Montmorillonite K-10 and KSF as remarkable acetylation catalysts

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Montmorillonite K-10 and KSF catalyse the acetylation of alcohols, thiols, phenols and amines with acetic anhydride in excellent yield.

The protection of hydroxy, thiol and amino groups by the formation of esters and amides is of great importance in organic synthesis.[1] Although a variety of procedures use the transesterification methodology,[2] the acylation of alcohols and phenols is routinely carried out using acid anhydrides or acid chlorides in the presence of tertiary amines such as triethylamine and pyridine.[3] DMAP is particularly noteworthy as an efficient catalyst for the acylation of tertiary alcohols.[4] Recently, Vedejs and co-workers reported tributylphosphine to be a similar catalyst for the acylation of alcohols.[5] In addition to the above catalysts, protonic acids such as toluene-*p*-sulfonic acid[6] and Lewis acids such as zinc chloride,[7] cobalt chloride[8] and scandium trifluoromethanesulfonate[9] are also known to catalyse the acylation of alcohols and phenols. Nevertheless, there is still a great demand for acid catalysts to generate esters under mild conditions.

Montmorillonite clays, a class of inexpensive and noncorrosive solid acids, have been used as efficient catalysts for a variety of organic reactions.[10] In a recent study on the preparation of 1,1-diacetates from aldehydes catalysed by montmorillonite clays, we found that hydroxy groups were protected as acetates in hydroxy-containing aromatic aldehydes.[11] In connection with our ongoing work on montmorillonite clay catalysis,[12] we now give a preliminary account of our study of the acetylation of alcohols, phenols, thiols and amines catalysed by montmorillonite K-10 and KSF.

As shown in Table 1, a series of alcohols, phenols, thiols and amines were acetylated with acetic anhydride under catalysis by montmorillonite K-10 and KSF. Generally K-10 worked better than KSF in terms of reaction time, temperature and/or yield

Table 1 Acetylation of alcohols, phenols, thiols and amines with acetic anhydride catalysed by K-10 and KSF

Entry	Substrate	Catalyst	Solvent	Ratio[a]	*T*/°C	*t*/h	Product[b]	Yield[c] (%)
1	Octanol	K-10	none	2 : 1	room temp.	1	Octyl acetate	96
		KSF	none	2 : 1	room temp.	4	Octyl acetate	96
2	Benzyl alcohol	KSF	none	2 : 1	room temp.	1	Benzyl acetate	90
3	Ethylene glycol	KSF	$CHCl_3$	4 : 1	62	2	Ethane-1,2-diyl diacetate	76
4	Glycerol	KSF	$CHCl_3$	6 : 1	62	1.5	Propane-1,2,3-triyl triacetate	95
5	Cholesterol	K-10	CH_2Cl_2	2 : 1	room temp.	2	Cholesteryl acetate	98
		KSF	$CHCl_3$	2 : 1	62	2	Cholesteryl acetate	98
6	Dihydrobetulin	K-10	CH_2Cl_2	4 : 1	40	3	3β,28-Diacetoxylupane	94
7	Triphenylmethanol	KSF	CCl_4	2 : 1	76	2	No reaction	—
8	*tert*-Butyl alcohol	KSF	none	2 : 1	80	0.25	2-Methylpropene	94
9	3α-Methyl-5α-cholestan-3β-ol	K-10	CH_2Cl_2	2 : 1	40	2	3β-Acetoxy-3α-methyl-5α-cholestane	23
							3-Methyl-5α-cholest-2-ene	49
10	3β-Methyl-5α-cholestan-3α-ol	K-10	CH_2Cl_2	2 : 1	35	1	3α-Acetoxy-3β-methyl-5α-cholestane	27[d]
							3-Methyl-5α-cholest-2-ene	49[d]
11	2-Mercaptoethanol	KSF	CH_2Cl_2	1 : 1	40	0.25	Ethyl 2-mercaptoacetate	20
12	2-Mercaptoethanol	KSF	CH_2Cl_2	4 : 1	40	1.5	2-Acetylthioethyl acetate	92
13	Benzenethiol	K-10	none	2 : 1	room temp.	2	*S*-Phenyl thioacetate	97
		KSF	none	2 : 1	room temp.	5	*S*-Phenyl thioacetate	92
14	Phenol	KSF	none	2 : 1	room temp.	3.5	Phenyl acetate	83
15	α-Naphthol	KSF	$CHCl_3$	2 : 1	62	4	α-Naphthyl acetate	87
16	β-Naphthol	K-10	CH_2Cl_2	2 : 1	room temp.	2.5	β-Naphthyl acetate	98
		KSF	CH_2Cl_2	2 : 1	40	2	β-Naphthyl acetate	98
17	3-Nitrophenol	KSF	none	2 : 1	room temp.	5	3-Nitrophenyl acetate	98
18	2-Nitrophenol	KSF	$CHCl_3$	2 : 1	62	7	2-Nitrophenyl acetate	93
19	4-Nitrophenol	KSF	CH_2Cl_2	2 : 1	40	2.5	4-Nitrophenyl acetate	98
20	2-Methylphenol	KSF	none	2 : 1	room temp.	3.5	2-Methylphenyl acetate	90
21	4-Methoxyphenol	KSF	none	2 : 1	room temp.	4.5	4-Methoxyphenyl acetate	92
22	Hydroquinone	KSF	none	4 : 1	room temp.	2	Benzene-1,4-diyl diacetate	98
23	Catechol	KSF	none	4 : 1	room temp.	3	Benzene-1,2-diyl diacetate	98
24	Resorcinol	KSF	$CHCl_3$	4 : 1	62	3	Benzene-1,3-diyl diacetate	78
25	Benzene-1,3,5-triol	KSF	$CHCl_3$	6 : 1	62	4.5	Benzene-1,3,5-triyl triacetate	83
26	2-Aminophenol	KSF	CH_2Cl_2	2 : 1	40	1	*N*-(2-Hydroxyphenyl)acetamide	72
27	2-Aminophenol	KSF	CH_2Cl_2	4 : 1	40	3	*N*-(2-Acetoxyphenyl)acetamide	70
28	Diisopropylamine	KSF	CH_2Cl_2	4 : 1	40	2	*N*-Diisopropylacetamide	98
29	2-Nitroaniline	K-10	CH_2Cl_2	2 : 1	40	3.5	2-Nitroacetanilide	98
		KSF	CH_2Cl_2	2 : 1	40	3.5	2-Nitroacetanilide	87

[a] Acetic anhydride: substrate (mol : mol). [b] All products were identified by their ^{1}H NMR spectra and/or by comparison of their bp or mp with authentic samples. [c] Isolated yield. [d] Net yield, conversion rate of the material is 27.5%.

(entries 1, 5, 13, 16 and 29). Primary and secondary alcohols and phenols can be easily acetylated at room temperature or in refluxing CH_2Cl_2 or $CHCl_3$. No selectivity between primary and secondary hydroxy groups was observed (entries 4 and 6). Different results were obtained for several tertiary alcohols. For example, triphenylmethanol remained unchanged even when the reaction was performed in refluxing CCl_4 for 2 h (entry 7). *tert*-Butyl alcohol gave 2-methylpropene (entry 8). 3β-Methyl-5α-cholestan-3α-ol afforded mainly 3-methyl-5α-cholest-2-ene, with a minor amount of 3α-acetoxy-3β-methyl-5α-cholestane (27% net yield based on 27.5% conversion rate) (entry 10). The hydroxy equatorial epimer, 3α-methyl-5α-cholestan-3β-ol, gave the corresponding acetate in better yield (23%) and 3-methyl-5α-cholest-2-ene (entry 9). It is noteworthy that 3-methyl-5α-cholest-2-ene was the exclusive dehydration product in both reactions. These results indicated that K-10 and KSF were not efficient catalysts for acetylation of tertiary alcohols. Polyhydroxy compounds were transformed into the corresponding polyacetates (entries 3, 4, 6, 22, 23, 24 and 25). In the presence of K-10 or KSF, thiols and amines were also converted into the corresponding acetamides and thioacetates (entries 12, 13, 26, 27, 28 and 29). Acetylation of thiols was slower than hydroxy groups (entry 11). Amino groups could be preferentially acetylated in the presence of hydroxy groups (entry 26).

In a typical procedure, a mixture of octan-1-ol (650 mg, 5.00 mmol), K-10 (or KSF) (purchased from Fluka and used directly) (100 mg) and acetic anhydride (1.02 g, 10.0 mmol) was stirred at room temperature for 1 h (or 4 h). The catalyst was removed by filtration and washed with CH_2Cl_2. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give octyl acetate (813 mg, 96%).

In conclusion, K-10 and KSF are good acetylation catalysts for primary and secondary alcohols, phenols, thiols and amines but not for tertiary alcohols. The present method has the additional advantages of mild conditions, high yield, easy separation and inexpensive and environmentally friendly catalysts.

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