. Similarly, benzoylation and cinnamoylation of **1a** gave the corresponding

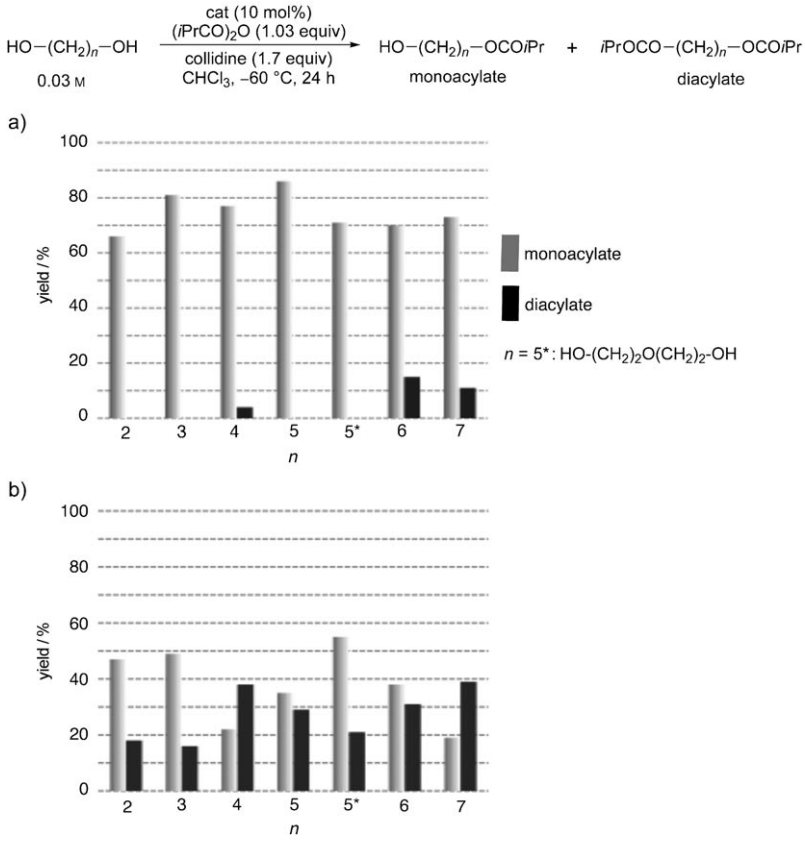
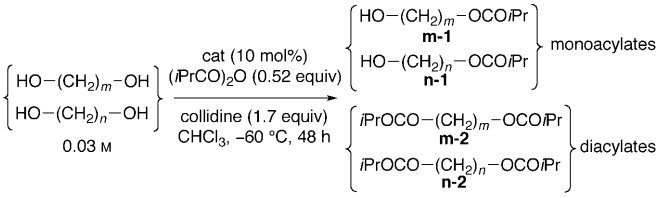


Figure 1. Ratios of the mono- and diacylate in the acylation of various linear diols. a) Acylation catalyzed by **4**. b) Acylation catalyzed by DMAP.

monoacylates exclusively in 64% and 65% yield, respectively, without the formation of the corresponding diacrylates, together with 32% and 30% recovered starting material, respectively (see the Supporting Information for graphical data).

The results in Figure 1a suggest that the catalyst **4** might recognize the molecular lengths of the linear diols. Therefore, we examined the competitive acylation between two diols with different molecular lengths (Table 3). Treatment of a 1:1

Table 3: Competitive acylation between different diols catalyzed either **4** or DMAP.



Entry	*m*, *n*	Cat.	*m*-1/*m*-2/*n*-1/*n*-2	Fast-reacting diol	Chemo-selectivity[a]
1	4, 5	**4**	37:≈0:60:≈0	HO-$(CH_2)_5$-OH	2.0
2	4, 5	DMAP	17:17:23:12	–	1.0
3	5, 6	**4**	74:≈0:23:0	HO-$(CH_2)_5$-OH	5.2
4	5, 6	DMAP	24:11:16:17	–	1.1
5	5, 7	**4**	66:≈0:15:0	HO-$(CH_2)_5$-OH	6.6
6	5, 7	DMAP	14:15:12:21	–	1.2

[a] k(fast-reacting diol)/k(slow-reacting diol) = ln{1−conversion[1+|(*m*-1+*m*-2)−(*n*-1+*n*-2)|/(*m*-1+*m*-2)+(*n*-1+*n*-2)]}/ln{1-conversion[1−|(*m*-1+*m*-2)−(*n*-1+*n*-2)|/(*m*-1+*m*-2)+(*n*-1+*n*-2)]}. |(*m*-1+*m*-2)−(*n*-1+*n*-2)| indicates the absolute value of the difference between (*m*-1+*m*-2) and (*n*-1+*n*-2). Conversion was calculated based on the total amount of two diols.

mixture of 1,4-butane diol (HO-$(CH_2)_m$-OH, $m = 4$) and 1,5-pentanediol (**1a**; HO-$(CH_2)_n$-OH, $n = 5$) with isobutyric anhydride (0.52 equiv of the total amount of the diols) in the presence of 10 mol% of **4** in $CHCl_3$ at −60 °C gave monoacylate of the former diol (*m*-1) and monoacylate of the latter diol (*n*-1) in 37% and 60% yield, respectively, without the formation of diacylates (*m*-2) and (*n*-2, entry 1). Chemoselectivity of the acylation of 1,4-butanediol versus **1a** was determined to be 2.0 according to the equation shown in the footnote [a] of Table 3.[10] In the presence of **4**, 1,5-pentanediol (**1a**) was chemoselectively acylated by a factor of 5.2 in the competitive acylation between **1a** and its analogue that is one carbon atom longer (entry 3). Similarly, **1a** was preferentially acylated 6.6 times faster than 1,7-heptanediol in a competitive acylation reaction (entry 5). In contrast, negligible chemoselectivity was observed in DMAP-catalyzed competitive acylation of these diols (entries 2, 4, and 6). Relatively high chemoselectivity was observed in the competitive acylation between 1,5- versus 1,6-diols and 1,5- versus 1,7-diols (entries 3 and 5), whereas low chemoselectivity was observed in the competitive acylation between 1,5- versus 1,4-diols (entry 1). Thus, catalyst **4** appears to chemoselectively acylate 1,*n*-linear diols whose chain length (*n*) is five carbon atoms or less.

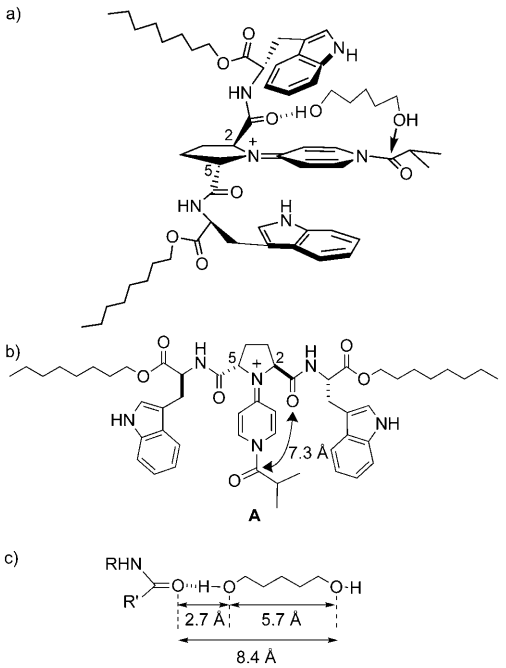


Figure 2. a) A possible transition-state model for monoacylation of 1,5-pentandiol promoted by **4**. b) The assumed distance between an oxygen atom of the amide carbonyl group and the carbon atom of the acyl group in acylpyridinium ion **A** generated by a molecular modeling search. c) The longest possible distance (8.4 Å) between the oxygen atom of the amide carbonyl group of **A** and the reacting OH of **1a**.

A hypothetical transition-state model for the acylation of **1a** catalyzed by **4** is shown in Figure 2a. Hydrogen-bonding interactions between the substrate and catalyst are suggested based on the solvent and temperature effects upon the monoacylation selectivity. We assume that the nonreacting OH group would serve as the hydrogen-bond donor, and the amide carbonyl groups at C2 and C5 of the catalyst **4** would be the hydrogen-bond acceptors. The latter assumption was based on the fact that the amide carbonyl groups are the common structural subunit in catalysts **4**–**7**, which gave the monoacylate selectively in the acylation of **1a** (Table 1, entries 2–5). A stable conformer of the expected reactive intermediate **A**[11] was generated by a molecular modeling search (Figure 2b),[12] in which the distance between the oxygen atom of the amide carbonyl group and the carbon atom of the reactive acyl group is approximately 7.3 Å. The distance between the two oxygen atoms in the extended conformation of **1a** is estimated to be approximately 5.7 Å by molecular modeling (Figure 2c). The sum of the length (8.4 Å) of 5.7 Å and the hydrogen-bonding distance (2.7 Å) might be the possible longest distance for hydrogen-bonding-assisted acylation as shown in Figure 2a. This could be one of the reasons why the selectivity of monoacylation diminishes in the cases where the chain length of the linear diols is longer than five (Figure 1a).[13] Although this is a merely hypothetical explanation without the experimental proof, the strong temperature effects on the selectivity observed in Table 2 appear consistent with this hypothesis because it suggests significant contribution of the activation entropy to

the monoacylation process through the molecular recognition process as shown in Figure 1a.

We then examined kinetic studies for acylation of **1a** and **2a** catalyzed by DMAP as well as **4** at 20 °C. The relative rate (k_{rel} **1a**/**2a**) for acylation of **1a** and **2a** by DMAP catalysis was determined to be 0.7 under the pseudo-first-order conditions using an excess amount (10 equiv) of isobutyric anhydride (Figure 3a). In contrast, the acylation of **1a** proceeded 2.4 times faster than that of **2a** in the presence of **4** at 20 °C (Figure 3b). These contrasting results roughly accounts for the selectivity tendency of monoacylation of **1a** at 20 °C shown in entries 5 and 8 in Table 2.[14,15]

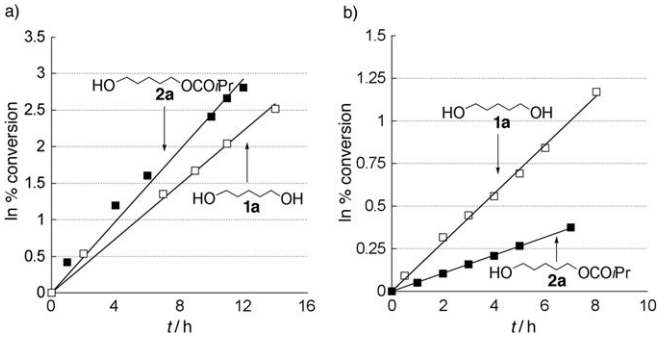
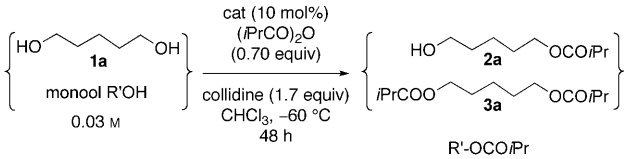


Figure 3. Pseudo-first-order kinetics for acylation of **1a** and **2a** at 20 °C catalyzed by a) DMAP and b) catalyst **4**. The reaction conditions for the kinetic studies: 0.03 M substrate, 0.003 M catalyst, 0.30 M isobutyric anhydride, 0.050 M collidine at 20 °C in $CHCl_3$.

Competitive acylation between **1a** and the monools was then examined under reaction conditions identical to those employed for the reactions depicted in Figure 1a, the exceptions being the use of a smaller amount (0.70 equiv) of the anhydride and a longer reaction time (48 h; Table 4). A 1:1 mixture of **1a** and **2b** was treated with isobutyric anhydride (0.70 equiv of the total amount of **1a** and **2b**) in the presence of 10 mol% of **4** in $CHCl_3$ at −60 °C gave the mono- and diacylate of **1a** (**2a** and **3a**) and the acylate of **2b** (**8**: R′ = $(CH_2)_5OAc$), in 91%, 8%, and 4% yield, respectively (entry 1). The rate of acylation of diol **1a** in the presence of **4** was estimated to be 113 times larger than that of monool **2b**, according to the equation shown in the footnote [a] in Table 4.[10] In contrast, the monool **2b** was acylated at a rate equal to that of **1a** in the presence of DMAP (entry 2). While the intrinsic reactivity of **2b** seems to be equal to that of **1a** based on the results from the DMAP-catalyzed reaction (entry 2), catalyst **4** promotes acylation of **1a** much faster than that of monool **2b**. Catalyst **4** also promotes acylation of diol **1a** 53–56 times faster than the monool such as 5-methoxypentan-1-ol or 2-phenylethanol (entries 3 and 4). Thus, catalyst **4** seems to be able to recognize the structure of 1,5-pentanediol in the presence of monools having a similar molecular length, and promote chemoselective acylation of 1,5-pentanediol.

In conclusion, a method for the organocatalytic chemoselective monoacylation of linear 1,*n*-diols has been developed.[16] Catalyst **4** seems to be able to recognize diol structure specifically in the presence of monools and also recognize molecular length of linear diols, thus promoting preferential acylation of 1,5-pentanediol in the presence of other diols and monools.

Table 4: Competitive acylation of diol **1a** and monools catalyzed by either **4** or DMAP.



Entry	Monool, R′OH	Cat.	**2a**/**3a**/**8**	Fast-reacting alcohol	Chemoselectivity[a]
1	$AcO(CH_2)_5OH$ (**2b**)	**4**	91:8:4	**1**	113
2	**2b**	DMAP	38:13:52	–	1.0
3	$MeO(CH_2)_5OH$	**4**	92:6:7	**1**	53
4	$PhCH_2CH_2OH$	**4**	90:7:6	**1**	56

[a] k(fast-reacting alcohol)/k(slow-reacting alcohol) = ln{1-conversion [1+|(**2a**+**3a**)−**8**|/(**2a**+**3a**)+**8**]}/ln{1-conversion[1−|(**2a**+**3a**)−**8**|/(**2a**+**3a**)+**8**]}. |(**2a**+**3a**)-**8**| indicates the absolute value of the difference between (**2a**+**3a**) and **8**. Conversion was calculated based on the total amount of the two alcohols.

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Keywords: acylation · alcohols · chemoselectivity · molecular recognition · organocatalysis

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[11] The structure of acylpyridinium ion is tentatively drawn as shown in **A** with iminium N^{+}=C substructure because of the reported X-ray structure of several *N*-acyl-4-dialkylaminopydinium ions; see: a) P. G. Jones, K. Linoh, A. Z. Blaschette, *Z. Naturforsch. B* **1990**, *45*, 267; b) C. Lohse, S. Hollenstein, T. Laube, *Angew. Chem.* **1991**, *103*, 1678; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1656; c) S. Hollenstein, C. Lohse, T. Laube, *Croat. Chem. Acta* **1992**, *65*, 727; d) B. Tao, J. C. Ruble, D. A. Hoic, G. C. Fu, *J. Am. Chem. Soc.* **1999**, *121*, 5091.

[12] The stable conformer **A** was generated by a molecular modeling search using the AMBER* force field with the GB/SA solvation model for chloroform using MacroModel V 9.0 (200000 steps MCMM). The most-stable conformer was found to be 0.79 kcal mol^{-1} more stable than **A**. We chose **A**, however, as the model of the reactive intermediate because of its C_2-symmetry structure. Conformer **A** was the most-stable one among those with C_2-symmetry. The stereoview of the calculated structure **A** was shown in the Supporting Information.

[13] The distance between the two oxygen atoms of the extended conformation of 1,6-hexanediol is estimated to be 7.3 Å by molecular modeling. The sum (10.0 Å) of 7.3 Å and the hydrogen-bonding distance (2.7 Å) seems too long for effective molecular recognition by acylpyridinium ion **A**. This could be the reason of poor selectivity of monoacylation of diols such as 1,6-hexanediol and 1,7-heptanediol. In contrast, acylation of diols having a chain length shorter than five atoms proceeds with high selectivity for monoacylation. The effective distance (7.3 Å) shown in Figure 2b is expected to be adjustable and therefore shortened by the bond rotation around C2–CO(NHR).

[14] The predominant formation of the monoacylate **2a** (**2a**/**3a** = 3.5) by DMAP-catalysis observed in entry 8 in Table 2 is assumed to be due to the initial low concentration of **2a** in the reaction medium and low conversion (37% recovery of **1a**).

[15] Specific rate acceleration in acylation by peptide-based catalysts has been reported; see: a) E. R. Jarvo, G. T. Copeland, N. Paparioannou, P. J. Bonitatebus, Jr., S. J. Miller, *J. Am. Chem. Soc.* **1999**, *121*, 11638 – 11643; b) G. T. Copeland, S. J. Miller, *J. Am. Chem. Soc.* **2001**, *123*, 6496 – 6502.

[16] Direct monoacylation of linear diols may be useful in the preparation of insect pheromones and hybrid esters, see: a) R. Rossi, *Synthesis* **1971**, 817 – 836; b) C. A. Henrick, *Tetrahedron* **1977**, *33*, 1845 – 1889; c) reference [3a].

