with ether. The extract was washed successively with aqueous $NaHSO_3$ (to remove I_2 liberated) and water, dried (Na_2SO_4), and evaporated. Chromatography of the residue afforded **20** (17 mg), **18** (24 mg), **21** (23 mg), and **3** (12 mg, 12%).

Acknowledgment. The author is grateful to Professor Keizo Naya and Mr. Keiji Hirota (Kwansei Gakuin University) for the measurement of NMR spectra with a JEOL EX-90 spectrometer. He also thanks Mr. Hiroshi Nagao for technical assistance. Valuable comments by the reviewer are gratefully acknowledged.

Registry No. **1**, 2607-52-5; **2**, 128-39-2; **3**, 98543-00-1; **4**, 62078-82-4; **6**, 128-37-0; **8**, 14387-13-4; **9**, 2091-51-2; **10**, 137649-09-3; **17**, 809-73-4; **18**, 1516-94-5; **20**, 128-38-1; **21**, 2455-14-3; **24**, 118-82-1; **25**, 4359-97-1; **27**, 137649-10-6; **28**, 137668-00-9.

Highly Selective Monoacylation of Symmetric Diols Catalyzed by Metal Sulfates Supported on Silica Gel

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Several 1,*n*-diols, ranging from 1,2-ethanediol to 1,16-hexadecanediol, were monoacylated with high selectivity by reaction with esters in the presence of metal sulfates or hydrogen sulfates, like $Ce(SO_4)_2$ and $NaHSO_4$, supported on silica gel. Symmetrical secondary diols were also selectively monoformylated, by reaction with ethyl formate. This method of selective esterification is simple and practical. The yield of monoester depends upon both the composition and the volume of the solvent (an ester/alkane mixture). Unsupported $NaHSO_4$ also catalyzed monoacylation, but the selectivity was less than in monoacylations catalyzed by the supported reagent. The selectivity can be explained by the following reasons: (1) monoacylated products are formed selectively because the diol, but not the monoester, is preferentially adsorbed on the surface of the catalysts, where esterification then occurs, and (2) thin diol layers are formed on the surface of the catalysts due to limited solubility of the diols in the solvent.

Introduction

It is important for organic chemists to develop methods that permit the selective protection or functionalization of multiple identical functional groups that exist in similar chemical environments. In some cases the monoprotection of 1,*n*-diols can be achieved by careful control of the reaction conditions;[1] by continuous extraction;[2] by the use of alumina,[3] phase-transfer catalysts,[4] or insoluble polymer supports;[5] or via the formation of cyclic compounds.[6] The use of supported reagents often has advantages over that of their homogeneous counterparts.[7] During a study of the dehydration of alcohols catalyzed by metal sulfates and hydrogen sulfates supported on silica gel,[8] we found that the alcohols were acylated, via transesterification, when esters were used as solvents[9,10] and that 1,*n*-diols were monoacylated.[11] Here we describe the selective monoacylation in more detail.

$$HO(CH_2)_pOH + R^1CO_2R^2 \xrightarrow{M_m(SO_4)_n\text{-}SiO_2} R^1CO_2(CH_2)_pOH + [R^1CO_2(CH_2)_pOCOR^1] \quad (1)$$

Results and Discussion

Selective Monoacylation of Symmetric Diols. The monoacylations were performed by heating together a diol (1 mmol), $M_m(SO_4)_n$–SiO_2 catalyst (3 mmol metal sulfate/g SiO_2), and an ester/hexane (or octane) mixture. The reactions were monitored by TLC and GLC. Table I shows that all of the 1,*n*-diols that were examined, ranging from 1,2-ethanediol to 1,16-hexadecanediol, gave the corresponding monoesters in acceptable yields.[12] Lowering the reaction temperature or reducing the amount of catalyst led to an increase in selectivity, although longer reaction times were necessary. Symmetrical secondary diols were also monoformylated, with moderate selectivity, by reaction with ethyl formate.[13]

Rationalization of the Selectivity. Figure 1 shows the yields of the products as a function of time for the acylation of 1,4-butanediol by methyl isobutyrate. The

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[12] Changing the identity of the catalyst did not significantly affect the selectivity of the reaction as long as the catalytic activity of the salt was high. In the $Fe_2(SO_4)_3$-catalyzed acylation of 1,4-butanediol, changing the solid support from silica gel to neutral alumina, Celite-535, or powdered 3A molecular sieves led both to a decrease in activity of the catalyst and a decrease in selectivity.

[13] No products other than esters were formed during the reaction of secondary diols in ethyl formate/hexane and of primary diols in any solvent. However, substantial quantities of olefins were produced, along with the expected esters, during reaction of secondary diols in EtOAc/hexane.

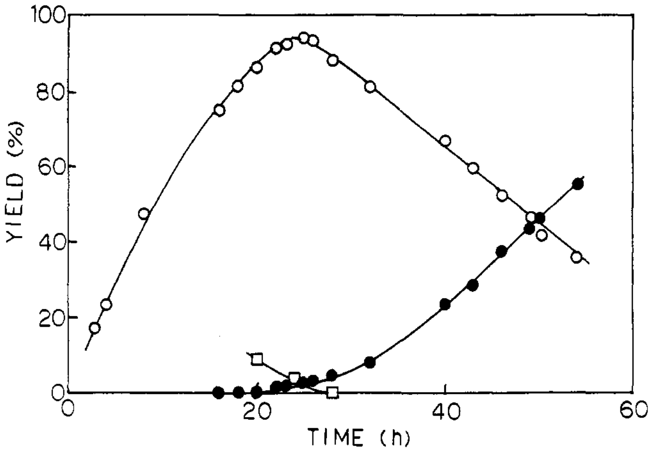

Figure 1. Plots of yield vs time for the NaHSO$_4$-SiO$_2$ (0.125 mmol) catalyzed acylation of 1,4-butanediol (1 mmol) in 1:4 (vol/vol) methyl isobutyrate/hexane (10 mL) at 60 °C: monoester (○); diester (●); unreacted diol (□).

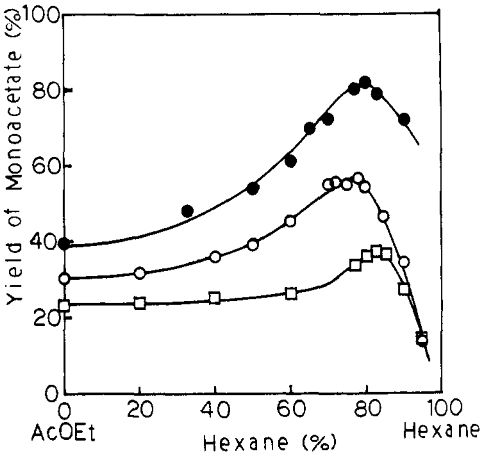

Figure 2. Plots of yield of the monoester (at yield of the diacetate = 5%) diol vs solvent composition for the acylation of 1,4-butanediol (1 mmol) at 60 °C in EtOAc/hexane (10 mL) catalyzed by NaHSO$_4$-SiO$_2$ (●), NaHSO$_4$ (○), and methanesulfonic acid (□) (0.125 mmol).

diester began to appear when the yield of the monoester reached 92% and most of the diol had already been consumed. Figure 1 shows that the maximum rate of monoester formation is roughly twice that of diester formation. This suggests that the reactivity of the hydroxyl groups of the diol and the monoester are virtually identical, as long as both compounds react on the surface of the catalyst. The yield or the monoester increased almost linearly over a long period, which suggests that the diol is adsorbed on the surface of the catalyst. Similar behavior was observed in the acylation of 1,4-butanediol by methyl propionate,[11] which implies that the phenomena are general.

In the acetylation of 1,4-butanediol, when composition of the ethyl acetate/hexane mixture was varied, the yield of the monoacetate at the point where the yield of the diester was 5% reached a maximum value when the proportion of hexane in the solvent was ca. 80% (Figure 2). The maximum yields of the monoester, as a function of catalyst, were 82% (NaHSO$_4$-SiO$_2$), 57% (NaHSO$_4$), and 37% (methanesulfonic acid). Similar results were obtained for the acylation of 1,4-butanediol in methyl isobutyrate-/hexane mixtures (Figure 3). When the proportion of hexane in the solvent was ca. 80%, the maximum yields of monoester at the point where the yield of the diester was 2% were 96% and 70% when the catalysts were NaHSO$_4$-SiO$_2$ and unsupported NaHSO$_4$, respectively.

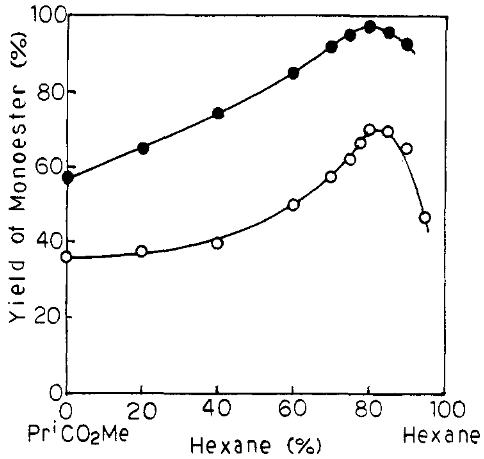

Figure 3. Plots of yield of the monoester (at yield of the diester = 2%) vs solvent composition for the acylation of 1,4-butanediol (1 mmol) at 60 °C in methyl isobutyrate/hexane (15 mL) catalyzed by NaHSO$_4$-SiO$_2$ (●), or NaHSO$_4$ (○) (0.125 mmol).

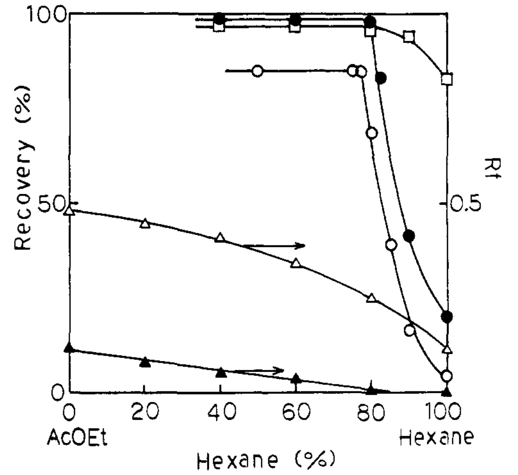

Figure 4. Plots of the amounts of 1,4-butanediol and 4-acetoxy-1-butanol present in solution (recovery) and R_f vs solvent composition. Amounts of 1,4-butanediol (●) and 4-acetoxy-1-butanol (□) present in the supernate after stirring the diol or the monoacetate (1 mmol) at 50 °C in EtOAc/hexane (10 mL). Diol (○) present in the supernate after introduction of NaHSO$_4$-SiO$_2$ (0.125 mmol). R_f values of the diol (▲) and the monoacetate (△) on TLC plates developed by the solvents.

The increased selectivity observed in the presence of silcia gel can be explained, at least in part, by postulating (1) only the alcohols that were adsorbed on the surface of the catalyst were esterified, (2) the diol reacted preferentially as long as it was present, (3) and the monoester was adsorbed but reacted only after most of the adsorbed diol had been consumed. The greater tendency of the diol to be adsorbed is indicated by the fact that the diol shows less mobility during TLC than does the monoester (Figure 4).

However, the considerable selectivity observed in the reactions catalyzed by both NaHSO$_4$ and methanesulfonic acid and the dependence of the selectivity on the solvent composition observed in the reactions catalyzed by both supported and unsupported catalysts cannot be entirely explained in terms of selective adsorption. Thus, after 1,4-butanediol was stirred in ethyl acetate/hexane for 5 min in the absence of a catalyst, the amount of diol that was present in the supernate was measured and found to depend on the composition of the solvent (Figure 4; see also the Experimental Section). When the proportion of hexane exceeded 80%, the amount of diol present in the supernate decreased sharply. This suggests that the diol

Table I. Selective Monoacylation of Diols by the $M_m(SO_4)_n$–SiO_2 Catalyzed Reaction[a] with $R^1CO_2R^2$

diol	ester R^1	ester R^2	ester %[b]	catalyst (M (mmol))	temp (°C)	time (h)	yield of monoester (%)	yield of diester (%)	recovered diol (%)
1,2-ethanediol	Me	Et	25	NaH (0.15)	50	5	78	3	14
1,3-propanediol	Me	Et	20	NaH (0.125)	50	4	65	5	27
1,4-butanediol	Me	Et	20	Ce(IV) (0.063)	50	4	68	0	30
1,4-butanediol	Me	Et	20	Ce(IV) (0.063)	50	6	78	4	15
1,4-butanediol	Me	Et	20	NaH (0.125)	50	6	81	5	11
1,4-butanediol	Et	Me	20	NaH (0.1)	70	2.2	95	4	0
1,4-butanediol	*i*-Pr	Me	20	NaH (0.125)	60	24	94	1	7
1,4-butanediol	*i*-Pr	Me	20	NaH (0.125)	60	33	96	2	0
cis-1,4-butenediol	Me	Et	20	NaH (0.1)	50	3	79	4	15
cis-1,4-butenediol	Me	Et	20	NaH (0.125)	50	4.5	89	12	2
1,4-butynediol	Me	Et	20	NaH (0.1)	50	7	76	6	16
1,5-pentanediol	Me	Et	20	Ce(IV) (0.063)	50	5	71	0	31
1,5-pentanediol	Me	Et	20	NaH (0.125)	50	6	88	6	5
1,5-pentanediol	Me	Et	20	NaH (0.125)	50	5	78	3	19
1,6-hexanediol	Me	Et	20	Ce(IV) (0.083)	50	5	80	6	15
1,6-hexanediol	Me	Et	17	NaH (0.125)	50	4	58	0	44
2,5-hexanediol	H	Et	20	NaH (0.01)	rt	6	69	7	16
1,4-cyclohexanediol	H	Et	25	NaH (0.01)	rt	4	69	3	21
1,4-cyclohexanediol	H	Et	25	NaH (0.01)	rt	6	80	11	2
1,8-octanediol	Me	Et	15	NaH (0.125)	50	7	76	5	7
1,10-decanediol[c]	Et	Me	8	NaH (0.1)	78	2.5	78	7	10
1,10-decanediol[c]	*i*-Pr	Me	20	NaH (0.125)	85	3	73	3	22
1,12-dodecanediol[d]	Et	Me	6	NaH (0.125)	95	3.5	71	3	22
1,12-dodecanediol[c]	*i*-Pr	Me	10	NaH (0.125)	88	4.5	82	9	8
1,16-hexadecanediol[d]	Et	Me	9	NaH (0.1)	105	3	62	9	26
1,16-hexadecanediol[c]	Me	Pr	6	NaH (0.083)	97	2.5	73	9	15
1,16-hexadecanediol[c]	Me	Pr	6	NaH (0.083)	97	3	79	13	10

[a] The diol (1 mmol) and a catalyst were heated together in an ester/hexane mixture (15 mL). Yields were determined by GLC. [b] Volume % of the ester in the solvent. [c] Octane was used in place of hexane (6 mL). [d] Octane was used in place of hexane (5 mL).

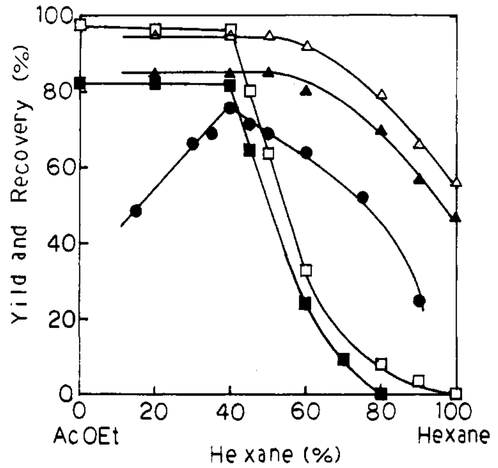

Figure 5. Plots of the yield of monoester and the amounts of diol and monoester present in solution (recovery) vs solvent composition: yield of the monoester (at yield of the diester = 5%) from the acylation of 1,2-ethanediol (1 mmol) catalyzed by $NaHSO_4$–SiO_2 (0.125 mmol) at 50 °C in EtOAc/hexane (10 mL) (●): amount of 1,2-ethanediol present in solution (□) and 2-acetoxyethanol present in solution (△) in the absence of $NaHSO_4$–SiO_2; the amount of diol (■) and the amount of monoester (▲) present in the supernate in the presence of the catalyst (see Experimental Section).

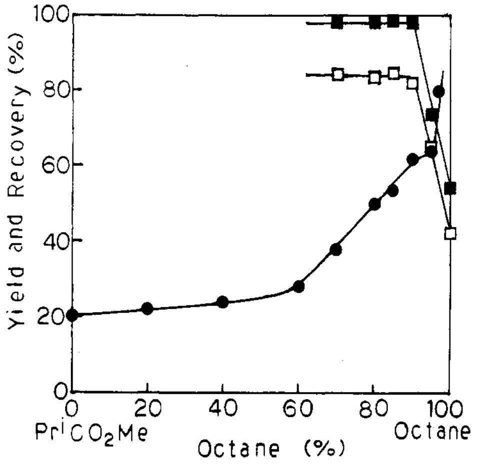

Figure 6. Plots of yield of monoester and diol present in solution (recovery) vs solvent composition: yield of the monoester (at yield of the diester = 2%) in the acylation of 1,10-decanediol (1 mmol) catalyzed by $NaHSO_4$–SiO_2 (0.1 mmol) at 80 °C in methyl isobutyrate/octane (10 mL) (●): amount of the diol in solution in the absence of the catalyst (■) and the amount of the diol in the supernate in the presence of $NaHSO_4$–SiO_2 (□) (see Experimental Section).

did not dissolve completely when the proportion of hexane was high and that in the presence of solid catalysts the undissolved diol forms a thin film on the surface. In contrast, the amount of 4-acetoxy-1-butanol that was present in the supernate decreased little at any solvent composition. Thus, little, if any, monoester separated from solution. This suggests that when the monoester forms, it migrates away from the layer of diol formed on the surface of solid catalysts into the ester/hexane phase by a process resembling continuous extraction and remains there without reacting further. The reasons for the lower selectivity observed for solvents containing a high proportion of hexane will be discussed later. Figure 4 also shows that the amount of diol present in the supernate decreased by ca. 10% when $NaHSO_4$–SiO_2 was added. This also suggests that the diol was adsorbed on the surface of the catalyst. The low selectivity observed in the methanesulfonic acid catalyzed reaction can be explained by postulating the following: (1) when the diol separated from solutions that contained a high proportion of hexane, most of the acid collected in the diol layer and there catalyzed the esterification of the diol; (2) the phenomenon described in 1 led to an increase in selectivity; and (3) the acid that was present in the ester/hexane phase catalyzed the acylation of the monoester, thereby lowering the selectivity. The relationship between selectivity and diol

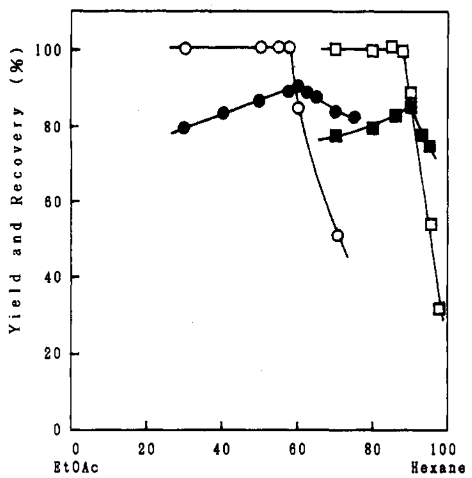

Figure 7. Plots of yield of monoester and diol present in solution (recovery) vs solvent composition: yield of the monoester (at yield of the diester = 5%) from the acylation of 1,4-butanediol (1 mmol) catalyzed by $NaHSO_4$–SiO_2 in EtOAc/hexane at 50 °C. Amount of the catalyst and the volume of solvent = 0.083 mmol and 3.3 mL, respectively (●), 0.125 mmol and 30 mL, respectively (■): amount of diol present in solution when the volume was 3.3 mL (○) and 30 mL (□) without the catalyst (see Experimental Section).

solubility observed in the case of 1,4-butanediol seems to be general because similar phenomena were observed with 1,2-ethanediol and 1,10-decanediol, although the solvent compositions at which maximum selectivity was achieved were different (Figures 5 and 6). In the acylation of 1,10-decanediol in methyl isobutyrate/octane, the yield of the monoester at the point where the yield of the diester was 2% appeared to have peaked when the proportion of octane in the solvent was ca. 90%. The amount of diol present in the supernate began to decrease at that solvent composition (Figure 6). However, the high selectivity that was observed when the proportion of octane was ca. 95% was probably due to the fact that the amount of methyl isobutyrate present was only five times that of the diol. Thus, the high selectivity in the monoesterification is believed to be a result of the selective adsorption of diols on the surface of the supported catalysts and the formation of a diol layer of appropriate thickness on the surface of the catalysts. Evidence in support of this latter belief is the observation that, in the acylation of both 1,8-octanediol and 1,10-decanediol, the selectivity decreased considerably when the reaction temperature was lower than the melting point of the diol.

In the acetylation of 1,4-butanediol, when the volume of the solvents were tripled (from 10 to 30 mL), the maximum yield of monoester was obtained when the proportion of hexane in the solvent was 90%, whereas when the volume of the solvent was reduced by two-thirds (from 10 to 3.3 mL), the maximum yield of monoester was obtained when hexane constituted 60% of the solvent (Figure 7). The amount of diol in the supernate began to decrease at those proportions of hexane. These results reflect the fact that the longer chain of methylene groups in the diol, the more closely the diol resembles an alkane structurally. Thus, increasing the volume of the solvent has the same effect as an increase in the solubility of the diol. These results further suggest that the monoacylation will occur selectively when the composition or the volume of the solvent is adjusted to the point where the amount of diol present in supernate just begins to decrease.

Initial Rate of Reaction. The initial rate of the acylation of 1,4-butanediol in methyl isobutyrate/hexane showed little dependence on the composition of the solvent until the proportion of hexane reached ca. 85%, whereupon the rate dropped off sharply. This suggests that the surface of the catalyst is now completely covered with the diol and that the reactivity of the adsorbed diol does not depend on the polarity of the solvent as long as the supply of the reactant ester is not disrupted by the formation of an overly thick diol layer. A comparison of Figures 3 and 8 suggests that the decrease in selectivity that is observed when the proportion of alkane in the solution is high is a result of a decrease in the reactivity of the diol.

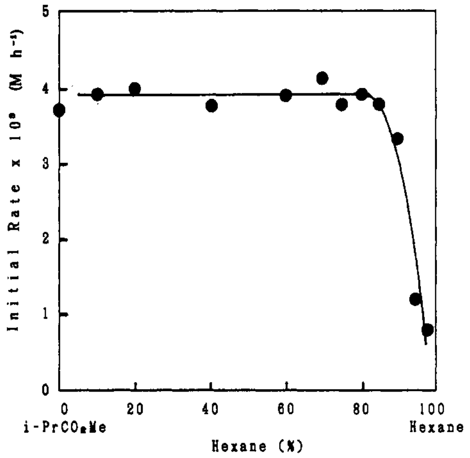

Figure 8. Plot of initial rate vs solvent composition for the acylation of 1,4-butanediol (1 mmol) catalyzed by $NaHSO_4$–SiO_2 (0.125 mmol) at 60 °C in methyl isobutyrate/hexane (15 mL).

Alcohols are also formed from the esters that are present in the solvents. Both the initial rate of monoester formation and the selectivity were lowered considerably upon introduction of an alcohol. For example, both the yield of the monoester at the point where the yield of the diester was 5% and the initial rate of formation of the monoester were decreased, from 83 to 66%, and from 9.8×10^{-4} to 7.8×10^{-4} M min^{-1}, respectively, when ethanol (1 mmol) was added during the reaction of 1,4-butanediol (1 mmol) and $NaHSO_4$–SiO_2 (0.125 mmol) at 50 °C in 1:4 (vol/vol) EtOAc/hexane (5 mL). These results may be explained by postulating that the presence of ethanol raised both the polarity of the solvent and the solvent's ability to dissolve the diol and also that the ethanol competed with the diol for the acylating agent, i.e., the ester.

Because the high selectivity that is observed seems to be the result of both the preferential adsorption of diol on the surface of $M_m(SO_4)_n$–SiO_2 and the limited solubility of diols in ester/alkane mixtures, selective monoprotection is presumed to occur when the polarity or the solubility successively decreases from a starting material to a final product. This interpretation is supported by the observation that symmetrical diols can be selectively monoetherated by reaction with dihydropyran in the presence of $M_m(SO_4)_n$–SiO_2.[14]

Experimental Section

Reagents, solvents, and chromatographic silica gel WB-300 (FUji-Davison) were used without purification. However, what brand of silica gel was used was not important. Solvents were stored over 3A molecular sieves before use. Supported reagents were prepared by the method described earlier.[6] The load of the metal salts on the silica gel was 3 mmol/g. $NaHSO_4$–SiO_2 was

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[14] Nishiguchi, T.; Kawamine, K. *J. Chem. Soc., Chem. Commun.* 1990, 1766.

dried at 160 °C for 1 h in vacuo ((4–10) × 10^2 Pa) with stirring. Unsupported $NaHSO_4$ was dried under the same conditions and then was pulverized. GLC analyses were performed with an instrument equipped with a direct injector. The column was a 30 m × 0.53 mm i.d. fused silica capillary column coated with either OV-1 or OV-1701. Analytical TLC was performed with precoated silica gel $60F_{254}$ (E. Merck) plates.

Analytical-Scale Monoacylation of 1,*n*-Diols. The acylation of 1,4-butanediol is typical. A stirred mixture of 1,4-butanediol (88.5 μL, 1 mmol), $NaHSO_4$–SiO_2 (56.5 mg, 0.125 mmol), and 1:4 (vol/vol) methyl isobutyrate/hexane (15 mL) was warmed at 60 ± 1 °C. After 10 min, tridecane (GLC internal standard, 50 μL) was added. Samples of the supernatant liquid were then removed periodically and were analyzed by GLC (OV-1 column). The retention times of the monoester and the diester were identical to those of authentic samples prepared by conventional methods.

When an amount of the unreacted diol was measured, the reaction was terminated at an appropriate conversion by removing the catalyst by filtration and the separated solid was eluted with ethanol (10 mL). The filtrate and the eluent were combined and a sample was analyzed by GLC.

The yield of monoester at a given yield of diester was derived from a plot of product yield vs time, such as that shown in Figure 1.

Synthetic-Scale Selective Monoacylation of 1,*n*-Diols. The acylation of 1,4-butanediol is again typical. A stirred mixture of 1,4-butanediol (0.44 mL, 5 mmol), $NaHSO_4$–SiO_2 (189 mg, 0.42 mmol), and 2:3 (vol/vol) EtOAc/hexane (16 mL) was warmed at 50 °C. The reaction was monitored by TLC (EtOAc/hexane (1:2) and GLC. After 5 h, the appearance of 1,4-diacetoxybutane was observed. The reaction mixture was then filtered. The catalyst that was separated was washed with CCl_4 (10 mL). The filtrate and washing were combined and concentrated. Column chromatography on silica gel (EtOAc/hexane (1:4)) of the residue gave 4-acetoxy-1-butanol (0.54 g, 82%). The ^1H NMR (60 MHz) and IR spectra and the GLC retention time of the compound were identical to those of an authentic sample synthesized independently.

Independent Synthesis of Authentic Monoesters and Diesters. The synthesis of the mono- and diisobutyrate of 1,4-butanediol is typical.

To an ice-cooled stirred suspension of NaH (0.68 g of a 60% dispersion in mineral oil which had been washed twice with 5 mL dry hexane) and dry THF (20 mL) were added, successively, drop-by-drop, 1,4-butanediol (0.8 mL, 9 mmol) and isobutyric anhydride (1.48 mL, 8.9 mmol). The mixture was allowed to stand overnight, and then the solvent was evaporated. The residue was treated with a mixture of ice and aqueous Na_2CO_3 (50 mL), and the whole was extractd with Et_2O (15 mL × 3). The Et_2O extract was washed with brine and was concentrated. The residue was twice purified by column chromatography on silica gel (EtOAc/hexane (1:6)) to give the monoester (0.42 g, 29%) and the diester (0.48 g, 23%).

Monoester: IR (neat) 3600–3300 (br), 1740 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 1.14 (6 H, d, J = 7 Hz), 1.63 (4 H, m), 2.35 (1 H, s), 2.44 (1 H, m, J = 7 Hz), 3.57 (2 H, t, J = 6 Hz), 4.06 (2 H, t, J = 6 Hz). Diester: IR (neat) 1740 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 1.14 (12 H, d, J = 7 Hz), 1.65 (4 H, m), 2.42 (2 H, m, J = 7 Hz), 4.04 (4 H, t, J = 6 Hz).

Authentic samples of other diesters and monoesters, which were used to prepare GLC calibration curves, were synthesized in a similar manner, i.e., via the corresponding acid anhydride. The diacetates of 1,2-ethanediol, 1,3-propanediol, and 1,4-butanediol were available commercially. Formates were prepared by the transesterification of the diols by ethyl formate.

Determination of the Amount of Diol in the Supernate. The determination of the amount of 1,4-butanediol in the supernate is typical. A mixture of 1,4-butanediol (88.5 μL, 1 mmol), dodecane (50 μL, GLC internal standard), and 1:4 (vol/vol) EtOAc/hexane mixture (10 mL) was heated, with stirring, for 5 min at 50 ± 1 °C. The mixture was then allowed to stand, unstirred, for 5 min at 50 ± 1 °C. A sample of the supernatant was then analyzed by GLC (OV-1 column). It is noteworthy that the amount of the diol and the solvent and the reaction temperature were the same as those in the reaction shown in Figure 2.

When $NaHSO_4$–SiO_2 (56.5 mg, 0.125 mmol) was added before heating, the corresponding mono- and diacetate were not to be found.

Registry No. $HO(CH_2)_2OH$, 107-21-1; $HO(CH_2)_3OH$, 504-63-2; $HO(CH_2)_4OH$, 110-63-4; (Z)-$HOCH_2CH{=}CHCH_2OH$, 6117-80-2; $HOCH_2C{\equiv}CCH_2OH$, 110-65-6; $HO(CH_2)_5OH$, 111-29-5; $HO(CH_2)_6OH$, 629-11-8; $H_3CCH(OH)(CH_2)_2CH(OH)CH_3$, 2935-44-6; $HO(CH_2)_8OH$, 629-41-4; $HO(CH_2)_{10}OH$, 112-47-0; $HO(CH_2)_{12}OH$, 5675-51-4; $HO(CH_2)_{16}OH$, 7735-42-4; $H_3CC(O)OEt$, 141-78-6; $H_3CCH(CH_3)CH_2C(O)OMe$, 547-63-7; $HC(O)OEt$, 109-94-4; $H_3CCH_2C(O)OMe$, 554-12-1; $H_3CC(O)OPr$, 109-60-4; $H_3CC(O)O(CH_2)_2OH$, 542-59-6; $H_3CC(O)O(CH_2)_3OH$, 36678-05-4; $H_3CC(O)O(CH_2)_4OH$, 35435-68-8; $H_3CCH_2C(O)O(CH_2)_4OH$, 33498-48-5; (Z)-$H_3CC(O)OCH_2CH{=}CHCH_2OH$, 64196-68-5; $H_3CC(O)OCH_2C{\equiv}CCH_2OH$, 83466-88-0; $H_3CC(O)O(CH_2)_5OH$, 68750-23-2; $H_3CC(O)O(CH_2)_6OH$, 68750-24-3; $HC(O)OCH(CH_3)(CH_2)_2CH(CH_3)OH$, 123674-08-8; $H_3CC(O)O(CH_2)_8OH$, 40646-17-1; $H_3CCH_2C(O)O(CH_2)_{10}OH$, 137174-86-8; $H_3CCH_2C(O)O(CH_2)_{12}OH$, 137174-87-9; $H_3CCH_2C(O)O(CH_2)_{16}OH$, 137174-88-0; $H_3CC(O)O(CH_2)_{16}OH$, 137174-89-1; $NaHSO_4$, 7681-38-1; $H_2SO_4{\cdot}xCe$, 24670-27-7; $MeSO_3H$, 75-75-2; $H_3CC(O)O(CH_2)_2OC(O)CH_3$, 111-55-7; $H_3CC(O)O(CH_2)_3OC(O)CH_3$, 628-66-0; $H_3CC(O)O(CH_2)_4OC(O)CH_3$, 628-67-1; $H_3CCH_2C(O)O(CH_2)_4OC(O)CH_2CH_3$, 1572-92-5; ($Z$)-$H_3CC(O)OCH_2CH{=}CHCH_2OC(O)CH_3$, 25260-60-0; $H_3CC(O)OCH_2C{\equiv}CCH_2OC(O)CH_3$, 1573-17-7; $H_3CC(O)O(CH_2)_5OC(O)CH_3$, 6963-44-6; $H_3CC(O)O(CH_2)_6OC(O)CH_3$, 6222-17-9; $HC(O)OCH(CH_3)(CH_2)_2CH(CH_3)OC(O)H$, 137174-90-4; $H_3CC(O)O(CH_2)_8OC(O)CH_3$, 3992-48-1; $H_3CCH_2C(O)O(CH_2)_{10}OC(O)CH_2CH_3$, 42236-22-6; $H_3CCH_2C(O)O(CH_2)_{12}OC(O)CH_2CH_3$, 42236-51-1; $H_3CCH_2C(O)O(CH_2)_{16}OC(O)CH_2CH_3$, 42237-31-0; $H_3CC(O)O(CH_2)_{16}OC(O)CH_3$, 42237-30-9; $H_3CCH(CH_3)C(O)O(CH_2)_4OH$, 123641-46-3; $H_3CCH(CH_3)C(O)O(CH_2)_{10}OH$, 137174-91-5; $H_3CCH(CH_3)C(O)(CH_2)_{12}OH$, 137174-92-6; $H_3CCH(CH_3)C(O)O(CH_2)_4OC(O)CH(CH_3)CH_3$, 1572-74-3; $H_3CCH(CH_3)C(O)O(CH_2)_{12}OC(O)CH(CH_3)CH_3$, 137174-93-7; $Fe_2(SO_4)_3$, 10028-22-5; 1,4-cyclohexanediol, 556-48-9; 4-hydroxycyclohexyl formate, 137174-94-8; 4-formylcyclohexyl formate, 137174-95-9.