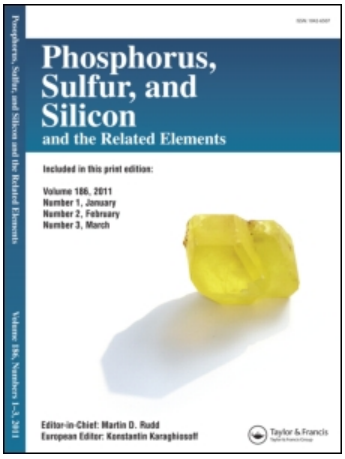


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

N,N'-Dibromo-*N,N'*-1,2-ethanediylbis(benzene sulfonamide) as an Efficient Catalyst for Acetylation and Formylation of Alcohols Under Mild Conditions

Ardeshir Khazaei[a]; Amin Rostami[b]; Zahra Rosta[a]; Ali Alavi[a]
[a] Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran [b] Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran

Online publication date: 28 December 2009

To cite this Article Khazaei, Ardeshir , Rostami, Amin , Rosta, Zahra and Alavi, Ali(2010) '*N,N'*-Dibromo-*N,N'*-1,2-ethanediylbis(benzene sulfonamide) as an Efficient Catalyst for Acetylation and Formylation of Alcohols Under Mild Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 1, 181 — 186
To link to this Article: DOI: 10.1080/10426500902758337
URL: http://dx.doi.org/10.1080/10426500902758337

Phosphorus, Sulfur, and Silicon, 185:181–186, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902758337

Taylor & Francis
Taylor & Francis Group

N,N′-DIBROMO-*N,N′*–1,2-ETHANEDIYLBIS(BENZENE SULFONAMIDE) AS AN EFFICIENT CATALYST FOR ACETYLATION AND FORMYLATION OF ALCOHOLS UNDER MILD CONDITIONS

Ardeshir Khazaei,[1] Amin Rostami,[2] Zahra Rosta,[1] and Ali Alavi[1]

[1]*Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran*
[2]*Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran*

An efficient method for the acylation and formylation of alcohols and phenols by using an acylating/formylating agent (acetic anhydride and formic acid) in the presence of a catalytic amount of N,N′-dibromo-N,N′–1,2-ethanediylbis(benzene sulfonamide) under mild and solvent-free conditions at room temperature in good to excellent yields is described. The use of protic acids and metal Lewis acids is avoided.

Keywords Acetic anhydrides; acetylation; alcohols; *N,N′*-dibromo-*N,N′*-1,2-ethanediylbis (benzene sulfonamide); formic acid; formylation; phenols

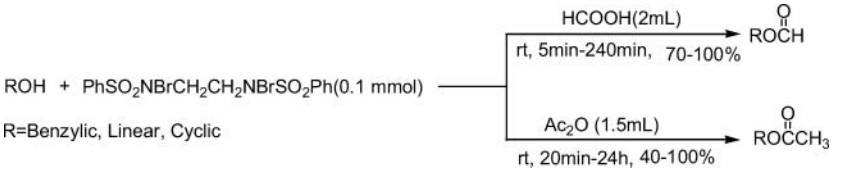
INTRODUCTION

Among the various protecting groups used for the hydroxyl function, the acetyl is the most common because of its ease of formation as well as mild conditions for deprotection. O-Formylation is also a very important process, because the formate esters serve as a useful synthetic reagent and intermediate.[1] Due to the instability of the anhydride and the acid chloride of formic acid, formylation of alcohols by formic acid and transesterfication using ethyl formate are important synthetic reactions. Lewis acid catalysts have been used to mediate the reaction between a hydroxyl group and acylating/formylating agent.[2–15] Despite a number of methods that are currently available, new and efficient methods are still in strong demand. On the other hand, these acetylation/formylation methodologies suffer from disadvantages such as stringent and complicated conditions; use of hazardous, strongly acidic, and costly materials; water-sensitive catalysts, etc.

Received 5 September 2008; accepted 19 January 2009.
The authors acknowledge the Bu-Ali Sina University and Kurdistan University Research Councils for partial support of this work.
Address correspondence to Ardeshir Khazaei, Faculty of Chemistry, Bu-Ali Sina University, Hamadan 65178-38683, Iran. E-mail: khazaei_1326@yahoo.com

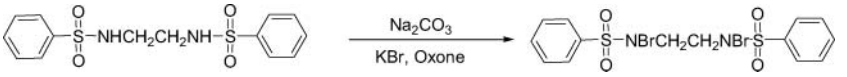
RESULTS AND DISCUSSION

Recently, we described the silylation of alcohols and phenols[16] and tetrahydropyranylation/depyranylation of hydroxy groups[17] by *N,N′*-dibromo-*N,N′*–1,2-ethanediylbis (benzene sulfonamide) (BNBBS). In continuation of our studies in the applications of *N*-halo reagents,[18–20] which are inexpensive, low in toxicity, highly stable towards humidity, and air stable,[21] we found that a catalytic amount of BNBBS is able to promote quantitative acetylation and formylation of alcohols and phenols at room temperature, in good to high yields, and requires only a short reaction time, in solvent-free conditions, with a simple method and easy workup procedure (Scheme 1).



Scheme 1

Initially, BNBBS was prepared using the recently reported green method for preparation of *N*-halosaccharin.[22] In this method, the use or handling of the toxic and corrosive molecular bromine and dichloromethane as solvent is avoided (Scheme 2). Also, the reaction condition is mild, the yield is moderate, the isolation of the product in high purity is simple, and water is the reaction solvent.



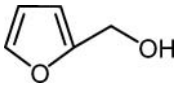
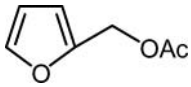
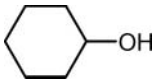
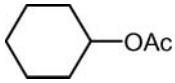
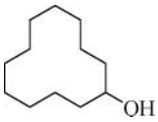
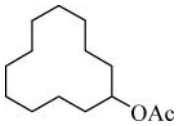
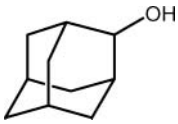
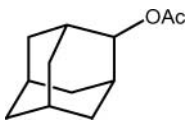
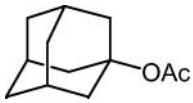
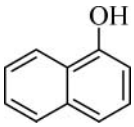
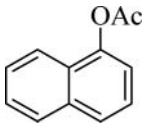
Scheme 2

The catalytic application of BNBBS was investigated for the acetylation of various hydroxyl compounds using acetic anhydride under solvent-free conditions at room temperature (Table I).

Subsequently, we discovered that the formylation of different types of alcohols can be performed with formic acid in the presence of a catalytic amount of BNBBS under solvent-free conditions at room temperature with good to high yields (Table II). Under these reaction conditions, there were no side products.

The actual role of BNBBS is not clear. However, on the basis of the previously reported mechanism,[27] one explanation for this process is that BNBBS probably generates small quantities of in situ HBr, which may be the actual catalyst for the acetylation and formylation reactions (as a protic acid). Another explanation is that BNBBS might act as a source for the formation of Br^+, which in turn activates the carbonyl group of Ac_2O to produce the highly reactive acylating agent (as a Lewis acid). However, at this time the

Table I Acetylation of the alcohols or phenols (1 mmol) using Ac_2O (1.5 mmol) catalyzed with BNBBS (0.1 mmol) under solvent-free conditions at room temperature

Entry	Substrate	Time (min)	Product[a]	Yields[b] (%)	[Ref][c]
1	4-OMe−$C_6H_4CH_2OH$	60	4-OMe−$C_6H_4CH_2OAc$	80	6, 10, 11, 5, 15, 2, 3
2	4-Cl−$C_6H_4CH_2OH$	60	4-Cl−$C_6H_4CH_2OAc$	91	12, 5, 11,3
3	4-NO_2−$C_6H_4CH_2OH$	120	4-NO_2−$C_6H_4CH_2OAc$	40	18, 12, 2,3
4		120		93	—
5	$PhCH_2CH_2OH$	300	$PhCH_2CH_2OAc$	93	18, 10, 11, 4, 2, 3
6	PhCH(OH)Ph	360	PhCH(OAc)Ph	92	21, 10, 4, 5,
7	$CH_3CH(Ph)OH$	180	$CH_3CH(Ph)OAc$	80	10, 13, 5, 2,3, 4
8	$CH_3(CH_2)_4CH(OH)CH_3$	15	$CH_3(CH_2)_4CH(OAc)CH_3$	87	18
9		10		90	8, 15, 11, 12, 2, 3, 4
10		20		94	18
11		20		95	8
12		360		50	5, 6, 12, 8, 7
13		20		88	15

[a]All products were characterized by comparison of their spectral data (^{1}H NMR, IR) with those of authentic samples.[23–26]

[b]Isolated yields.

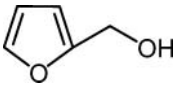
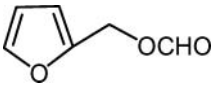
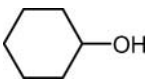
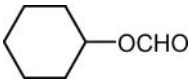
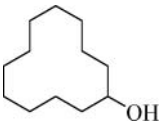
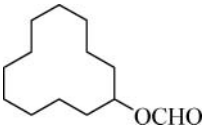
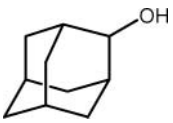
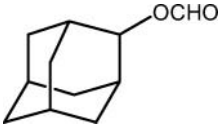
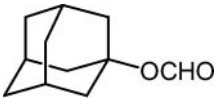
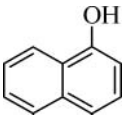
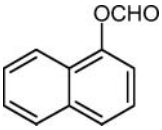
[c]References for previously reported products.

precise role of BNBBS is not clear, and the actual role of this reagent should be studied in further detail.

CONCLUSION

In summary, we have developed the catalytic application of BNBBS for acetylation and formylation of hydroxyl compounds, essentially under neutral and solvent-free conditions. In addition, the most notable advantages of this methodology are mild condition (room temperature), low cost, easy preparation, low toxicity, easy workup, and high yield. The use of protic acids and metal Lewis acids is avoided.

Table II Formylation of alcohols using HCOOH (20 mmol) in the presence of a catalytic amount of BNBBS (0.1 mmol) at room temperature

Entry	Substrate	Time (min)	Product[a]	Yields[b] (%)	[Ref][c]
1	4-OMe−$C_6H_4CH_2OH$	3	4-OMe−$C_6H_4CH_2OCHO$	88	7,3, 4
2	4-Cl−$C_6H_4CH_2OH$	60	4-Cl−$C_6H_4CH_2OCHO$	94	9,13,2,3,4
3	4-NO_2−$C_6H_4CH_2OH$	240	4-NO_2−$C_6H_4CH_2OCHO$	70	4, 13,2,3
4		immediate		95	—
5	$PhCH_2CH_2OH$	40	$PhCH_2CH_2OCHO$	93	11, 2,3,4
6	PhCH(OH)Ph	60	PhCH(OCHO)Ph	93	5, 4
7	$CH_3CH(Ph)OH$	90	$CH_3CH(Ph)OCHO$	75	9, 3
8	$CH_3(CH_2)_4CH(OH)CH_3$	45	$CH_3(CH_2)_4CH(OCHO)CH_3$	87	—
9		80		85	7, 2, 3, 4
10		90		95	14
11		55		92	14, 13
12		90		70	7, 13
13		180		Trace	—

[a]All products were characterized by comparison of their spectral data (^{1}H NMR, IR) with those of authentic Samples.[23–26]

[b]Isolated yields.

[c]References for previously reported products.

EXPERIMENTAL

Preparation of *N,N′*-Dibromo-*N,N′*–1,2-ethanediylbis(benzene sulfonamide) [BNBBS][19]

To solution of the sulfonamide (50 mmol, 25.0 g), Na_2CO_3 (25 mmol, 2.65 g), and KBr (50 mmol) in water (250 mL), a solution of oxone (30.75 g, 50 mmol) in water (30 mL) was added slowly at 0°C. After stirring for 24 h at room temperature, the solid was filtered off, washed with cold distilled water, and dried to give the pure BNBBS.

^{1}H NMR ($CDCl_3$), δ (ppm): 3.29 (4H, s), 7.26 (2H, m), 7.55 (4H, m), 7.85 (4H, m); EIMS: (m/z) = 495 (M+); CHN Anal. Calcd for $C_{14}H_{14}Br_2N_2O_4S_2$: C 33.75, H 2.83, N 5.62, S 12.87. Found: C 33.80, H 2.86, N 5.68, S 12.81.

General Procedure for Acetylation of Alcohols and Phenols Using Ac_2O Catalyzed with BNBBS Under Solvent-Free Conditions

To a solution of alcohol or phenol (1 mmol) and acetic anhydride (1.5 mL), BNBBS (0.1 mmol, 50 mg) was added, and the mixture was stirred at room temperature for the specified time (Table I). After completion of the reaction, the reaction was quenched with saturated $NaHCO_3$ (10 mL). The product was extracted with CH_2Cl_2 (3 × 10 mL), and the organic layer was dried over anhydrous Na_2SO_4. CH_2Cl_2 was evaporated under reduced pressure to afford almost pure products. For further purification, the resulting mixture was applied on a silica gel pad and was washed with a mixture of *n*-hexane:acetone (10:1).

General Procedure for Formylation of Alcohols Using Formic Acid Catalyzed with BNBBS Under Solvent-Free Conditions

To a solution of alcohol (1 mmol) and formic acid (2 mL), BNBBS (0.1 mmol, 50 mg) was added, and the mixture was stirred at room temperature for the specified time (Table II). After completion of the reaction (TLC), the reaction was quenched with saturated $NaHCO_3$ (10 mL). The product was extracted with CH_2Cl_2 (3 × 10 mL), and the organic layer was dried over anhydrous Na_2SO_4. The CH_2Cl_2 was evaporated under reduced pressure to give almost pure products. In the some cases, the reaction mixture was passed through a short column of silica gel using *n*-hexane:acetone (10:1) as an eluent.

REFERENCES

1. P. J. Kocienski, *Protecting Groups* (Thieme, Stuttgart, Germany, 1994).
2. N. Iranpoor, H. Firouzabadi, and M. A. Zolfigol, *Synth. Commun.*, **28,** 1923 (1998).
3. M. H. Habibi, S. Tangestaninejad, V. Mirkhani, and B. Yadollahi, *Tetrahedron*, **57,** 8333 (2001).
4. F. Shirini, M. A. Zolfigol, and M. K. Mohammadi, *Phosphorus, Sulfur, and Silicon*, **178,** 1617 (2003).
5. B. Karimi and J. Maleki, *J. Org. Chem.*, **68,** 4951 (2003).
6. A. K. Chakraborti, L. Sharma, R. Gulhane, and Shivani, *Tetrahedron*, **59,** 7661 (2003), and references cited therein.
7. V. Mirkhani, S. Tangestaninejad, M. Moghadam, B. Yadollahi, and L. Alipanah, *Monatsh. fur Chem.*, **135,** 1257 (2004).
8. F. Shirini, M. A. Zolfigol, and M. Abedini, *Monatsh. fur Chem.*, **135,** 279 (2004).
9. F. Shirini, M. A. Zolfigol, and B. Mallakpour, *Russ. J. Org. Chem.*, **41,** 634 (2005).
10. J. S. Yadav, A. V. Narsaiah, B. V. S. Reddy, A. K. Basak, and K. Nagaiah, *J. Mol. Catal. A: Chem.*, **230,** 107 (2005).
11. N. Iranpoor, H. Firouzabadi, and A. Jamalian, *Tetrahedron Lett.*, **46,** 7963 (2005).
12. R. Tayebee1 and M. H. Alizadeh, *Monatsh fur Chem.*, **137,** 1063 (2006).
13. F. Shirini, K. Marjani, H. Taherpour-Nahzomi, and M. A. Zolfigol, *Phosphorus, Sulfur, and Silicon*, **182,** 1245 (2007).
14. M. A. Zolfigol, G. Chehardoli, M. Dehghanian, K. Niknam, F. Shirini, and A. Khoramabadi-Zada, *J. Chin. Chem. Soc.*, **55,** 885 (2008).

15. F. Rajabi, *Tetrahedron Lett.*, **50**(4), 395 (2009).
16. A. Khazaei, A. Rostami, S. Rahmati, and M. Mahboubifar, *Phosphorus, Sulfur, and Silicon*, **182,** 537 (2007).
17. A. Khazaei, A. Rostami, and M. Mahboubifar, *Catal. Commun.*, **8,** 383 (2007).
18. A. Khazaei, A. Rostami, Z. Tanbakochian, and Z. Zinati, *J. Braz. Chem. Soc.*, **17,** 206 (2006).
19. A. Khazaei, A. Rostami, A. Raiatzadeh, and M. Mahboubifar, *Can. J. Chem.*, **85,** 336 (2007).
20. A. Rostami, A. Khazaei, M. Mahboubifar, and S. Rahmati, *Org. Prep. Pro. Inter.*, **40,** 303 (2008).
21. E. Kolvari, A. Ghorbani-Choghamarani, P. Salehi, F. Shirini, and M. A. Zolfigol, *J. Iran. Chem. Soc.*, **4,** 126 (2007).
22. S. P. L. De Souza, J. F. M. Da Silva, and M. C. S. De Mattos, *Synth. Commun.*, **33,** 935 (2003).
23. C. J. Pouchart and B. Jacqlynn, Eds., *The Aldrich Libraray of ^{13}C and ^{1}H FT NMR Spectra* (Aldrich Chemical, Milwaukee, WI, USA, 1993, Vol. I, I.
24. TCI, *Organic Chemicals Catalog*, 2002–2003, No. 36.
25. Merck Index, 2005–2007.
26. *CRC Handbook of Chemistry & Physics*, 83rd ed, 2002–2003.
27. B. Karimi, G. R. Ebrahimian, and H. Seradj, *Org. Lett.*, **1,** 737 (1999).