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KF–Al_2O_3 is an efficient solid support reagent for the acetylation of amines, alcohols, and phenols. Impeding effect of solvent on the reaction rate

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Abstract—KF–Al_2O_3 brings about rapid acetylation of a range of amines, alcohols, and phenols with Ac_2O/AcCl. Aliphatic alcohols are acetylated chemoselectively in the presence of phenols. 1° alcohols react several times faster than 2° alcohols. 3° alcohols do not react.

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1. Introduction

The acetylation of alcohols and amines is an important reaction in organic synthesis.[1] Pyridine and 4-dialkylaminopyridines are the most commonly used basic catalysts.[2] More recently, a variety of new catalysts have been reported which are either basic or acidic. Amongst the basic catalysts, Bu_3P,[3] $MgBr_2$–R_3N,[4] and an aminophosphine superbase[5] are significant. $CoCl_2$,[6] $MgBr_2$,[7] $Sc(OTf)_3$,[8] $Sc(NTf_2)_3$,[9] $TiCl_4$–$2AgClO_4$,[10] $TiCl(OTf)_3$,[11] $Sn(OTf)_2$,[12] TMSOTf,[13] $La(OTf)_3$,[14] $Cu(OTf)_2$,[15] $TaCl_5$[16] and montmorillonite K-10[17] represent the acidic catalysts. The transesterifications catalyzed by $NaHSO_4{\cdot}SiO_2$[18] and distannoxane[19] are very successful for selective reactions. *Pseudomonus cepacia* PS lipase[20] and twisted amides[21] have been used for the chemoselective acetylation of aliphatic alcohols present in hydroxyalkylphenols. NaH and 3-acetylthiazolidine-2-thione[22] and hindered amines and AcCl[23] are employed for the selective reactions of 1° alcohols. The direct acetylation of 1° and 2° alcohols and phenols with no apparent discrimination using zeolite HSZ-360[24] is also efficient.

KF–Al_2O_3 has been used earlier for the *O*-alkylation of alcohols and phenols,[25] Michael addition,[26] β-elimination,[27] aldol condensation,[27] Darzens[27] and Knoevenagel[28] reactions, and the oxidation of electron-deficient alkenes.[29] The high efficacy and ease of product isolation prompted us to investigate its use for acetylation purposes. This has resulted in a simple and economical method that we report herein.

2. Results and discussion

The results of the reactions of a diverse range of alcohols and amines are collected in Table 1. Several features deserve comment. While AcCl is preferred over Ac_2O for the reactions of alcohols, Ac_2O was superior to AcCl for amines. Alcohols of both 1° and 2° nature, including allylic and benzylic alcohols, reacted very well (entries 1–9). It was gratifying to observe that the neopentylic 2° alcohol present in testosterone acetylated quantitatively with AcCl in <2.5 h (entry 9). Linalool, an allylic and 3° alcohol, did not react at all with Ac_2O and it was recovered quantitatively (entry 10). However, it decomposed when the acetylation was attempted with AcCl. This observation raised the genuine possibility of selective acetylation of 1° and 2° alcohols in the presence of a 3° one. Indeed, the reaction of 2-methyl-2,7-octanediol with 1.1 equiv. of Ac_2O furnished only the monoacetate of the 2° alcohol (entry 11). The reaction with AcCl caused elimination of the 3° alcohol and the acetate of 7-methyl-6-octen-2-ol was isolated as the predominant product. Diols possessing 1° and 2° alcohol functions were conveniently transformed into diacetates (entries 12–15). Enolizable 1,3-diketones that do not exist in cyclic hydrogen-bonded structures reacted to form enol-acetates. This is exemplified by the quantitative transformation of 1,3-cyclohexanedione (entries 16).

The reactions of *p*-bromophenol and β-naphthol with AcCl (entries 17 and 18) were very slow in comparison to the reactions of aliphatic alcohols. Even after vigorous stirring for 30 h at 25°C, ~10% of the phenols were left unchanged. This raised the possibility of selective acetylation of 1°/2° aliphatic alcohols in the presence of phenols. Indeed, 3-(2-hydroxyphenyl)propanol furnished, on reaction with AcCl (1.1 equiv.), only the expected monoacetate (entry

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Keywords: KF–Al_2O_3; acetylation; chemoselectivity; solvent effect.

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Table 1. Acetylation of alcohols, amines, and phenols promoted by KF–Al_2O_3 in toluene

Entry	Substrate	Ac_2O/AcCl	Time (h)	Rxn (%)	Yield (%)
1	Citronellol	Ac_2O	14	90	–
	Citronellol	AcCl	1	100	98
2	3-Phenyl-1-propanol	AcCl	1.7	100	96[a]
3	Menthol	Ac_2O	18	85	–
	Menthol	AcCl	2	100	95[b]
4	Geraniol	Ac_2O	14	93	–
	Geraniol	AcCl	2	100	98[b]
5	Cinnamyl alcohol	Ac_2O	14	92	–
	Cinnamyl alcohol	AcCl	1	100	98[b]
6	3-Methyl-2-cyclohexenol	Ac_2O	12	80	–
	3-Methyl-2-cyclohexenol	AcCl	2	100	95
7	Benzyl alcohol	Ac_2O	6	90	–
	Benzyl alcohol	AcCl	0.7	100	96[b]
8	Methyl mandelate	AcCl	10	100	98
9	Testosterone	Ac_2O	38	65	–
	Testosterone	AcCl	2.5	100	98[b]
10	Linalool	Ac_2O	48	NR	–
11	2-Methyl-2,7-octanediol	Ac_2O	20	100	95
12	1,2-Propanediol	Ac_2O	1.5	100	92[b,c]
	1,2-Propanediol	AcCl	0.5	100	93
13	1-Phenyl-1,2-ethanediol	AcCl	2	100	96
14	1,3-Butanediol	AcCl	0.5	100	94[b,c]
15	1,6-Heptanediol	AcCl	0.5	100	95[c]
16	1,3-Cyclohexanedione	Ac_2O	15	90	–
	1,3-Cyclohexanedione	AcCl	5	100	96[b]
17	*p*-Bromophenol	AcCl	30	90	–
18	β-Naphthol	AcCl	30	90	–[d]
19	3-(2-Hydroxyphenyl)propanol	AcCl	4	100	96[e]
20	*tert*-Butyl amine	Ac_2O	0.2	100	92
21	Morpholine	Ac_2O	0.2	100	95[f]
22	4-Chloroaniline	Ac_2O	0.1	100	96[g]
23	4-Nitroaniline	Ac_2O	4	100	97[h]

Reaction % indicates the percentage of starting material reacted. The yield % is the overall yield of the product (acetate or diacetate).

[a] Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4560–4567.

[b] The spectral data of the acetate/diacetate corresponded to those of the commercially available materials.

[c] The corresponding diacetate was prepared.

[d] *Handbook of Proton-NMR Spectra and Data*, Ed. Asahi Research Center, 1985; Vol. 4, p 260.

[e] Ref. 20.

[f] *Handbook of Proton-NMR Spectra and Data*, Ed. Asahi Research Center, 1986; Vol. 6, p 242.

[g] *Handbook of Proton-NMR Spectra and Data*, Ed. Asahi Research Center, 1985; Vol. 3, p 82.

[h] *Handbook of Proton-NMR Spectra and Data*, Ed. Asahi Research Center, 1985; Vol. 3, p 89.

19). In this respect, the KF–Al_2O_3 reagent resembles the distannoxane-catalyzed transesterification.[19]

Aliphatic amines such as *t*-butyl amine and morpholine reacted very quickly (entries 20 and 21). Aromatic amines that were substituted by electron-withdrawing groups, e.g. 4-nitroaniline, reacted remarkably slowly than those that are substituted otherwise, e.g. 4-chloroaniline. While 4-chloroaniline reacted almost instantly with Ac_2O (entry 22), 4-nitroaniline took 4 h for complete reaction (entry 23). Such a large rate-difference must be helpful in selective reactions. No such discrimination is achieved with the use of $Cu(OTf)_2$.[15]

We then investigated the species that possessed both a 1° and a 2° alcohol with the aim of studying their relative kinetics of acetylation. In the event when 1,3-butanediol and 1,6-heptanediol were allowed to react with 1.1 equiv. of AcCl and 1.5 equiv. of KF–Al_2O_3 for 1 h, we obtained a mixture of 1° and 2° acetates and the unreacted diol. About 70% of the diol had reacted in each instance. The average ratio of the 1° and 2° acetates was 4:1 from 1,3-butanediol

Table 2. Acetylation of alcohols and amines catalyzed by KF–Al_2O_3 (no solvent)

Entry	Substrate	Ac_2O/AcCl	Time (min)	Rxn (%)	Yield (%)
1	3-Phenyl-1-propanol	AcCl	5	100	96
2	Benzyl alcohol	AcCl	4	100	95
3	Methyl mandelate	AcCl	15	100	98
4	1,2-Propanediol	AcCl	5	100	95[a]
5	1,6-Heptanediol	AcCl	5	100	95[a]
6	β-Naphthol	AcCl	30	100	97
7	4-Nitroaniline	Ac_2O	15	100	97

[a] The corresponding diacetate was prepared.

and 5.4:1 from 1,6-heptanediol over two runs. Small amounts of diacetates were also formed.

There was enormous rate enhancement in the acetylation of alcohols with AcCl in the absence of solvent. The acetylation of 3-phenylpropanol with AcCl was at least 20 times faster than the reaction in toluene. Benzyl alcohol and methyl mandelate reacted, respectively, 10 and 40 times faster than those in toluene. Even β-naphthol could be acetylated completely within 30 min. Remarkably, the corresponding reaction in toluene was only 90% complete in 30 h. Rate enhancement was also observed for the bisacetylation of diols. The reactions of both 1,2-propanediol and 1,6-heptanediol were 6 times faster than the reactions in toluene. The acetylation of amines was also accelerated: the reaction of *p*-nitroaniline with Ac_2O, for example, was complete in 15 min as against 4 h in toluene. These results are collected in Table 2.

3. Conclusions

In conclusion, we have presented a new, economical, and operationally simple method for the acetylation of amines, alcohols, and phenols with Ac_2O/AcCl. The present method is much more efficient than most other often-used methods. An aliphatic alcohol can be acetylated in the presence of phenols with high selectivity. 1° alcohols react several times faster than the 2° alcohols; 3° alcohols do not react.

4. Experimental

^1H and ^{13}C spectra were recorded on JEOL JNM-400 in $CDCl_3$. The signal positions are reported in ppm (δ scale) relative to TMS used as an internal standard. For every OH/NH function in the substrate, 1.5 equiv. of KF were used. Furthermore, for every OH/NH function in the substrate, 1.5 equiv. of Ac_2O or 1.1 equiv. of AcCl were used. The reaction mixtures were vigorously stirred magnetically and the progress of the reaction monitored by TLC. When complete, the mixture was diluted with Et_2O and filtered. The solvents were evaporated on Rotovap under reduced pressure (water aspirator) to furnish the product. The chromatographic separations, whenever needed, were performed by silica gel (100–200 mesh) column chromatography. Mixtures of hexanes and EtOAc were used to elute the material(s) off the column.

4.1. Preparation of $KF–Al_2O_3$

Anhydrous KF (5.8 g, 100 mmol) was dissolved in distilled H_2O (10 mL) and mixed with neutral Al_2O_3 (10 g). The water was removed at 50°C on a rotovap under reduced pressure. The impregnated Al_2O_3 was further dried at 75°C for 30 h in a vacuum drying oven. The free-flowing material, thus obtained, was stored in a plastic bottle at room temperature and used for the present investigation.

4.2. General procedure for the acetylation of monohydric aliphatic alcohols, amines, and phenols

Ac_2O (1.5 mmol) or AcCl (1.1 mmol) was added, in one portion, to a suspension of $KF–Al_2O_3$ (0.238 g, 1.5 mmol KF) and the alcohol (1 mmol) in toluene (4 mL). The resultant mixture was stirred vigorously and the reaction monitored by TLC. The reaction mixture was diluted with Et_2O and filtered. The solvents were removed to furnish the product.

4.3. General procedure for the bisacetylation of aliphatic diols

Ac_2O (3.0 mmol) or AcCl (2.2 mmol) was added, in one portion, to a suspension of $KF–Al_2O_3$ (0.475 g, 3.0 mmol KF) and the diol (1.0 mmol) in toluene (4 mL). The resultant mixture was stirred vigorously and the reaction monitored by TLC. The reaction mixture was worked up as above.

4.4. Chemoselective monoacetylation of aliphatic diols and hydroxyalkyl phenols

AcCl (1.1 mmol) was added, in one portion, to a suspension of $KF–Al_2O_3$ (0.238 g, 1.5 mmol KF) and the substrate to be acetylated (1 mmol) in toluene (4 mL). The resultant mixture was stirred vigorously and the reaction monitored by TLC. The reaction mixture was diluted with Et_2O and filtered. The solvents were removed to furnish the product(s). For the reaction of a diol that contained a 3° alcohol, Ac_2O was used in place of AcCl. AcCl caused extensive dehydration of the 3° alcohol.

4.5. General procedure for acetylation in the absence of solvent

Ac_2O (1.5 mmol) or AcCl (1.1 mmol) was added, in one portion, to a dispersion of the alcohol (1 mmol) over $KF–Al_2O_3$ (0.238 g, 1.5 mmol KF). The resultant dispersion was rotated mechanically and the progress of the reaction monitored by TLC. The reaction mixture was diluted with Et_2O and filtered. The solvent was removed to furnish the product.

4.5.1. 1,6-Heptanediol. A solution of 7-methyl-2-oxepanone (0.190 g, 1.48 mmol) in dry THF (5 mL) was slowly added to a stirred suspension of LAH (0.078 g, 2 mmol) in dry THF (5 mL) at 0°C. This was allowed to warm up to 25°C and then refluxed for 3 h. The reaction mixture was cooled to 0°C and the excess of LAH was destroyed by adding EtOAc. This was filtered and the solid residue was washed with EtOAc and filtered. The solvents were removed from the combined solution and the residue was filtered through a short silica gel column to furnish the diol, 0.188 g (liquid); 96% yield.

^1H NMR δ 3.79–3.73 (1H, m), 3.61 (2H, t, J=6.6 Hz), 2.60 (2H, bs), 1.56 (2H, m), 1.44–1.34 (6H, m), 1.16 (3H, d, J=6.4 Hz). ^{13}C NMR δ 67.8, 62.4, 39.0, 32.5, 25.6, 25.4, 23.3. Anal. Calcd for $C_7H_{16}O_2$: C, 63.58; H, 12.20. Found: C, 63.40; H, 12.04.

4.5.2. 2-Methyl-2,7-octanediol. MeI (0.373 mL, 6 mmol) was added slowly at 0°C over 5 min to a suspension of Mg turnings (0.145 g, 6 mmol) in Et_2O (8 mL) under nitrogen. After all the Mg had dissolved, a solution of

7-methyl-2-oxepanone (0.256 g, 2 mmol) in Et_2O (5 mL) was added. The mixture was gradually warmed to 25°C and then refluxed for 2 h. The reaction mixture was cooled to 25°C and mixed with saturated aqueous NH_4Cl (5 mL) and stirred for 10 min. The layers were separated and the organic layer was washed with H_2O (2×5 mL) and brine (1×5 mL). This was dried and concentrated to furnish a residue which was chromatographed over Al_2O_3 to isolate the product, 0.255 g, liquid; 80% yield.

^{1}H NMR δ 3.82–3.60 (1H, m), 1.65–1.25 (10H, m), 1.21 (6H, s), 1.19 (3H, d, J=6.4 Hz). ^{13}C NMR δ 70.9, 67.9, 43.8, 39.2, 29.2, 29.1, 26.2, 24.2, 23.5. Anal. Calcd for $C_9H_{20}O_2$: C, 67.44; H, 12.59. Found: C, 67.32; H, 12.40.

4.5.3. Ethyl 3-(2-Hydroxyphenyl)acrylate. Salicyclaldehyde (0.610 g, 5 mmol) was added to a stirred solution of $Ph_3P{=}CHCO_2Et$ (3.48 g, 10 mmol) in MeOH (15 mL). After 30 min, the solvent was removed and the oily residue was purified by silica gel chromatography to furnish pure ethyl 3-(2-hydroxyphenyl)acrylate, 0.865 g, liquid; 90% yield.

^{1}H NMR δ 8.08 (1H, d, J=16.1 Hz), 7.65 (1H, s), 7.44 (1H, dd, J=7.8, 1.5 Hz), 7.24–7.19 (1H, dt, J=7.7, 1.7 Hz), 6.91–6.86 (2H, m), 6.65 (1H, d, J=16.1 Hz), 4.28 (2H, q, J=7.1 Hz), 1.34 (3H, t, J=7.1 Hz). ^{13}C NMR δ 168.9, 155.8, 141.2, 131.5, 129.1, 121.6, 120.4, 117.9, 116.4, 60.8, 14.2.

4.5.4. 3-(2-Hydroxyphenyl)propanol. A solution of ethyl 3-(2-hydroxyphenyl)acrylate (0.540 g, 2.82 mmol) in dry THF (10 mL) was added slowly to a suspension of LAH (0.078 g, 2 mmol) in THF (5 mL) at 0°C. The reaction mixture was allowed to reach 25°C and refluxed for 4 h. It was brought back to 0°C and the excess LAH was destroyed by adding EtOAc. The contents were filtered and the solid washed with Et_2O. The solvents were removed and the residue was purified by silica gel column chromatography to obtain the desired product, 0.345 g, liquid; 80% yield.

^{1}H NMR δ 7.76 (1H, bs), 7.08–7.04 (2H, m), 6.86–6.80 (2H, m), 3.60 (2H, t, J=5.9 Hz), 2.74 (2H, t, J=7.1 Hz), 1.87–1.81 (2H, m). ^{13}C NMR δ 154.2, 130.6, 127.4, 120.7, 115.8, 60.9, 32.2, 25.3. Anal. Calcd for $C_9H_{12}O_2$: C, 71.01; H, 7.95. Found: C, 70.85; H, 7.78.

4.5.5. β-Citronellol acetate (liquid). ^{1}H NMR δ 5.08 (1H, t, J=7.1 Hz), 4.15–4.05 (2H, m), 2.03 (3H, s), 2.00–1.87 (2H, m), 1.68 (3H, s), 1.70–1.62 (1H, m), 1.60 (3H, s), 1.58–1.50 (1H, m), 1.47–1.41 (1H, m), 1.40–1.30 (1H, m), 1.23– 1.14 (1H, m), 0.91 (3H, d, J=6.4 Hz). ^{13}C NMR δ 171.1, 131.3, 124.5, 63.0, 36.9, 35.4, 29.4, 25.7, 25.3, 21.0, 19.4, 17.6. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19. Found: C, 72.45; H, 10.96.

4.5.6. Methyl mandelate acetate (liquid). ^{1}H NMR δ 7.47–7.44 (2H, m), 7.39–7.36 (3H, m), 5.92 (1H, s), 3.69 (3H, s), 2.17 (3H, s). ^{13}C NMR δ 170.1, 169.1, 133.6, 129.1, 128.6, 127.5, 74.3, 52.4, 20.5. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.44; H, 5.81. Found: C, 63.30; H, 5.65.

4.5.7. 3-Methyl-2-cyclohexen-1-ol acetate (liquid). ^{1}H NMR δ 5.46 (1H, bs), 5.24 (1H, bs), 2.04 (3H, s), 2.03–1.86 (2H, m), 1.70 (3H, d, J=0.08 Hz), 1.82–1.60 (4H, m). ^{13}C NMR δ 170.9, 141.1, 120.0, 68.8, 29.9, 28.0, 23.7, 21.5, 19.0. Anal. Calcd for $C_9H_{14}O_2$: C, 70.08; H, 9.16. Found: C, 69.90; H, 8.96.

4.5.8. 1,6-Heptanediol diacetate (liquid). ^{1}H NMR δ 4.93–4.85 (1H, m), 4.05 (2H, t, J=6.6 Hz), 2.05 (3H, s), 2.03 (3H, s), 1.65–1.27 (8H, m), 1.20 (3H, d, J=6.4 Hz). ^{13}C NMR δ 171.2, 170.7, 70.8, 64.4., 35.7, 28.5, 25.7, 25.0, 21.3, 20.9, 19.9. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.07; H, 9.33. Found: C, 59.90; H, 9.20.

4.5.9. 2-Methyl-2,7-octanediol monoacetate (liquid). ^{1}H NMR δ 4.94–4.86 (1H, m), 2.03 (3H, s), 1.21 (6H, s), 1.65–1.20 (9H, m), 1.16 (3H, d, J=7.3 Hz). ^{13}C NMR δ 170.8, 70.91, 70.90, 43.7, 35.8, 29.21, 29.17, 25.9, 24.1, 21.3, 19.9. Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.30; H, 10.97. Found: C, 65.15; H, 10.80.

4.5.10. 1-Phenyl-1,2-ethanediol diacetate (liquid). ^{1}H NMR δ 7.36–7.26 (5H, m), 6.02 (1H, dd, J=7.9, 3.9 Hz), 4.36–4.26 (2H, m), 2.11 (3H, s), 2.05 (3H, s). ^{13}C NMR δ 170.5, 169.9, 136.4, 128.5, 126.6, 73.2, 66.0, 21.0, 20.6. Anal. Calcd for $C_{12}H_{14}O_4$: C, 58.04; H, 7.58. Found: C, 57.90; H, 7.45.

4.5.11. 7-Methyl-6-octene-2-ol acetate (liquid). ^{1}H NMR δ 5.09 (1H, t, J=7.0 Hz), 4.93–4.85 (1H, m), 2.03 (3H, s), 2.00–1.94 (2H, m), 1.69 (3H, s), 1.60 (3H, s), 1.65–1.55 (2H, m), 1.55–1.40 (2H, m), 1.40–1.25 (2H, m), 1.20 (3H, d, J=6.3 Hz). ^{13}C NMR δ 170.8, 131.7, 124.2, 71.0, 35.5, 27.7, 25.66, 25.60, 21.3, 19.9. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.68; H, 10.95. Found: C, 71.54; H, 10.80.

4.5.12. *tert*-Butyl amine acetate (mp 95–97°C). ^{1}H NMR δ 5.69 (1H, bs), 1.92 (3H, s), 1.34 (9H, s). ^{13}C NMR δ 169.6, 51.2, 28.7, 24.4. Anal. Calcd for $C_6H_{13}NO$: C, 62.55; H, 11.38. Found: C, 62.40; H, 11.15.

4.5.13. *p*-Bromophenol acetate (liquid). ^{1}H NMR δ 7.47 (2H, d, J=8.5 Hz), 6.97 (2H, d, J=8.5 Hz), 2.28 (3H, s). ^{13}C NMR δ 169.1, 149.6, 132.4, 123.3, 118.9, 21.0.

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