
Dodecylbenzenesulfonic acid as an efficient, chemoselective and reusable catalyst in the acetylation and Formylation of alcohols and phenols under solvent-free conditions at room temperature

M. Esmailpour and A. R. Sardarian*

Chemistry Department, College of Sciences, Shiraz University, Shiraz 71454, Iran
E-mail: sardarian@susc.ac.ir

Abstract

Dodecylbenzenesulfonic acid (DBSA) was used as an efficient, cheap and stable Brønsted catalyst for acetylation of alcohols and phenols and formylation of alcohols under solvent-free conditions. Various primary, secondary and tertiary alcohols were acetylated with acetic anhydride as an acetylating agent under solvent-free conditions in the presence of catalytic amount of DBSA at room temperature. Also, formylation of alcohols was catalyzed by DBSA with ethyl formate in high to excellent yields. This method showed high selectivity in acetylation and formylation of various alcohols and phenols. DBSA was recovered and reused in four successive runs without significant deterioration in catalytic activity.

Keywords: Dodecylbenzenesulfonic acid; acetylation; formylation; solvent-free; Reusable catalyst

1. Introduction

Functional group protection strategies are central to target molecule synthesis. Among the many protecting groups of hydroxyl group of alcohols and phenols, acetylation and formylation reactions are one of the most important methods because of easy and fast formation of acetate and formate under mild conditions, their considerable stability under acidic conditions and easy removal of acetyl and formyl groups by alkaline hydrolysis (Rao et al., 2002). Acetyl halides and acetic anhydrides are usually employed as acetylating agents for acetylation of hydroxyl group in alcohols and phenols in the presence of acid or base catalysts (Rao et al., 2002), including 4-pyrrolidinopyridine (PPY) and 4-(dimethylamino)pyridine (DMAP) (Scriven, 1983), InCl_3 (Chakraborti and Gulhane, 2003), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Ghosh et al., 2005), TaCl_5 (Chandrasekhar et al., 1998), metal triflates such as $\text{Al}(\text{OTf})_3$ (Kamal et al., 2007), $\text{Gd}(\text{OTf})_3$ (Alleti et al., 2005), $\text{Sc}(\text{OTf})_3$ (Lee and Park, 2003), $\text{Ce}(\text{OTf})_3$ (Dalpozzo et al., 2003), ZnO (Sarvari and Sharghi, 2005), LiClO_4 (Bandgar et al., 2002), $\text{Mg}(\text{ClO}_4)_2$ (Bartoli et al., 2003), SmI_2 (Ishii et al., 1996), $\text{NH}_2\text{SO}_3\text{H}$ (Jin et al., 1998), $\text{Al}(\text{HSO}_4)_3$ (Shirini et al., 2004), ionic liquids (Lee and Park, 2003), distannoxane (Orita et al., 1999), and solid supported reagents and lipase enzymes (Berger et al., 1991).

Ethyl formate is the choice of formylating reagent for alcohols and phenols because of its availability, its relatively low cost, its easy handling and the instability of the anhydride and the acid chloride of formic acid. Several catalysts have been reported in the literature that are able to perform the formylation reaction by ethyl formate, such as $\text{Bi}(\text{III})$ salts (Mohammadpoor-Baltork et al., 2001a), $\text{Ce}(\text{OTf})_4$ (Iranpoor and Shekarriz, 1999), $\text{In}(\text{OTf})_3$ (Chauhan et al., 1999), silica triflate (Shirini et al., 2007), $\text{TiCl}_3(\text{OTf})$ (Firouzabadi et al., 2008), Chloral (Ram and Meher, 2002), $\text{Mg}(\text{HSO}_4)_2$ (Shirini et al., 2002), heteropoly acids (Habibi et al., 2001) and cerium poly oxometalate (Mirkhani et al., 2004).

However, some of these methods for the acetylation and formylation of alcohols and phenols suffer from one or several of the following disadvantages, such as: harsh reaction conditions, use of toxic solvents and metal containing catalysts, low yields of the desired products, tedious work-up procedure and long reaction times. Therefore, new methods and catalysts for the preparation of esters are still in demand.

We wish to report a simple, efficient, eco-friendly and selective method for the acetylation of alcohols and phenols with acetic anhydride and formylation of alcohols with ethyl formate using 4-dodecylbenzenesulfonic acid (DBSA) as a stable catalyst at room temperature.

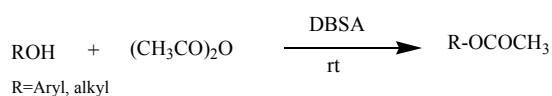
*Corresponding author

2. Results and discussion

2.1. Acetylation of alcohols and phenols

In continuation of our systematic evaluation of the efficacy of DBSA as a catalyst, we report, herein, our results on acylation of alcohols, phenols using DBSA at room temperature under solvent-free conditions (Scheme 1).

Initially, the reaction between benzyl alcohol (1mmol) and acetic anhydride (1.2 mmol), as a model reaction, was examined in the presence of varying amount of the catalyst under solvent-free conditions at ambient temperature and the results were presented in Table 1.



Scheme 1

According to these data, the highest yield of the desired product was obtained in shortest time when 0.1 mmol of DBSA was loaded in the reaction mixture (Table 1, entry 4). In order to elucidate the role of the catalyst, a control reaction was conducted using benzyl alcohol and acetic anhydride in the absence of catalyst and only 5% of benzyl acetate was formed after 12 h at room temperature under solvent-free conditions (Table 1, entry 1). Using higher amount of DBSA made the yield of the reaction lower and the reaction time longer (Table 1, entries 5-7).

On the other hand, this catalyst was not efficient in the presence of common organic solvents such as CH_2Cl_2 , H_2O , CHCl_3 , CH_3CN and $\text{CH}_3\text{CO}_2\text{Et}$ at room temperature (Table 2, entries 1-5). This observation confirms that the solvent-free condition plays an important role in this acetylation reaction and a rate enhancement was carried out without any solvent (Table 2, entry 6).

Table 1. Effect of the amount of DBSA on the conversion of benzyl alcohol to benzyl acetate at room temperature under solvent-free conditions^a

Entry	DBSA (mmol)	Time (min)	Yield ^b (%)
1	None	720	5
2	0.05	15	81
3	0.075	8	86
4	0.1	2	97
5	0.125	4	94
6	0.15	5	93
7	0.2	5	90

^aReaction conditions: benzyl alcohol (1mmol) and acetic anhydride (1.2 mmol), r.t.

^bIsolated yield.

For showing generality and scope of the reaction, the acylation reaction of a wide variety of alcohols and phenols was studied under the optimization

conditions and the results were summarized in Table 3. Although all primary and secondary alcohols carried out the acetylation reaction easily, fast and in quantitatively yields (Table 3, entries 1-3, 13, 18, 19, and 21), primary alcohols reacted with acetic anhydride faster than secondary ones (Table 3, entries 1-3, 13, 18, and 19).

Table 2. Effect of solvent on the acetylation of benzyl alcohol^a

Entry	Solvent	Time (min)	Yield ^b (%)
1	CH_2Cl_2	6	45
2	H_2O	10	52
3	CHCl_3	4	58
4	CH_3CN	3	87
5	$\text{CH}_3\text{CO}_2\text{Et}$	3	91
6	Solvent-free	2	97

^aReaction conditions: benzyl alcohol (1mmol), acetic anhydride (1.2 mmol) and DBSA (0.1 mmol), room temperature.

^bIsolated yield

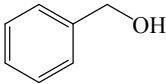
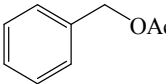
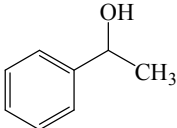
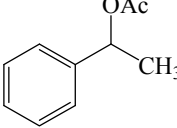
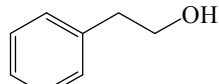
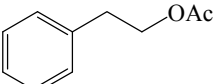
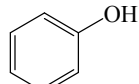
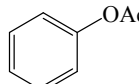
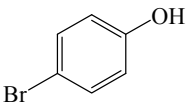
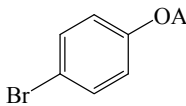
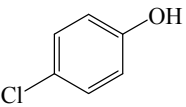
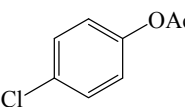
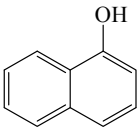
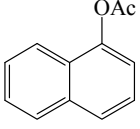
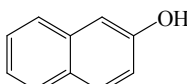
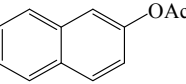
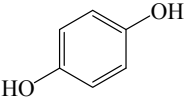
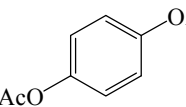
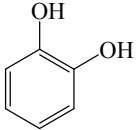
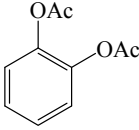
3-Phenyl-2-methyl-2-propanol, as a tertiary alcohol, was also acylated smoothly in high yield without any side product but in longer reaction time in compare to primary and secondary alcohols (Table 3, entry 20).

Phenols were also acetylated in short reaction times with acetic anhydride in the presence of DBSA catalyst under optimized conditions. The acetylation of phenols with electron-donor groups was faster than those with electron-withdrawing groups (Table 3, entries 5, 6, 9-12, 14-17).

Selective acetylation among the different type of alcohols and phenols was checked by using competitive method. In these experiments, a mixture of substrates, 1mmol of each, was treated with 1 mmol of acetic anhydride under solvent-free condition in the presence of DBSA at room temperature. The results were summarized in Table 4. According to these data, it was possible to acetylate primary alcohol selectively against secondary alcohol (Table 4, entry 1) and phenol (Table 4, entry 4). Also, secondary alcohol and phenol were selectively acetylated in the presence of tertiary alcohol (Table 4, entry 2) and lesser active phenols, such as *p*-bromophenol and *p*-nitrophenol, (Table 4, entry 3) respectively.

A comparison among DBSA and the other acid catalysts, which were reported in the literature, in acetylation of alcohols and phenols revealed advantages of DBSA over most of them in terms of lower reaction temperature, shorter reaction times, and higher yields in the acid catalyzed acetylation reaction of alcohols and phenols (Tables 5-7). To show the effect of dodecyl group on the benzene ring of DBSA, the acetylation of benzyl alcohol, (-)-menthol and phenol was explored in the presence of *p*-TSA (Tables 5-7, entry 2). Therefore, the key factor in such chemical transformation is probably not only the acid strength, but also the amphipathic behavior of DBSA which plays an important role in accelerating the reaction (Shrikhande Janhavi, 2007).

Table 3. Acetylation of alcohols and phenols catalyzed by DBSA at room temperature under solvent-free conditions with acetic anhydride^a

Entry	Substrate	Product ^b	Time (min)	Yield ^c (%)	Ref.
1			2	97	(Bartoli et al., 2003)
2			4	94	(Bartoli et al., 2003)
3			2	96	(Bartoli et al., 2003)
4			4	96	(Sarvari and Sharghi, 2005)
5			5	93	(Bartoli et al., 2003)
6			5	94	(Bartoli et al., 2003)
7			6	92	(Bartoli et al., 2003)
8			5	93	(Bartoli et al., 2003)
9			3	94	(Bartoli et al., 2003)
10			4	93	(Bartoli et al., 2003)

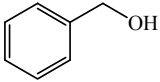
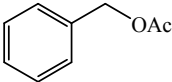
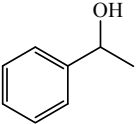
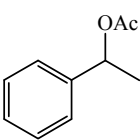
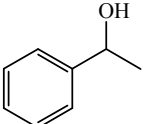
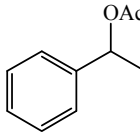
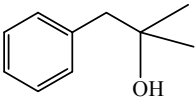
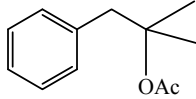
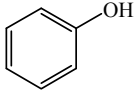
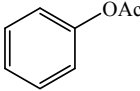
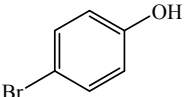
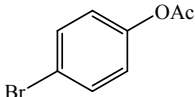
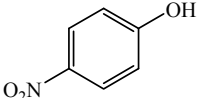
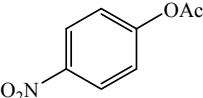
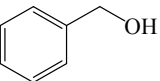
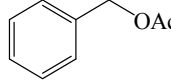
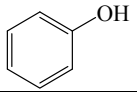
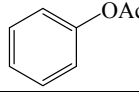
11			4	92	(Bartoli et al., 2003)
12			7	89	(Farhadi and Zaidi, 2009)
13			3	95	(Bartoli et al., 2003)
14			6	88	(Bartoli et al., 2003)
15			3	92	(Yoon et al., 2008)
16			4	94	(Ghosh et al., 2005)
17			4	90	(Bartoli et al., 2003)
18			2	96	(Alleti et al., 2005)
19			3	93	(Sarvari and Sharghi, 2005)
20			20	84	(Niknam and Saberi, 2009b)
21			4	95	(Firouzabadi et al., 2008)

^aReaction conditions: Substrate (1mmol), Ac₂O (1.2 mmol), DBSA (0.1 mmol), room temperature

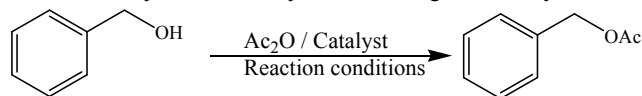
^bThe known products were identified by comparison of their IR, ¹H NMR and ¹³C NMR spectra with those reported in the literature

^cIsolated yield

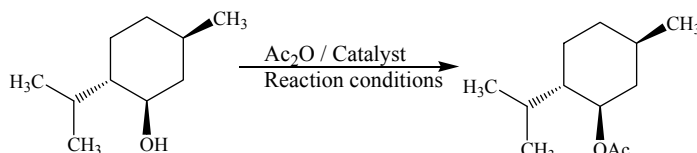
Table 4. Selective acetylation of different alcohols and phenols^a

Entry	Substrate	Product	Yield(%) ^b
1			94
			0
2			89
			0
3			91
			0
			0
4			93
			0

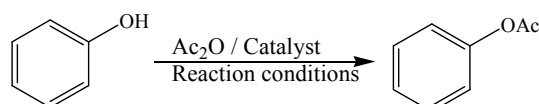
^aReaction conditions: Substrate (1mmol), Ac₂O (1 mmol), DBSA(0.1 mmol), room temperature^bIsolated yield

Table 5. Comparison of some of the reported acid catalysts with DBSA in acetylation of benzyl alcohol using acetic anhydride

Entry	Catalyst	Solvent	Temp (°C)	Time (min)	Yield (%) ^b	Ref.
1	DBSA	Solvent-free	rt	2	97	Present work
2	<i>p</i> -TSA	Solvent-free	rt	5	96	--- ^a
3	SBNPSA	Solvent-free	rt	20	98	(Niknam and Saberi, 2009b)
4	Sulfuric acid ([3-(3-silica propyl) sulfanyl] propyl) ester	Solvent-free	rt	5	96	(Niknam and Saberi, 2009a)
5	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	Solvent-free	rt	72	95	(Heravi et al, 2006)
6	Sulfamic acid	Solvent-free	rt	120	99	(Jin et al., 1998)
7	Cu(BF ₄) ₂	Solvent-free	rt	60	96	(Chakraborti et al, 2004)
8	BiCl ₃	Solvent-free	rt	35	98	(Mohammadpoor-Boltark et al., 2001b)
9	CMPSIM-Gd	DMSO	rt	90	99	(Yoon et al., 2008)

^aThis experiment was performed by the authors^bIsolated yield**Table 6.** Comparison of some of the reported acid catalysts with DBSA in acetylation of (-)-menthol using acetic anhydride

Entry	Catalyst	Solvent	Temp. (°C)	Time (min)	Yield (%) ^b	Ref.
1	DBSA	Solvent-free	rt	3	95	Present work
2	<i>p</i> -TSA	Solvent-free	rt	12	93	--- ^a
3	Saccharinsulfonic acid	CH ₂ Cl ₂	reflux	90	92	(Shirini et al., 2009)
4	Sulfamic acid	CHCl ₃	62	120	NR	(Jin et al., 1998)
5	Cu(BF ₄) ₂	Solvent-free	rt	30	95	(Chakraborti et al, 2004)
6	BiCl ₃	Solvent-free	reflux	20	94	(Mohammadpoor-Boltark et al., 2001b)
7	CMPSIM-Gd	DMSO	rt	24h	18	(Yoon et al., 2008)

^aThis experiment was performed by the authors^bIsolated yield**Table 7.** Comparison of some of the reported acid catalysts with DBSA in acetylation of phenol using acetic anhydride

Entry	Catalyst	Solvent	Temp. (°C)	Time (min)	Yield (%) ^b	Ref.
1	DBSA	Solvent-free	rt	4	96	Present work
2	<i>P</i> -TSA	Solvent-free	rt	10	95	--- ^a
3	SBNPSA	Solvent-free	rt	360	92	(Niknam and Saberi, 2009b)
4	Sulfuric acid ([3-(3-silica propyl) sulfanyl]propyl) ester	Solvent-free	rt	120	0	(Niknam and Saberi, 2009a)
5	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	Solvent-free	rt	60	95	(Heravi et al, 2006)
6	Sulfamic acid	CH ₂ Cl ₂	rt	120	98	(Jin et al., 1998)
7	Cu(BF ₄) ₂	Solvent-free	rt	30	97	(Chakraborti et al, 2004)
8	BiCl ₃	Solvent-free	reflux	50	97	(Mohammadpoor-Boltark et al., 2001b)
9	CMPSIM-Gd	DMSO	rt	5	94	(Yoon et al., 2008)

^aThis experiment was performed by the authors^bIsolated yield

Recyclability of DBSA was examined using the reaction of benzyl alcohol and acetic anhydride under the optimized conditions. The recycled catalyst was reused four times without any additional treatment and considerable loss of activity (Fig. 1).

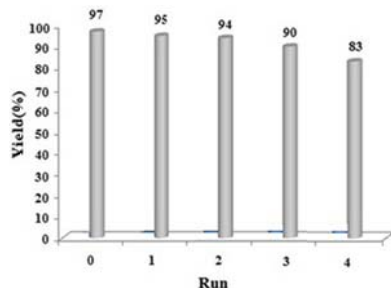
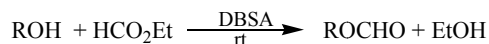


Fig. 1. Investigation of reusability of DBSA in acetylation of benzyl alcohol^a

^aReaction conditions: benzyl alcohol (1 mmol), acetic anhydride (1.2 mmol), DBSA (0.1 mmol), without solvent at room temperature

2.2. Formylation

In this part, formylation of different type of alcohols by ethyl formate in the presence DBSA at room temperature is considered (Scheme 2).



Scheme 2

The reaction conditions for formylation of alcohols was optimized using the reaction of benzyl alcohol (1mmol) with ethyl formate (2mmol), as a model reaction, in the presence of different amounts of DBSA (0-0.3mmol) at room temperature under solvent-free conditions and the results were collected in Table 8. These data revealed 0.2 mmol of DBSA was enough to produce the highest yield of benzyl formate in shortest time at room temperature under solvent-free condition (Table 8, entry4). The formylation reaction did not proceed under similar condition in the absence of DBSA even after 12 h (Table 8, entry 6).

Table 8. Effect of the amounts of DBSA on the conversion of benzyl alcohol to benzyl formate at room temperature under solvent-free conditions^a

Entry	DBSA (mmol)	Time (min)	Yield(%) ^b
1	0.05	20	76
2	0.1	15	78
3	0.15	12	81
4	0.2	10	92
5	0.3	10	90
6	No catalyst	12h	0

^a Reaction conditions: benzyl alcohol (1 mmol), ethyl formate (2 mmol), room temperature

^b Isolated yield

The effect of common organic solvents such as CH_2Cl_2 , CHCl_3 , CH_3CN , $\text{CH}_3\text{CO}_2\text{Et}$ and H_2O was explored on the model reaction and according to the data obtained (Table 9, entries 1-5) the reaction took a longer time to be completed and provided lower yield in compared to the solvent-free conditions.

The effect of amount of ethyl formate in the reaction with benzyl alcohol (1mmol) was also studied and the results were summarized in Table 9. According to these data, using 2 mmol of ethyl formate produced the highest yield of the product in the shortest time under solvent free condition (Table 9, entry 6).

With optimized conditions in hand, the formylation of various alcohols was performed at room temperature and under solvent-free conditions (Table 10).

The experimental results showed that primary and secondary alcohols are converted to their corresponding formates in the presence of 0.2 mmol of the catalyst in high yields (Table 10, entry 1-9), whereas under the same condition tertiary alcohols such as 2-methyl-1-phenylpropan-2-ol carried out the reaction in lower yield after 12h (Table 10, entry 10).

Table 9. Effect of solvent on the formylation of benzyl alcohol at room temperature^a

Entry	Solvent	DBSA (mmol)	Time (min)	Yield ^b (%)
1	CH_2Cl_2	0.2	20	61
2	CHCl_3	0.2	15	65
3	CH_3CN	0.2	15	73
4	$\text{CH}_3\text{CO}_2\text{Et}$	0.2	12	81
5	H_2O	0.2	12	86
6	Solvent-free	0.2	10	92
7	Solvent-free	0.25	10	91
8	Solvent-free	0.15	15	85
9	Solvent-free	0.1	20	79

^aReaction conditions: benzyl alcohol (1 mmol), ethyl formate (2 mmol), DBSA (0.2 mmol), room temperature

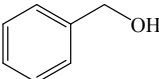
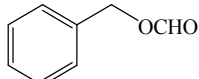
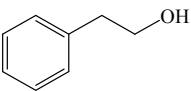
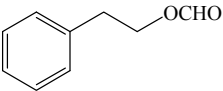
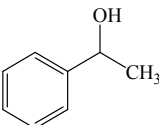
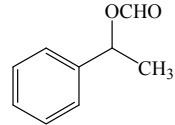
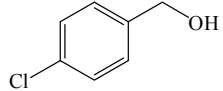
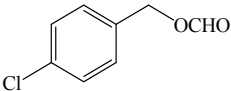
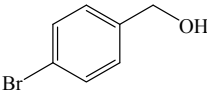
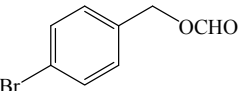
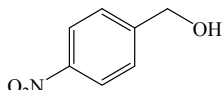
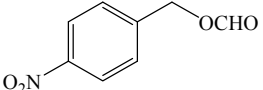
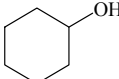
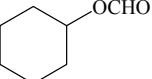
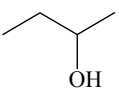
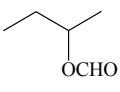
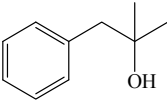
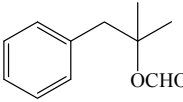
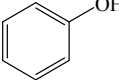
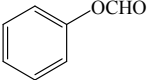
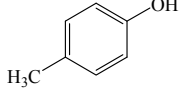
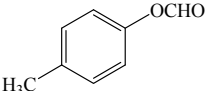
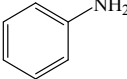
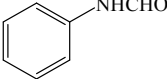
^bIsolated yield

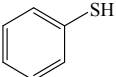
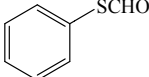
Electron-withdrawing substituents on the aromatic ring of benzyl alcohols, such as *p*-nitrobenzyl alcohol, reacted slower than benzyl alcohol (Table 10, entry4-6). However, phenols, aniline and thiophenol remained intact under the similar conditions (Table 10, entry 11-14).

To show the selectivity of the formylation reaction, using competitive method, an equimolar mixture of a primary and secondary alcohol, secondary and tertiary alcohol, and benzyl alcohol and phenol were subjected to formylation under the optimization condition (Table 11).

This method was shown to be highly selective for formylation of primary alcohols versus secondary alcohols, secondary alcohols in the presence of tertiary alcohols. Also, benzyl alcohol completely carried out formylation in the presence of phenol and phenol was recovered unchanged.

Table 10. Formylation of alcohols with ethyl formate in the presence of DBSA catalyst at room temperature under solvent-free conditions^a

Entry	Substrate	Product ^b	Time (min)	Yield (%) ^c	Ref.
1			10	92	(Niknam and Saberi, 2009b)
2			10	91	(Niknam and Saberi, 2009b)
3			20	89	(Niknam and Saberi, 2009b)
4			25	85	(Shirini et al., 2007)
5			20	84	(Shirini et al., 2007)
6			80	71	(Shirini et al., 2007)
7			25	87	(Niknam and Saberi, 2009b)
8			25	85	(Iranpoor et al., 2005)
9	CH ₃ (CH ₂) ₇ OH	CH ₃ (CH ₂) ₇ OCHO	15	88	(Niknam and Saberi, 2009b)
10			16h	53	(Niknam and Saberi, 2009b)
11			160	NR	-
12			160	NR	-
13			150	NR	-

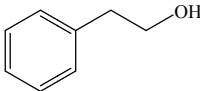
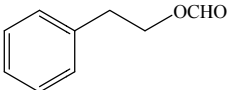
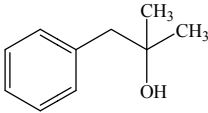
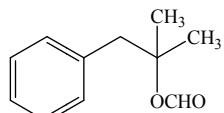
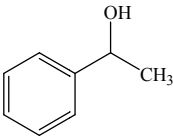
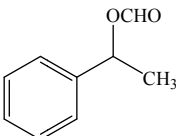
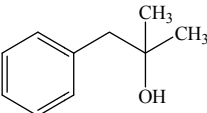
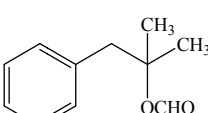
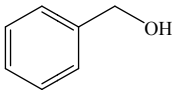
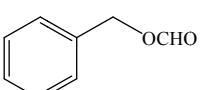
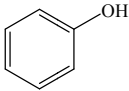
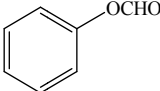
14			150	NR	-
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^aReaction conditions: substrate (1 mmol), ethyl formate (2 mmol), DBSA (0.2 mmol)

^bThe known products were identified by comparison of their IR, ¹H NMR and ¹³C NMR spectra with those reported in the literature

^cIsolated yield

Table 11. Selective formylation of different type of alcohols in the presence of DBSA^a

Entry	Substrate	Product	Yield (%) ^b
1			91
			0
2			87
			0
3			90
			0

^aReaction conditions: substrate (1 mmol), ethyl formate (2 mmol), and DBSA catalyst (0.2 mol), room temperature

^bIsolated yield

Recycling the catalyst was examined using the reaction of benzyl alcohol and ethyl formate under the optimized conditions. The recycled catalyst was reused three times without any additional treatment and without distinct deterioration in catalytic activity (Fig. 2).

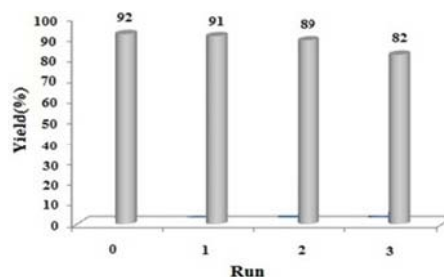


Fig. 2. Investigation of reusability of DBSA for formylation of benzyl alcohol^a

^aReaction conditions: benzyl alcohol (1 mmol), ethyl formate (2 mmol), DBSA (0.2 mmol), without solvent at room temperature

3. Experimental

3.1. General

Chemical materials were purchased from the Merck, Flucka Chemical Company in high purity. The formylated products were characterized by comparison of their spectral and physical data such as NMR, FT-IR, and melting point with available literature data.

The NMR spectra were recorded on a Bruker avance DPX 250MHz spectrometer in chloroform (CDCl_3) using tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer

3.2. General procedure for acetylation with acetic anhydride

To a mixture of substrate (1 mmol) and acetic anhydride (1.2 mmol), DBSA (0.1 mmol) was added and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, CH_2Cl_2 (10mL) and saturated NaHCO_3 (10mL) were added and organic layer was extracted from aqueous layer. The organic layer was washed twice with water ($2 \times 10\text{mL}$), dried over anhydrous Na_2SO_4 , filtered, and concentrated to afford the crude product. If needed, further purification was performed by column chromatography on silica gel to product the pure acetate. Aqueous layer, which includes catalyst salt, was acidified by HCl (5%, 15mL) and then Et_2O (10mL) was added. DBSA catalyst was recovered and regenerated by extraction of this acidic solution and evaporation of diethyl ether under reduced pressure. It is noteworthy that DBSA could be reused without significant decrease in activity.

3.3. General procedure for formylation of alcohols with ethyl formate

DBSA (0.2 mmol) was added to a mixture of substrate (1 mmol) and ethyl formate (2 mmol) and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, CH_2Cl_2 (10mL) and saturated NaHCO_3 (10mL) was added and organic layer was extracted from aqueous layer. The organic layer was washed twice with water ($2 \times 10 \text{ mL}$), dried over anhydrous Na_2SO_4 , filtered, and concentrated to afford the crude product. If needed, further purification was performed by column chromatography on silica gel which produced the pure acetate. Aqueous layer, which includes catalyst salt, was acidified by HCl (5%,

15mL) and then Et_2O (10 mL) was added to the previous solution. DBSA catalyst was recovered and regenerated by extraction of this acidic solution and evaporation of diethyl ether under reduced pressure. It is noteworthy that DBSA could be reused without significant decrease in activity.

4. Conclusion

In conclusion, we have shown that DBSA, which is a cheap, commercially available and stable combined Brønsted acid-surfactant-catalyst (BASC) (Manabe et al., 2001; Sanzhong et al., 2007; Shrikhande Janhavi, 2007), is an efficient, eco-friendly, recyclable, versatile and chemoselective catalyst for the acetylation of alcohols and phenols and formylation of alcohols at room temperature under mild conditions. The method has advantages in term of short reaction times, operation at room temperature, excellent yields and ease of operation, and excellent chemoselectivity. In addition, even hindered substrates can be acetylated with acetic anhydride in high yields at room temperature.

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