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N,N'-Diiodo-*N,N*'-1,2-ethanediylbis(*p*-toluenesulfonamide) as an Efficient Catalyst for Acetylation of Alcohols, Phenols, Amines, and Thiols Under Solvent-Free Conditions

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***N,N'*-DIIDO-*N,N'*-1,2-ETHANEDIYLBIS(*p*-TOLUENESULFONAMIDE) AS AN EFFICIENT CATALYST FOR ACETYLATION OF ALCOHOLS, PHENOLS, AMINES, AND THIOLS UNDER SOLVENT-FREE CONDITIONS**

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****N,N'*-Diiodo-*N,N'*-1,2-ethanediylbis(*p*-toluenesulfonamide) (NIBTS) is a highly efficient catalyst for the acetylation of alcohols, phenols, amines, and thiols under solvent-free conditions. Primary, secondary, tertiary alcohols; phenols; amines; and thiols can be easily acetylated in good to excellent yields at 80 °C.***

Keywords Acetic anhydride; acetylation; alcohols; amines; NIBTS; phenols; thiols

INTRODUCTION

Protection of functional groups is highly essential in organic synthesis. Among various protecting methods, acetylation of alcohols, phenols, amines, and thiols is typically performed using acetic anhydride with the aid of either base or acid catalysts.^{1,2} A variety of procedures is routinely performed for the preparation of acetyl derivatives, including homogeneous or heterogeneous catalysts such as 4-(dimethylamino)pyridine (DMAP),³ 4-pyrrolidinopyridine (PPY),⁴ *N,N,N,N'*-tetramethylethylenediamine,⁵ tributylphosphine,⁶ alumina,⁷ iodine,⁸ La(NO₃)₃ · H₂O,⁹ cobalt chloride,¹⁰ zinc chloride,¹¹ montmorillonite K-10 and KSF,¹² zeolite HSZ-360,¹³ zirconium sulfophenyl phosphonate,¹⁴ Sc(OTf)₃,¹⁵ In(OTf)₃,¹⁶ Cu(OTf)₂,¹⁷ Al(OTf)₃,¹⁸ TMSOTf,¹⁹ magnesium bromide,²⁰ bromodimethylsulfonium bromide,²¹ ferric perchlorate adsorbed on silica-gel,²² RuCl₃,²³ InCl₃,²⁴ ZrCl₄,²⁵ Mg(ClO₄)₂,²⁶ NBS,²⁷ AlPW₁₂O₄₀,²⁸ ZrOCl₂ · 8H₂O,²⁹ zeolite H-FER,³⁰ and MoO₃/Al₂O₃.³¹ Although a large number of methods for acetylation are available, most of the aforementioned methods have one or more drawbacks, which include long reaction times, harsh reaction conditions, and often, poor yields of the desired products. Furthermore, most of the metal triflates are rather expensive, and some of them must be used under critically anhydrous conditions for optimum results. Also, most of the catalysts are usually used in environmentally harmful organic solvents, thereby generating large amounts of corrosive

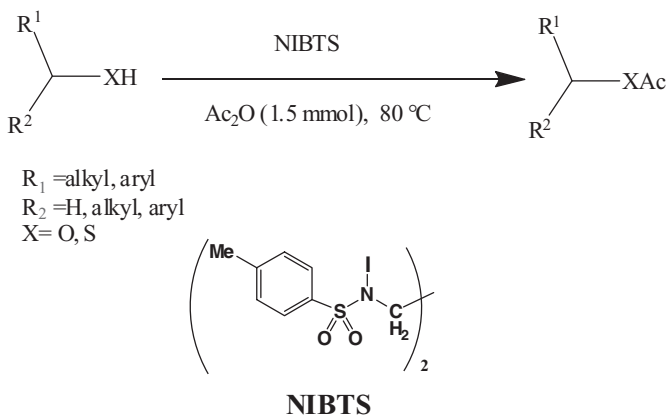
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and toxic waste products.³² Hence, there is a need for improved reagents for the acetylation of selected substrates.

Recently, the use of *N*-halo reagents in organic reactions has become an important part of our research program.^{33–38} In continuation of these studies, in this article we report the application of *N,N'*-Diiodo-*N,N'*-1,2-ethanediylbis(*p*-toluenesulfonamide) (NIBTS)³⁹ as a recyclable catalyst for acetylation of alcohols, phenols, amines, and thiols with acetic anhydride, at 80°C under solvent-free conditions in excellent yields (Scheme 1).



Scheme 1

RESULTS AND DISCUSSION

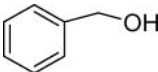
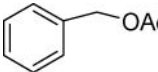
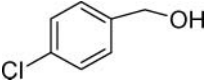
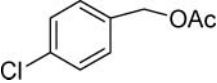
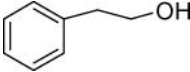

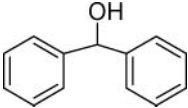
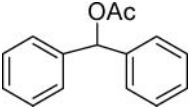
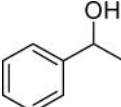
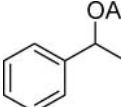
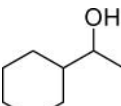
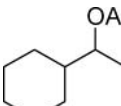
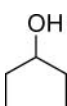
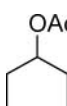
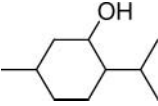
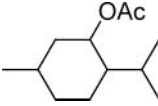
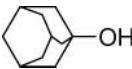
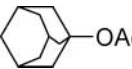
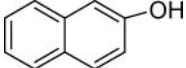
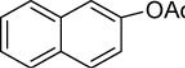
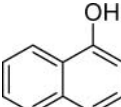
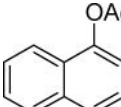
For optimized conditions for this reaction, we used benzyl alcohol. We found that 1 mmol benzyl alcohol and 1.5 mmol acetic anhydride in the presence of 0.06 mmol NIBTS at 80°C under solvent-free conditions afforded the best result (Table I, entry 1). Other compounds also reacted well under the same conditions, to give the corresponding acetylated products in excellent yields without any evidence for the formation of side products. The general applicability and efficiency of this reaction is evident from the wide range of compounds studied (Table I). For example, strongly deactivated *p*-nitrophenol (Table I, entry 15) quantitatively afforded the corresponding acetates within 1 min. Furthermore, nonactivated secondary alcohols such as menthol and hindered tertiary alcohols such as adamantanol could also be converted to corresponding acetylated products in good yields under similar reaction conditions (Table I, entries 9 and 10). In the absence of a catalyst, using the same reaction conditions, the corresponding product for phenol was obtained in low yield (25–30%) even after prolonged reaction time (1.5 h).⁸

We also found that NIBTS was a reusable catalyst; after several runs, the catalytic activity of the catalyst was almost the same as it was of fresh catalyst.

Since this catalyst contains iodine atoms that are attached to nitrogen atoms, it is possible that it releases I^+ in situ, which can act as a Lewis acid in the reaction medium.³⁹ We hoped that this would be sufficient to catalyze the acetylation of alcohols, phenols, amines, and thiols.

In order to show the merit of this method, Table II compares some of our results with some of the aforementioned methods for the acetylation of phenol, benzyl alcohol, and benzyl thiol.

Table I Acetylation of alcohols, phenols, amines, and thiols with Ac₂O using NIBTS

Entry	Substrate	Product	Time (min)	Yield% ^a	Ref.
1			10	99	17
2			20	98	21
3			13	97	9
4	CH ₃ (CH ₂) ₇ OH	CH ₃ (CH ₂) ₇ OAc	40	94	28
5			60	96	28
6			30	98	17
7			100	92	17
8			90	95	18
9			180	95	31
10			900	94	31
11			7	98	28
12			8	98	18

(Continued on next page)

Table I Acetylation of alcohols, phenols, amines, and thiols with Ac₂O using NIBTS (*Continued*)

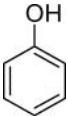
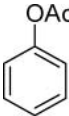
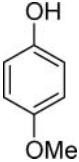
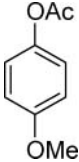


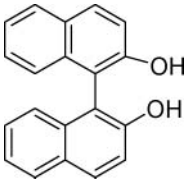
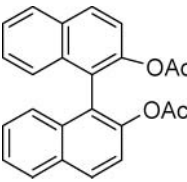
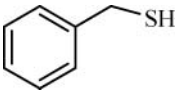
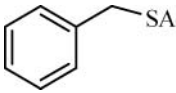
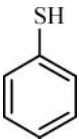
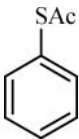
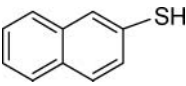
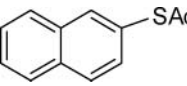
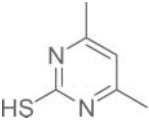
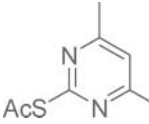
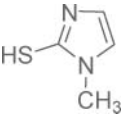
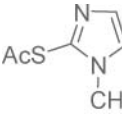
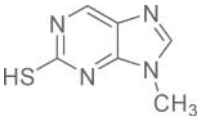
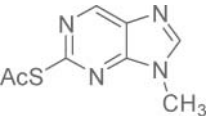
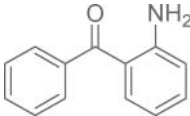
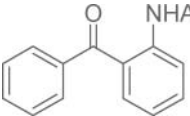
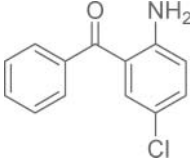
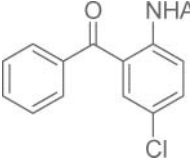
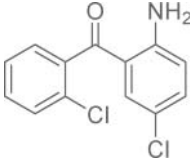
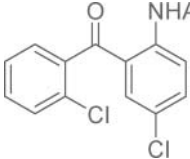
Entry	Substrate	Product	Time (min)	Yield% ^a	Ref.
13			2	99	18
14			2	99	18
15			1	98	18
16			15	97	17
17			50	97	28
18			90	85	18
19			180	86	17
20			20	72	—
21			40	67	—

Table I Acetylation of alcohols, phenols, amines, and thiols with Ac₂O using NIBTS (*Continued*)

Entry	Substrate	Product	Time (min)	Yield% ^a	Ref.
22			30	78	—
23			10	92	—
24			15	89	—
25			15	85	—

^aIsolated yield.

In conclusion, we have shown that NIBTS is a recyclable catalyst with no loss of activity for acetylation of alcohols, phenols, amines, and thiols with acetic anhydride under solvent-free conditions after several runs. The advantages of this procedure over earlier reported processes includes its simplicity, fast and clean reaction, high yield, and the absence of organic solvent.

EXPERIMENTAL

Products of the following procedures were characterized by their physical constants, and compared with authentic samples by IR and NMR spectroscopy.

Table II Reaction times and yields for previously published methods

Substrate	Conditions	Reaction time	Yield (%)	Ref.
Phenol	I ₂ / 85–90°C	5 min	99	8
Phenol	MoO ₃ / Al ₂ O ₃ / rt	60 min	94	31
Benzyl alcohol	I ₂ / 85–90°C	5 min	98	8
Benzyl alcohol	Zeolite H-FER/ 75°C	1.5 h	99	30
Benzyl thiol	Zeolite H-FER/ 75°C	5 h	94	30
Benzyl thiol	MoO ₃ / Al ₂ O ₃ / rt	45 min	95	31

General Procedure for Acetylation

To a stirred mixture of Ac_2O (1.5 mmol) and NIBTS (6 mol%) at 80°C , alcohols, phenols, amines, and thiols (1 mmol) were added with continued stirring at the same temperature for the indicated times (Table I). After completion of the reaction (TLC monitoring), the mixture was cooled to room temperature. Then CCl_4 (10 mL) was added, and the reagent was removed by filtration. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. If necessary, the product was purified by thin layer chromatography using n-hexane/acetone as the solvent system to afford the pure product (85–99%).

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