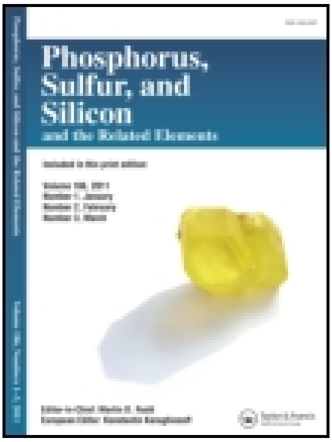
This article was downloaded by: [Karolinska Institutet, University Library]
On: 17 November 2014, At: 22:11
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

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

Ramin Ghorbani-Vaghei [a] & Zahra Toghraei-Semiromi [a]
[a] Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran

Published online: 02 Aug 2010.

To cite this article: Ramin Ghorbani-Vaghei & Zahra Toghraei-Semiromi (2010) 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, Phosphorus, Sulfur, and Silicon and the Related Elements, 185:8, 1701-1707, DOI: 10.1080/10426500903241721

To link to this article: http://dx.doi.org/10.1080/10426500903241721

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Phosphorus, Sulfur, and Silicon, 185:1701–1707, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903241721

Taylor & Francis
Taylor & Francis Group

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

Ramin Ghorbani-Vaghei and Zahra Toghraei-Semiromi
Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran

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] $La(NO_3)_3$. H_2O,[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] $RuCl_3$,[23] $InCl_3$,[24] $ZrCl_4$,[25] $Mg(ClO_4)_2$,[26] NBS,[27] $AlPW_{12}O_{40}$,[28] $ZrOCl_2.8H_2O$,[29] zeolite H-FER,[30] and MoO_3/Al_2O_3.[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

---

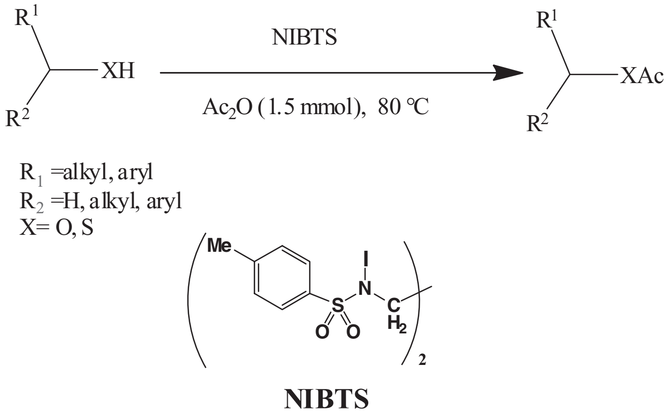
Received 16 March 2009; accepted 4 August 2009.

We are thankful to Bu-Ali Sina University, Center of Excellence and Development of Chemical Methods (CEDCM), for financial support.

Address correspondence to Ramin Ghorbani-Vaghei, Department of Organic Chemistry, Faculty of Chemistry Bu-Ali Sina University, Hamadan, Iran. E-mail: rgvaghei@yahoo.com

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

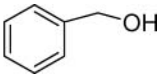
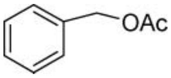
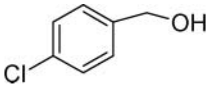
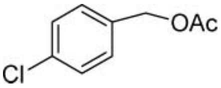
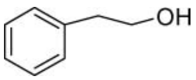
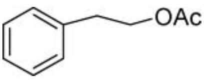
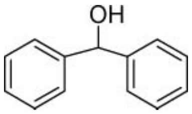
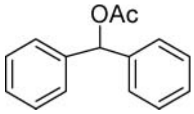
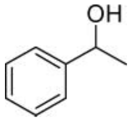
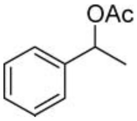
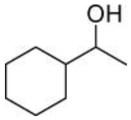
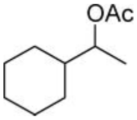
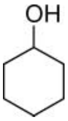
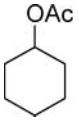
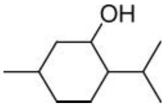
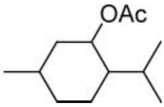
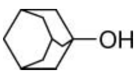
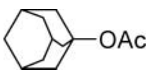
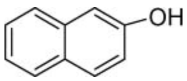
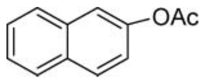
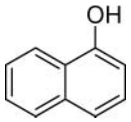
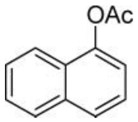
For optimized conditions for this reaction, we used benzyl alcohol. We found that 1 mmol benzyl alcohol and 1.5 mmol acetic anhydride in the presence of 0.06 mmol NIBTS at 80°C under solvent-free conditions afforded the best result (Table I, entry 1) Other compounds also reacted well under the same conditions, 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 Ac_2O using NIBTS

Entry	Substrate	Product	Time (min)	Yield%[a]	Ref.
1			10	99	17
2			20	98	21
3			13	97	9
4	$CH_3(CH_2)_7OH$	$CH_3(CH_2)_7OAc$	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 Ac_2O using NIBTS *(Continued)*

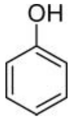
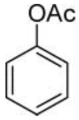
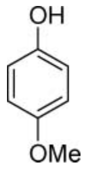
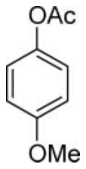
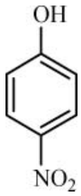
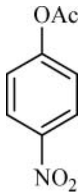
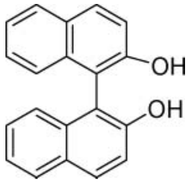
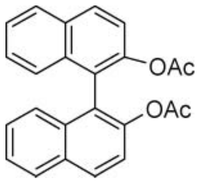
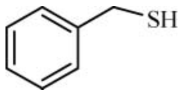
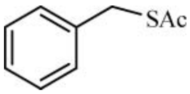
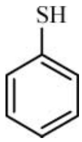
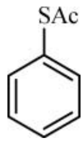
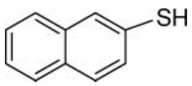
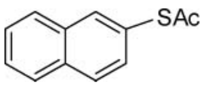
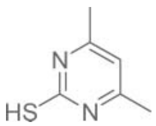
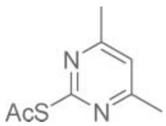
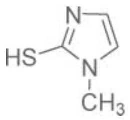
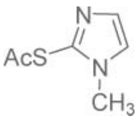
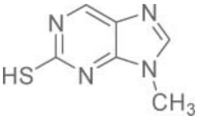
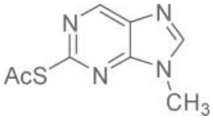
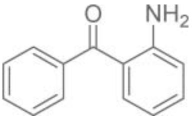
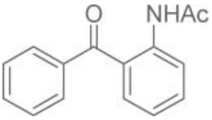
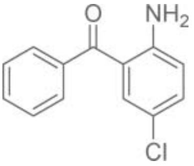
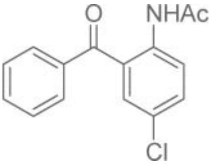
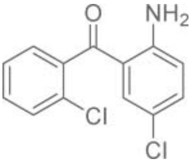
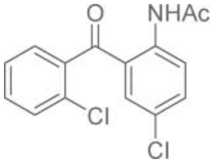
Entry	Substrate	Product	Time (min)	Yield%[a]	Ref.
13			2	99	18
14			2	99	18
15			1	98	18
16			15	97	17
17			50	97	28
18			90	85	18
19			180	86	17
20			20	72	—
21			40	67	—

Table I Acetylation of alcohols, phenols, amines, and thiols with Ac_2O using NIBTS *(Continued)*

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

[a] Isolated 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_2O_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_2O_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%).

REFERENCES

1. T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd ed. (Wiley, New York (1999).
2. R. C. Larock, In *Comprehensive Organic Transformations* (VCH, New York, 1989), p. 980.
3. G. Hofle, V. Steglish, and H. Vorbruggen, *Angew. Chem. Int. Ed. Engl.*, **17,** 569 (1978).
4. E. F. V. Scriven, *Chem. Soc. Rev.*, **12,** 129 (1983).
5. T. Sano, K. Ohashi, and T. Oriyama, *Synthesis*, 1141 (1999).
6. E. Vedejs, N. S. Bennett, L. M. Conn, S. T. Diver, M. Gingras, S. Lin, P. A. Oliver, and M. J. Peterson, *J. Org. Chem.*, **58,** 7286 (1993).
7. G. W. Breton, M. J. Kurtz, and S. L. Kurtz, *Tetrahedron Lett.*, **38,** 3825 (1997).
8. N. Ahmed and J. E. V. Lier, *Tetrahedron Lett.*, **47,** 5345 (2006).
9. Y. Srikanth Reddy, M. Narasimhulu, N. Suryakiran, K. Chinni Mahesh, K. Ashalatha, and Y. Venkateswarlu, *Tetrahedron Lett.*, **47,** 6825 (2006).
10. J. Iqbal and R. R. Srivastava, *J. Org. Chem.*, **57,** 2001 (1992).
11. R. H. Baker and F. G. Bordwell, *Organic Synthesis Collective*, **3,** 141 (1955).
12. A. X. Li, T. S. Li, and T. H. Ding, *Chem. Commun.*, 1389 (1997).
13. R. Ballini, G. Bosica, S. Carloni, L. Ciaralli, R. Maggi, and G. Sartori, *Tetrahedron Lett.*, **39,** 6049 (1998).
14. M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, and M. Rossi, *Synth. Commun.*, **30,** 1319 (2000).
15. H. Zhao, A. Pendri, and R. B. Greenwald, *J. Org. Chem.*, **63,** 7559 (1998).
16. K. K. Chauhan, C. G. Frost, I. Love, and D. Waite, *Synlett*, 1743 (1999).
17. P. Saravanan and V. K. Singh, *Tetrahedron Lett.*, **40,** 2611 (1999).
18. A. Kamal, M. N. A. Khan, K. S. Reddy, Y. V. V. Srikanth, and T. Krishnaji, *Tetrahedron Lett.*, **48,** 3813 (2007).
19. P. A. Procopiou, S. P. D. Baugh, S. S. Flack, and G. G. A. Inglis, *Chem. Commun.*, 2625 (1996).
20. S. V. Pansare, M. G. Malusare, and A. N. Rai, *Synth. Commun.*, **30**, 2587 (2000).
21. A. T. Khan, S. Islam, A. Majee, T. Chattopadhyay, and S. Ghosh, *J. Mol. Catal. A: Chem.*, **239,** 158 (2005).
22. A. Parma, J. Kaur, R. Goyal, B. Kumar, and H. Kumar, *Synth. Commun.*, **28,** 2821 (1998).
23. S. K. De, *Tetrahedron Lett.*, **45,** 2919 (2004).
24. A. K. Chakraborti and R. Gulhan, *Tetrahedron Lett.*, **44,** 6749 (2003).
25. A. K. Chakraborti and R. Gulhan, *Synlett*, 627 (2004).
26. G. Bartoli, M, Bosco, R. Dalpozzo, E. Marcantoni, M. Massaccesi, and L. Sambri, *Synlett*, 39 (2003).
27. B. Karimi and H. Seradj, *Synlett*, **4,** 519 (2001).
28. H. Firouzabadi, N. Iranpoor, F. Nourouzi, and K. Amani, *Chem. Commun.*, 764 (2003).
29. R. Ghosh, M. Swarupananda, and A. Chakraborty, *Tetrahedron Lett.*, **46,** 147 (2005).
30. S. P. Chavan, R. Anand, K. Pasupathy, and B. S. Rao, *Green Chemistry*, **3,** 320 (2001).

31. J. K. Joseph, S. L. Jain, and B. Sain, *J. Mol. Catal. A: Chem.*, **267,** 108 (2007).
32. H. J. Yoon, S. M. Lee, J. H. Kim, H. J. Cho, J. W. Choi, S. H. Lee, and Y. S. Lee, *Tetrahedron Lett.*, **49,** 3165 (2008).
33. R. Ghorbani-Vaghei, M. A. Zolfigol, M. Chegeny, and H. Veisi, *Tetrahedron Lett.*, **47,** 4505 (2006).
34. R. Ghorbani-Vaghei and H. Jalili, *Synthesis*, **7,** 1099 (2005).
35. R. Ghorbani-Vaghei and E. Shahbazee, *J. Braz. Chem. Soc.*, **16,** 647 (2005).
36. M. A. Zolfigol, R. Ghorbani-Vaghei, S. Mallakpour, G. Chehardoli, A. Ghorbani Choghamani, and A. Yazdi Hosain, *Synthesis*, **10,** 1631 (2006).
37. R. Ghorbani-Vaghei, H. Jalili, E. Shahbazee, and H. Veisi, *J. Chin. Chem. Soc.*, **53,** 379 (2006).
38. R. Ghorbani-Vaghei, E. Shahbazee, and H. Veisi, *Mendeleev Commun.*, 207 (2005).
39. R. Ghorbani-Vaghei, *Tetrahedron Lett.*, **44,** 7529 (2003).