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SULFAMIC ACID CATALYSED ACETYLATION OF ALCOHOLS AND PHENOLS WITH ACETIC ANHYDRIDE

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Abstract: An easy acetylation of alcohols and phenols with acetic anhydride has been carried out in excellent yield under catalysis of sulfamic acid.

The protection of hydroxyl of alcohols and phenols by formation of esters is of great importance in synthetic organic chemistry.[1] Although several methods are the use of transesterification manner,[2] the routinely acylation of alcohols and phenols is carried out by acid anhydrides or acid chlorides in the presence of tertiary amines such as triethylamine and pyridine.[3] 4-(Dimethylamino)pyridine (DMAP) as a much more efficient catalysts for acylation of tertiary alcohols is particularly noteworthy.[4] Vedejs *et al* reported tributylphosphine as a similar catalyst for acylation of alcohols.[5] Recently, iodine was reported to be used as an acetyl transfer catalyst.[6] In addition to the above catalysts, protonic acids such as *p*-toluenesulfonic acid,[7] Lewis acids such as zinc chloride,[8] cobalt chloride[9] and

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scandium trifluoromethanesulfonate[10] were also applied to catalyse the acylation of alcohols and phenols. Each of the above methods has its merit and some shortcomings. These methods have not been entirely satisfactory, such as triethylamine and pyridine[3] have unpleasant odour and are not so easy to remove, DMAP[4] is not easily obtained and expensive, and tributylphosphine[5] has irritant, highly flammable and still expensive. More recently, montmorillonite K-10 and KSF[11] and expansive graphite[12] were applied as solid catalysts for this purpose to obtain relatively better results.

Sulfamic acid has been used as efficient catalyst for a variety of organic reactions.[13] Herein we wish to report a simple, efficient and inexpensive method for acetylation of alcohols and phenols catalysed by sulfamic acid.

$$\underset{\mathbf{1}}{\mathrm{ROH}} + \underset{\mathbf{2}}{\mathrm{Ac_2O}} \xrightarrow[88\text{-}99\%]{\substack{\text{Sulfamic acid} \\ \mathrm{CH_2Cl_2} \text{ or } \mathrm{CHCl_3} \\ \text{r.t. or reflux, 0.5-4 h}}} \underset{\mathbf{3}}{\mathrm{ROAc}} + \mathrm{HOAc}$$

As shown in Table 1, a series of alcohols and phenols (**1**) were acetylated with acetic anhydride (**2**) under catalysis of sulfamic acid. Primary and secondary alcohols and phenols could be easily acetylated at room temperature or in refluxing CH_2Cl_2 or $CHCl_3$. No selective acetylation between primary alcohol and phenol was observed (entry 8). Polyhydroxyl compounds were converted into the corresponding polyacetates (entries 3, 17-20). However, tertiary alcohols gave different results. For example, triphenylmethanol (entry 6) remained unchanged even the reaction mixture was heated in refluxing $CHCl_3$ for 2 h. *tert*-Butyl alcohol (entry 5) gave 2-methylpropene as the exclusive product. These results indicated that sulfamic acid was not efficient catalyst for acetylation of tertiary alcohols. It is noteworthy that sulfamic acid could recovered easily by filtration and could be reused without significant decrease in activity.

Table 1. Acetylation of alcohols and phenols catalysed by sulfamic acid

Entry	Substrate	Solvent/T(°C) /t(h)	Yield (%)[a]	Product	Bp/torr or Mp(°C) (reported)
1	n-Octanol	none/rt/1	88	n-Octyl acetate	103-105/20 (98/15[4])
2	Benzyl alcohol	none/rt/2	99	Benzyl acetate	115-117/20(134/102[14])
3	Glycerol	$CHCl_3$/62/2	94	Triacetin	135-137/20(258[14])
4	Cholesterol	$CHCl_3$/62/2	96	Cholesteryl acetate	113-114(114-115[14])
5	*t*-Butyl alcohol	none/80/0.5	98	2-Methylpropene	-7/760(-6.6/760[14])
6	Triphenyl methanol	$CHCl_3$/62/2	-	No reaction	
7	Phenol	CH_2Cl_2/rt/2	98	Phenyl acetate	93-95/20(196/760[14])
8	Salicyl alcohol	CH_2Cl_2/40/3	95	2-Acetoxyphenzyl acetate	163/760 (162-164/760[15])
9	Benzoin	$CHCl_3$/62/4	92	Benzoin acetate	82-83(83[15])
10	4-Methoxy phenol	none/rt/2	96	4-Methoxyphenyl acetate	31-32(32[10])
11	4-Methyl phenol	CH_2Cl_2/rt/2	99	4-Methylphenyl acetate	103-105/20 (212-213/760[14])
12	2-Nitrophenol	CH_2Cl_2/62/4	90	2-Nitrophenyl acetate	39-40(40-41[14])
13	3-Nitrophenol	CH_2Cl_2/rt/4	96	3-Nitrophenyl acetate	54-55(55-56[14])
14	4-Nitrophenol	CH_2Cl_2/62/2	96	4-Nitrophenyl acetate	80-81(81-82[14])
15	α-Naphthol	CH_2Cl_2/rt/4	98	α-Naphthyl acetate	46-47(47-48[14])
16	β-Naphthol	CH_2Cl_2/rt/3	98	β-Naphthyl acetate	69-70(70[14])
17	Catechol	CH_2Cl_2/rt/3	98	Benzene-1,2-diyl diacetate	62-63(63.5[14])
18	Resorcinol	CH_2Cl_2/rt/2	96	Benzene-1,3-diyl diacetate	156-158/20(278[14])
19	Hydroquinone	CH_2Cl_2/rt/2	98	Benzene-1,4-diyl diacetate	69-70(70[14])
20	Benzene-1,3,5-triol	$CHCl_3$/62/4	96	Benzene-1,3,5-triyl triacetate	104-105(104[14])

[a] Isolated yield.

In conclusion, we have developed an efficient and high yield method for the acetylation of primary and secondary alcohols and phenols. This method has the additional advantages of mild conditions, easy of set up and of work up, inexpensive and reusable catalyst.

Experimental

Boiling and melting point were uncorrected. The products were characterised by IR, ^{1}H NMR and mass spectra and by comparison of their melting or boiling points with literature values.

General procedure for the acetylation of alcohols and phenols:

A mixture of the alcohol or phenol(**1**, 10 mmol), acetic anhydride(**2**, 2 equivalent to each hydroxyl group in the alcohol or phenol) and finely ground sulfamic acid (200 mg, 2.06 mmol) was stirred at room temperature or refluxing temperature for the length of time indicated in Table 1. For the reactions with solvent, CH_2Cl_2 or $CHCl_3$ (5 ml) was also added. The progress of reaction was monitored by TLC. After completion of the reaction, Et_2O (10 ml) was added to the mixture, the sulfamic acid was filtered off and washed with Et_2O(2 x 10 ml). The filtrate was washed with 5% HCl(15 ml), 5% $NaHCO_3$ (15 ml) and brine(2 x 10 ml) successively. After drying($MgSO_4$), the solvent was evaporated under reduced pressure and the crude product was purified by distillation in vacuum or by column chromatography on silica gel to give **3**.

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References

1. (a) Li, T.S.; Li, Y.L. and Liang, X.T. *Steroids*, **1990**, *55*, 263; (b) Rana, S.S.; Barlow, J.J. and Matta, K.L. *Tetrahedron Lett.* **1981**, *22*, 5007; (c)

Green, T.W. and Wuts, P.G.M. *Protective Groups in Organic Synthesis*, Wiley Interscience, New York, 2nd edn., **1991**, pp 87-118; 162-170.

2. (a) Otera, J. *Chem. Rev.*, **1993**, *93*, 1449; (b) Balaji, B.S.; Sasidharan, M.; Kumar, R. and Chanda, B. *Chem. Commun.*, **1996**, 707.
3. (a) Horton, D. *Org. Synth.*, **1973**, *Coll. Vol. 5*, 1; (b) Zhdanov, R.I. and Zhenodarova, S.M. *Synthesis*, **1975**, 222.
4. Scriven, E.F.V. *Chem. Soc. Rev.*, **1983**, *12*, 129.
5. Vedejs, E.; Bennett, N.S. Conn, L.M;. Diver, S.T.; Gingras, M.; Lin, S.; Oliver, P.A. and Peterson, M.J. *J. Org. Chem.*, **1993**, *58*, 7286.
6. Borah, R.; Deka, N. and Sarma, J. *J. Chem. Res. (S)*, **1997**, 110.
7. Cope, A.C. and Herrich, E.C. *Org. Synth.*, **1963**, *Coll. Vol. 4*, 304.
8. Baker, R.H. and Bordwell, F.G. *Org. Synth.*, **1955**, *Coll. Vol. 3*, 141.
9. Iqbal, J. and Srivastava, R.R. *J. Org. Chem.*, **1992**, *57*, 2001.
10. Ishihara, K.; Kubota, M.; Kurihara, H. and Yamamoto, H. *J. Org. Chem.*, **1996**, *61*, 2001.
11. Li, A.X.; Li, T.S. and Ding, T.H. *Chem. Commun.*, **1997**, 1389.
12. Jin, T.S.; Li, T.S. and Duan, G.B. *J. Chem. Res. (S)*, submitted.
13. (a) Rhoad, M.J.and Hory, P.J. *J. Am. Chem. Soc.*, **1950**, *72*, 2216; (b) Zhang, J.Q. *Huaxue Shijie*, **1996**, *37*, 423.
14. Buckingham, J. and Donghy, S.M. *Dictionary of Organic Compounds*, Chapman and Hall, New York, 5th edn., **1982**.
15. Heilbron, I and Bunbury, H.M. *Dictionary of Organic Compounds*, Eyre and Spottiswoode, London, **1953**.

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