Sulphuric Acid Adsorbed on Silica Gel. A Remarkable Acetylation Catalyst

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ABSTRACT: *Sulphuric acid adsorbed on silica gel is a practical and useful catalyst for acetylation of various alcohols, phenols and amines.*

KEY WORDS: *Sulphuric acid, Silica gel, Acetylation alcohols, Amines*

The protection of hydroxy and amino groups by the formation of esters and amides is of great importance in organic synthesis and have been the subject of intensive research in the last few decades [1]. The acetylation of alcohols and phenoles have classically involved acid anhydrides and acid chlorides in the presence of tertiary amines such as triethylamine and pyridine [2], tributylphosphine [3], toluene-*p*-sulfonic acid [4], zinc chloride [5], cobalt chloride [6] and scandium trifluoromethanesulfonate [7]. In addition to the above catalyst, montmorillonite K-10, KSF [8] and HSZ-360 zeolite [9] are also known for the acetylation of alcohols, phenols and amines.

The synthetic utility of supported reagents has been demonstrated during past ten years [10]. In recent years it has been shown that sulphuric acid adsorbed on silica gel can be used as a multipurpose acid catalyst [11]. Continuing our interest performing reaction on solid supports [12] we now report in this communication, the acetylation of alcohols, phenols and amines catalyzed by sulphuric acid adsorbed on silica gel.

A series of alcohols, phenols and amines were acetylated with acetic anhydride under catalysis of sulphuric acid adsorbed on silica gel (Table). Primary and secondary alcohols and phenols were acetylated at room temperature or in refluxing CH_2Cl_2 . Acetylation of tertiary alcohols was successful with this method. *t*-Butanol was acetylated in 87% yield, however triphenylmethanol remained unchanged even when the reaction was performed in refluxing CH_2Cl_2 and excess of catalyst for several hours.

Phenol was acetylated in 15 min in refluxing CH_2Cl_2 whereas resorcinol was not converted to acetylated product after 4 h.

In conclusion in comparison with the presently available synthetic methods for acetylation of alcohols, phenols and amines [1-9] which show draw back from the stand point of yield, price and limited availability of catalyst, the efficiency of the present method is apparent from the availability of inexpensive sulphuric acid and silica gel, easy work up procedure

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Table : Acetylation of alcohols, phenoles and amines with acetic anhydride catalyzed by sulphuric acid adsorbed on silica gel in CH_2Cl_2

Entry	Substrate	Ratio[a]	T/°C	t/m	Product	Yield[b]
1	Propanol	1.5:1	R.T	10	Propyl acetate	95
2	(+)Menthol	1.5:1	R.T	10	(+)Mentyl acetate	90
3	Octanol	1.5:1	R.T	10	Octyl acetate	96
4	Cyclohexanol	1.5:1	R.T	10	Cyclohexyl actate	94
5	Benzyl alcohol	1:1	R.T	B	Benzyl actate	95
6	4-Nitrobenzylalcohol	1:1	R.T	5	4-Nitrobenzyl acetate	95
7	Benzhydrol	3:1	R.T	10	Benzhydryl acetate	79
8	α-Methylbenzyl alcohol	1:1	R.T	5	α-Methylbenzyl acetate	70
9	*t*-Butanol	1:5	R.T	10	*t*-Butyl acetate	87
10	Phenol	4:1	40	15	Phenyl acetate	96
11	Resorcinol	4:1	40	100	—	0
12	α-naphthol	2:1	R.T	15	α-naphtyl acetate	93
13	Hydroquinone	1:1	40	15	Hydroquinyl diacetate	70
14	Benzylamine	1:1	R.T	3	Benzyl acetamide	97
15	4-Ethylaniline	1:1	R.T	3	4-Ethyl acetamide	97
16	2,4-Dimethoxyaniline	1:1	R.T	3	2,4-Dimethoxy acetamide	95
17	N-Methylaniline	1:1	R.T	3	N-Methyl acetamide	94
18	2,6-Diethylaniline	1:1	40	120	2,6-Diethyl acetamide	30
19	4-Methylaniline	6:1	R.T	3	4-Methyl acetamide	95
20	2-Nitroaniline	1:1	40	10	2-Nitro acetamide	90
21	Aniline	1:1	R.T	5	Acetanilide	96
22	1,4-Diamino benzene	1:1	R.T	5	1,4-Benzene diyl diacetamide	97

a) Acetic anhydride: Substrate (mol:mol)

b) Isolated yield

and high yields. Also due to the heterogeneous conditions, all reactions are clean and the work up is so simple that usually give good quality and yield. The catalyst itself is inexpensive and after the reaction it may be recovered in order to be recycled.

EXPERIMENTAL

Alcohols, phenols and amines were available from commercial sources. Acetylated compounds are known and their physical and spectroscopic data were compared with those of authentic samples.

Adsorbtion of sulphuric acid on silica gel

A solution of concentrated sulphuric acid (2 mL) in acetone (20 mL) is added to a solution of silica gel (100 g, Merck 60, 70-230) in acetone (200 mL) at room temperature for 1 h. The solvent is removed under reduced pressure. A yellow brown powder is obtained which can be stored in a desiccator for long period of times without any appreciable loss of activity.

Acetylation of alcohols, phenoles and amines. A typical procedure

A mixture of octan-1-ol (1.6 mL, 10 mmol) in CH_2Cl_2 (10 mL), sulphuric acid adsorbed on silica gel (40 mg) and acetic anhydride (1.4 mL, 15 mmol) was stirred at room temperature for 10 min. The

catalyst was removed by filteration 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 acetylated product (1.6 g, 93%).

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REFERENCES

[1] Greene, T. W. and Wuts, P. G. M., "Protective Groups in Organic Synthesis", John Wiley, New Yourk (1991).

[2] (a) Zhdanov, R. I. and Zhenodarova, S. M., *Synthesis.*, 222(1975); (b) Harton, D., "Organic Synthesis", Collective, **Vol. 5,** 1(1973).

[3] Vedejs, E. and Diner, S. T., *J. Am. Chem. Soc.*, **115,** 3358(1993).

[4] Cope, A. C. and Herick, E. C., "Organic Synthesis", Collective Vol. 4, p. 304(1963).

[5] Baker, R. H. and Bordwell, F. G., "Organic Synthesis", Collective Vol. 3, p. 141 (1955).

[6] Iqbal, J. and Srivastava, R. R., *J. Org. Chem.*, **57,** 2001(1992).

[7] Ishihara, K., Kubota, M., Kurihara, H. and Yamamoto, H. T., *J. Org. Chem.*, **61,** 4560(1996).

[8] Xiao Li, A., Li, T. Sh. and Ding, T. H., *Chem. Commun.*, 1389(1997).

[9] Ballini, R., Basic, G. and Carloxi, S., *Tetrahedron Lett.*, **39,** 6049(1998).

[10] (a) Mckillop, A. and Young, D. W., *Synthesis,* 401 and 481(1979); (b) Balogh, M. and Laszlo, P., "Organic Chemistry Using Clays", Springer Verlag, Berlin (1993).

[11] (a) Chavez, F. and Godinez, R., *Synth. Commun.*, 159, (1992); (b) Chavez, F., Suarez, S. and Diaz, M. A., *Synth. Commun.*, 2335(1994); (c) Riego, J. M., Sedin, Z., Xaldivar, J. M., Marziano, N. C. and Tortato, C., *Tetrahedron Lett.*, **37,** 513(1996); (d) Heravi, M. M., Ajami, D. and Ghassemzadeh, M., *Synth. Commun.*, **29,** 1013(1999).

[12] (a) Heravi, M. M., Ajami, D., Mojtahedi, M. M. and Tabar Hydar, K., *J. Chem. Res.*, 620(1998); (b) Heravi, M. M., Kiakoojori, R. and Tabar Hydar, K., *J. Chem. Res.*, 656(1998); (c) Heravi, M. M. and Ajami, D., *J. Chem. Res.*, 718(1998); (d) Heravi, M. M., Ajami, D. and Tabar Hydar, K., *Monatsch Chem.*, **129,** 1305(1998); (e) Tajbakhsh, M. and Heravi, M. M., *Synth. Commun.*, **22,** 135(1999); (f) Mirza Aghyan, M. and Heravi, M. M., *Synth. Commun.*, **29,** 785(1999); (g) Heravi, M. M., Ajami, D. and Ghassemzadeh, M., *Synthesis,* **3,** 393(1999); (h) Heravi, M. M., Ajami, D., Mojtahedi, M. M., and Ghassemzadeh, M., *Tetrahedron Lett.*, **40,** 561(1999).