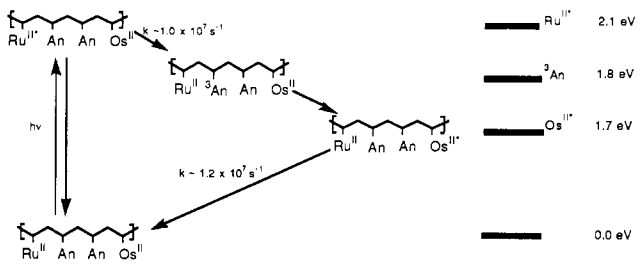
Scheme I



(DCE) in the mixed polymer, reaction 1, even though energy transfer is favored by 0.4 eV. The excited-state energies are 2.1 eV for Ru^{II*} and 1.7 eV for Os^{II*}.[11]

$$\xrightarrow{h\nu} [PS\text{-}Ru^{II}_2Ru^{II*}Os^{II}_3](PF_6)_{12} \rightarrow [PS\text{-}Ru^{II}_3Os^{II*}_1Os^{II}_2](PF_6)_{12} \quad (1)$$

In the absorption spectrum of $[PS\text{-}Ru^{II}_3An_{12}Os^{II}_3](PF_6)_{12}$ in polar organic solvents, $d\pi(Os) \rightarrow \pi^*(bpy)$ transitions appear in the region 410–700 nm, $d\pi(Ru,Os) \rightarrow \pi^*(bpy)$ transitions from 410 to 550 nm, and vibronically resolved $\pi \rightarrow \pi^*(An)$ transitions from 325 to 400 nm. Excitation of $[PS\text{-}Ru^{II}_3An_{12}Os^{II}_3](PF_6)_{12}$ in DCE at 460 nm results in a significant (90%) loss in the Ru^{II} emission at 620 nm compared to $[PS\text{-}Ru^{II}_2Ru^{II*}](PF_6)_6$, while the lower energy, Os^{II*}-based emission at 740 nm is enhanced compared to $[PS\text{-}Os^{II}_2Os^{II*}](PF_6)_6$. The lifetime of the Ru^{II*} emission is shortened to ~100 ns compared to the 753-ns lifetime for Ru^{II*} in $[PS\text{-}Ru^{II}_3](PF_6)_2$. Independent experiments on a polymer of composition $[PS\text{-}Ru^{II}_3An_{12}](PF_6)_6$ show the same shortened lifetime compared to $[PS\text{-}Ru^{II}_2Ru^{II*}](PF_6)_{12}$ and, from transient absorbance measurements, the appearance of the anthryl triplet at λ_{max} = 430 nm ($\tau > 5$ μs) following laser flash excitation at 460 nm. From these results, the loss in emission intensity and the decreased lifetimes in $[PS\text{-}Ru^{II}_2Ru^{II*}An_{12}Os^{II}_3](PF_6)_{12}$ and $[PS\text{-}Ru^{II}_2Ru^{II*}An_{12}](PF_6)_6$ can be attributed to intrapolymeric energy transfer from Ru^{II*} to An to give the anthryl triplet, ^3An, of energy 1.8 eV.[13]

$$\xrightarrow{h\nu} [PS\text{-}Ru^{II}_2Ru^{II*}An_{12}](PF_6)_6 \rightarrow [PS\text{-}Ru^{II}_3{}^3AnAn_{11}](PF_6)_6 \quad (2)$$

The origin of the quenching of Ru^{II*} in $[PS\text{-}Ru^{II}_3An_{12}Os^{II}_3](PF_6)_{12}$ is by $Ru^{II*} \rightarrow An$ energy transfer, but the excited-state energy ultimately reaches Os^{II}. From emission quantum yield studies as a function of excitation wavelength over the range 420–530 nm, Os^{II*} is reached with near unit efficiency even in regions (420–500 nm) where Ru^{II} is a significant light absorber.

The combination of anthryl quenching of Ru^{II*} and the appearance of Os^{II*} leads to the suggested quenching mechanism in Scheme I. Excitation at Ru^{II} is followed by energy transfer, first to An ($\tau \sim 100$ ns) and then to Os^{II}. From the composition of the polymer, on the average there are two intervening anthryl groups between the Ru^{II} and Os^{II} sites. The net effect of adding the anthryl groups to the polymer is to create an energy transfer "cascade" pathway, which allows long-range energy transfer to occur from Ru^{II*} to Os^{II}. The anthryl groups act as intervening energy-transfer relays and act as a "molecular light pipe" in providing a spatial link between the two emissive MLCT chromophores.

Acknowledgment. Financial support from the Department of Energy under Grant No. DE-FG05-86 ER 13633 and a NIH Postdoctoral Fellowship 1-F32-GM11 280-01A1 for J.N.Y. are gratefully acknowledged.

(11) Excited-state energies were calculated from the results of a two-mode Franck–Condon analysis of the emission band shapes that is described in detail elsewhere.[12] These values are in good agreement with excited-state energies estimated as the energy on the low-energy side of the spectral profile where the emission intensity had fallen by $^1/_4$ compared to the maximum.

(12) (a) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. F. *J. Am. Chem. Soc.* **1984**, *106*, 3492. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

(13) Birks, J. B. *Photophysics of Aromatic Molecules*; W. A. Benjamin: New York, 1967.

Selective Monoacylation of 1,*n*-Diols Catalyzed by Metallic Sulfates Supported on Silica Gel

Takeshi Nishiguchi* and Hisashi Taya

Faculty of Liberal Arts, Yamaguchi University
Yamaguchi 753, Japan

Received July 17, 1989

It is important for organic synthesis to establish general methods for selective and differential functionalization of the same kind of plural functional groups having similar stereoelectronic and steric factors. Monoprotection or monofunctionalization of polyols is achieved in some cases by carefully controlled reaction conditions,[1] by continuous extraction,[2] by the use of alumina[3] and insoluble polymer supports,[4] or via cyclic compound formation.[5] In the course of studying the dehydration of alcohols catalyzed by metallic sulfates supported on chromatographic silica gel (abbreviation: $M_m(SO_4)_n$–SiO_2),[6] we found that alcohols were acylated in high yields when esters were used as solvents. Here, we report highly selective monoacylation of 1,*n*-diols by transesterification catalyzed by $M_m(SO_4)_n$–SiO_2.

The acylation was quite easy to perform, and the results are summarized in Table I.[7] For the catalysts, several supported sulfates and hydrogen sulfates were examined and were found to show nearly the same order of activity as in the dehydration of alcohols.[6] This result suggests that the characteristics of these catalysts are alike in the acylation and in the dehydration of alcohols.[8] Table I shows that the larger the acyl group of the solvent, the slower the reaction rate of acylation and the higher the selectivity. Figure 1 shows the time dependence of the yields of the products in the acylation of 1,4-butanediol by methyl propionate. The diester appeared when the yield of the monoester reached 90% and most of the diol had been consumed. The maximum value of the slope showing the maximum rate of the monoester formation is roughly twice as large as the value showing the maximum rate of the diester formation. These results may

(1) (a) Wilkinson, S. G. In *Comprehensive Organic Chemistry*; Pergamon Press: New York, 1979; Vol. 1, p 681. (b) Greene, T. W. *Protective Groups in Organic Synthesis*; John Wiley & Sons, Inc.: New York, 1981. (c) Fuhuhop, J.; Penzlin, G. *Organic Synthesis*; Verlag Chemie: Weinheim, 1983; p 143.

(2) Babler, J. H.; Coghlan, M. J. *Tetrahedron Lett.* **1979**, 1971.

(3) (a) Ogawa, H.; Chihara, T.; Taya, K. *J. Am. Chem. Soc.* **1985**, *107*, 1365. (b) Ogawa, H.; Ichimura, Y.; Chihara, T.; Teratani, S.; Taya, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2481. (c) Ogawa, H.; Chihara, T.; Teratani, S.; Taya, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1337.

(4) Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327.

(5) (a) Takasu, M.; Naruse, Y.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 1947. (b) Takano, S.; Akiyama, M.; Sato, S.; Ogasawara, K. *Chem. Lett.* **1983**, 1593.

(6) (a) Nishiguchi, T.; Machida, N.; Yamamoto, Y. *Tetrahedron Lett.* **1987**, *28*, 4565. (b) Nishiguchi, T.; Kamio, C. *J. Chem. Soc., Perkin Trans. 1* **1989**, 707.

(7) For example, $M_m(SO_4)_n$–SiO_2 function as acid catalysts in the dehydration of alcohols.

(8) Changing the solid support from silica gel to neutral alumina, Celite-535, and powdered 3A molecular sieves lowered the catalytic activity and the selectivity in the acetylation of 1,4-butanediol catalyzed by $Fe_2(SO_4)_3$. Addition of methanol or ethanol lowered reaction rates and the selectivity. For example, 4% of the diester was detected at the 80% yield of the monoester when 2 mmol of methanol was added under the conditions shown in Figure 1.

0002-7863/89/1511-9102$01.50/0

Table I. Selective Monoesterification of Diols[a]

diol	catalyst salt	catalyst mmol	time, h	yield and recovery, % monoester	diester	alcohol
ethylene glycol[b]	$NaHSO_4$	0.15	5	78	3	14
1,4-butanediol	$Ce(SO_4)_2$	0.063	4	68	0	30
1,4-butanediol	$Ce(SO_4)_2$	0.063	6	78	4	15
1,4-butanediol	$NaHSO_4$	0.125	6	81	5	11
1,4-butanediol[c]	$NaHSO_4$	0.1	2.2	92	2	7
1,4-butanediol[d]	$NaHSO_4$	0.125	24	94	1	7
1,4-butanediol[d]	$NaHSO_4$	0.125	33	97	2	0
1,5-pentanediol	$NaHSO_4$	0.125	5	78	3	19
1,6-hexanediol	$Ce(SO_4)_2$	0.083	5	80	6	15
2,5-hexanediol[e]	$NaHSO_4$	0.01	6	69	7	23

[a] A diol (1 mmol) and a supported salt (3 mmol/g of SiO_2) were heated at 50 °C in ethyl acetate–hexane (1:4) (15 mL). Yields were measured by GLC. [b] Ethyl acetate:hexane = 1:3. [c] This run was done at 70 °C in methyl propionate–hexane (1:4). [d] This run was done at 60 °C in methyl isobutyrate–hexane (1:4). [e] This run was done at room temperature in ethyl formate–hexane (1:4).

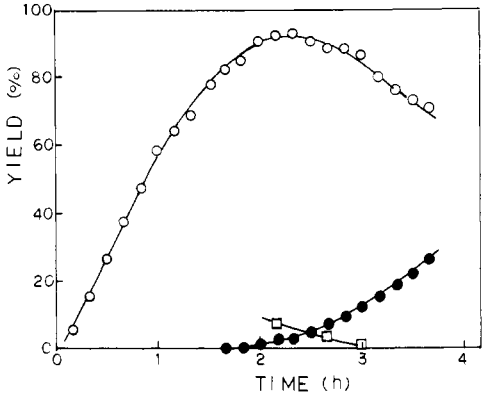


Figure 1. Yields and recoveries vs reaction time. 1,4-Butanediol (1 mmol) and $NaHSO_4$–SiO_2 (0.1 mmol) were heated in methyl propionate–hexane (1:4) at 70 °C: the monoester, ○; the diester, ●; the diol, □.

be explained by the following presumptions: (1) only the alcohols adsorbed on the catalyst surface reacted; (2) as long as the diol, which is more polar and more apt to be adsorbed than the monoester, remained, it reacted preferentially; (3) the monoester was adsorbed and reacted after most of the diol had been consumed; and (4) the reactivity per hydroxyl group is alike both in the diol and in the monoester as long as these compounds are adsorbed. When the ratio of hexane gradually increased in the acylation of 1,4-butanediol in the methyl isobutyrate–hexane mixture, the yields of the monoester at 2% yield of the diester rose at first, showed the maximum value (97%) at the hexane:methyl isobutyrate ratio of 4:1, and then began to decrease (Figure 2). The reason why the selectivity to the monoester depends on the polarity of the mixed solvent may be explained by the following assumptions: (1) when the polarity of the mixed solvent was high, there was little selectivity in the adsorption on the catalyst between the diol and the monoester; (2) when it was adjusted adequately by the addition of hexane, only the diol was selectively adsorbed and acylated; and (3) when it decreased further, the selectivity decreased because the monoester too was adsorbed. The R_f values of the substances on silica gel TLC plates developed by the mixed solvents are also shown in Figure 2 for reference. Using smaller amounts of the catalysts generally raised the selectivity. This may be due to reduced adsorption of the monoester in the presence of small amounts of the diol. It is inferred that the surface of silica gel forms a "reaction field" where reagents and substrates are accumulated by adsorption and binds more polar substances in preference to less polar ones. This inference suggests that such a selective reaction as this esterification generally occurs when the polarity decreases successively from starting materials to the final products. This suggestion is supported by the preliminary result that 1,*n*-diols are selectively monoprotected by pyranyl ether formation using dihydropyran in the presence of some kind of

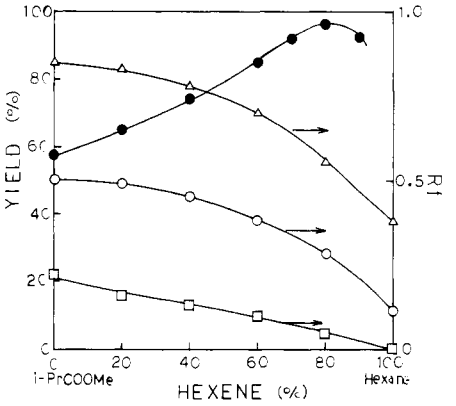


Figure 2. Yields of the monoester (●) at the 2% yield of the diester and R_f values of the diester (△), the monoester (○), and the diol (□) vs solvent composition. 1,4-Butanediol (1 mmol) and $NaHSO_4$–SiO_2 (0.125 mmol) were heated at 60 °C in the methyl isobutyrate–hexane mixture (15 mL). The R_f values were obtained by the use of silica gel 60 TLC plates (Merck).

$M_m(SO_4)_n$–SiO_2.

Registry No. $NaHSO_4$, 7681-38-1; $Ce(SO_4)_2$, 13590-82-4; ethylene glycol, 107-21-1; 1,4-butanediol, 110-63-4; 1,5-pentanediol, 111-29-5; 1,6-hexanediol, 629-11-8; 2,5-hexanediol, 2935-44-6; ethyl acetate, 141-78-6; methyl propionate, 554-12-1; methyl isobutyrate, 547-63-7; ethyl formate, 109-94-4; ethylene glycol monoacetate, 542-59-6; ethylene glycol diacetate, 111-55-7; 4-hydroxybutyl acetate, 35435-68-8; 1,4-butanediol diacetate, 628-67-1; 4-hydroxybutyl propionate, 33498-48-5; 1,4-butanediol dipropionate, 1572-92-5; 4-hydroybutyl isobutyrate, 123641-46-3; 1,4-butanediol diisobutyrate, 1572-74-3; 5-hydroxypentyl isobutyrate, 123641-47-4; 1,5-pentanediol diisobutyrate, 123641-48-5; 6-hydroxyhexyl isobutyrate, 101830-67-5; 1,6-hexanediol diisobutyrate, 101830-68-6; 2,5-hexanediol monoformate, 123674-08-8; 2,5-hexanediol diformate, 123641-49-6.

Synthesis of a Cyclic Phosphopeptide Containing a Phosphodiester Linkage

A. H. van Oijen, C. Erkelens, J. H. Van Boom, and R. M. J. Liskamp*

Department of Organic Chemistry
Gorlaeus Laboratories, University of Leiden
P.O. Box 9502 2300 RA Leiden, The Netherlands

Received July 24, 1989

Although protein phosphorylation is recognized as a major regulatory process[1,2] mediated by protein kinases, the molecular basis of changes induced by phosphorylation is virtually unknown. However, at least two examples in the recent literature may contribute to deepen our insight into this important posttranslational modification of peptides and proteins. In the first example,[3] the refined crystal structures of glycogen phosphorylase b and a, which differ only in one phosphorylated serine residue at position 14, were compared. This important study[3] may add to a further understanding of control by phosphorylation. For this reason, among others, we are interested in the synthesis and structure of phospho amino acids and phosphopeptides.[4,5] In the second

(1) Krebs, E. G. In *The Enzymes*, 3rd ed.; Boyer, P. D., Krebs, E. G., Eds.; Academic: New York, 1986; Vol. 17, p 3. Krebs, E. G.; Beavo, J. A. *Annu. Rev. Biochem.* **1979**, *48*, 923.
(2) Cohen, P. *Nature* **1982**, *296*, 613. Cohen, P. *Eur. J. Biochem.* **1985**, *151*, 439.
(3) Sprang, S. R.; Acharya, K. R.; Goldsmith, E. J.; Stuart, D. I.; Varvill, K.; Fletterick, R. J.; Madsen, N. B.; Johnson, L. N. *Nature* **1988**, *336*, 215.
(4) De Bont, H. B. A.; Veeneman, G. H.; Van Boom, J. H.; Liskamp, R. M. J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 641.
(5) De Bont, H. B. A.; Liskamp, R. M. J.; O'Brian, C. A.; Erkelens, C.; Veeneman, G. H.; Van Boom, J. H. *Int. J. Pept. Protein Res.* **1989**, *33*, 115.

0002-7863/89/1511-9103$01.50/0