

Efficient, Solvent-Free and Rapid Oxidation of Alcohols to Carbonyl Compounds with *N,N'*-Dibromo-*N,N'*-1,2-ethanediybis(benzene sulfonamide)

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N,N'-Dibromo-*N,N'*-1,2-ethanediybis(benzene sulfonamide) (BNBBS): a safe, neutral and efficient reagent was utilized for the rapid and selective oxidation of alcohols to carbonyl compounds with no side reactions such as oxidations of carbon-hydrogen bonds, over oxidation of aldehydes and bromination of aromatic rings; under solvent-free condition, at room temperature with excellent yield.

Key Words: Solvent-free, Oxidation, Alcohols, Carbonyl compounds, *N,N'*-Dibromo-*N,N'*-1,2-ethanediybis(benzene sulfonamide).

INTRODUCTION

Oxidation is one of the most important classes of reactions in synthetic organic chemistry. The development of new oxidizing agents and the modification of known reagents have been studied actively in recent years^{1,2}.

The known chemical methodologies for selective oxidation of alcohols to carbonyl compounds use either conventional mineral oxidants in stoichiometric amounts³⁻⁶ or environmentally benign oxidizing agents like molecular oxygen, hydrogen peroxide catalyzed by transition metal compounds⁷⁻¹⁸. The former method generates considerable amount of inorganic waste and is therefore environmentally not very attractive.

Nowadays, new synthetic methods must include as component the ecological point of view. It has become primordial to minimize the quantity of toxic waste and byproducts from chemical processes, to decrease the amount of solvents in the reaction media and/or during the following workups. This new behaviour imposed the recycling of solvents or the discovery of other alternative synthetic strategies, such as photoreactions^{19,20} or the use of solvents such as water or green solvents²¹. The best ecological solution is, of course, to use no solvent at all. And effectively, solvent-free reactions or solid-state reactions have been particularly developed²².

In connection with our ongoing research program directed toward the development of *N*-halo reagents²³, present research in this area is aimed at eliminating waste, maximizing the incorporation of raw materials into the final product, avoiding,

where possible, the use of auxiliary substances including solvents and employing (recyclable) reagent. Herein we report a fast, simple and convenient methodology for the oxidation of alcohols to the corresponding carbonyl compounds with use of *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(benzene sulfonamide) as a reagent.

EXPERIMENTAL

All the material were purchased from Merck Co. (Darmstadt, Germany).

Preparation of *N,N'*-1,2-ethanediybis(benzene sulfonamide) (1): Benzenesulfonyl chloride (30.0 g, 169.25 mmol) was placed in a beaker, then ethylenediamine (8 mL, 0.0789 mol) was added dropwise (for 0.5 h) and the mixture was stirred with a glass rod. The mixture was heated (90 °C) and stirred for 0.5 h. The 100 mL distilled H₂O and filtered off. Crude product was recrystallized by EtOH; yield: 88 %; m.p. 160 °C. IR (KBr, ν_{\max} , cm⁻¹): 3319 (m), 3272 (s), 1583 (w), 1327 (s), 1156 (s), 1092 (s), 998 (m), 906 (m), 840 (m), 754 (s), 687 (s). ¹H NMR (CDCl₃) δ (ppm): 3.28-3.56 ppm (4H, d), 5.5 (2H, s), 7.5-7.9 (5H, m).

Preparation of *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(benzene sulfonamide) (2): The sulfonamide (1) (10.0 g, 20 mmol) was dissolved in a slight molar excess of chilled aq. NaOH solution (3 M) at room temperature and the solution was transferred to a beaker. A solution of Br₂ (3 mL, 0.0584 mol) in CCl₄ (6 mL) was added to the solution with vigorous stirring. Immediately a yellow precipitate began to form. The

yellow precipitate was collected by suction on a Büchner funnel, washed with cold distilled water (30 mL) and then dried in a vacuum desiccator at room temperature for 6 h. The yield of pure product was (83 %). The product was stable at room temperature and not sensitive to air. IR (KBr, ν_{\max} , cm^{-1}): 2854 (m), 1310 (s), 1088 (m), 841 (m), 721 (s), 687 (m), 594 (m). $^1\text{H NMR}$ (CDCl_3) δ (ppm): 3.28-3.56 ppm (4H, d), 7.66 (2H, d), 7.93 (2H, d).

General procedure for oxidation of alcohols with BNBS:

Oxidant (1.5 mmol) and the alcohol (1 mmol) were added to mortar and the mixture was pulverized vigorously with a pestle. A spontaneous reaction took place at room temperature [Table-1, monitored by TLC (9:1, *n*-hexane/acetone)]. After completion of the reaction, *n*-hexane (15 mL) was added and the insoluble sulfonamide **1** was removed by filtration. Evaporation of the *n*-hexane under reduced pressure gave the corresponding carbonyl compounds in 80-94 % yields isolated as their 2,4-dinitrophenylhydrazone derivatives, which were recrystallized by ethanol.

TABLE-1
OXIDATION OF ALCOHOLS WITH BNBS UNDER SOLVENT-FREE CONDITIONS AT ROOM TEMPERATURE

Entry	ROH	Subst/ BNBS	Time (min)	Yield (%)*,**
1		1.0:1.5	2	87
2		1.0:1.5	4	94
3		1.0:1.5	5	90
4		1.0:1.5	6	92
5	$(\text{C}_2\text{H}_5)_2\text{CH}(\text{OH})$	1.0:1.5	4	80
6		1.0:1.5	5	80
7	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	1.0:1.5	7	83
8		1.0:1.5	35	87
9	$\text{CH}_3\text{CH}(\text{OH})(\text{CH}_2)_4\text{CH}_3$	1.0:1.5	6	85
10		1.0:1.5	5	80

*Products were characterized by melting points the corresponding of 2,4-dinitrophenylhydrazone derivatives and their IR and $^1\text{H NMR}$ spectra.

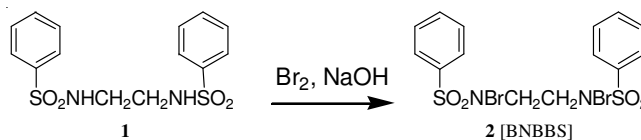
**Isolated yields as their 2,4-dinitrophenylhydrazone derivatives.

RESULTS AND DISCUSSION

Recently, we have shown that *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(*p*-toluene sulfonamide) (BNBTS) in presence of $(\text{CH}_3)_2\text{S}$ in CH_2Cl_2 at -15°C is a powerful reagent for the oxidation of primary and secondary alcohols to aldehydes and ketones²⁴. Some limitations of this reagent encouraged us to investigate the ability of another protocol for the efficient and highly rapid conversion of various type of alcohols to their corresponding carbonyl compounds.

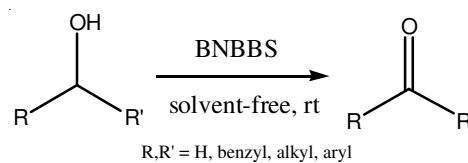
Therefore, we now introduced *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(benzene sulfonamide) (**2**) which is a stable

compound and can be stored and used for several months without any loss of activity. It is inexpensive and the preparation of this reagent is easy, also it is soluble in most of the organic solvents and is not explosive even when heated in solution. This reagent **2** was prepared similar to other reported reagent^{23a} from *N,N'*-1,2-ethanediybis(benzene sulfonamide) (**1**) by the action of molecular bromine in alkaline medium (**Scheme-I**).



Scheme-I

In view of this minor difference between this reagent (BNBS) and the older one (BNBTS) it is interesting to note that we found selective oxidation of a wide range of alcohols with this reagent (BNBS) **2**, is not only take place in more convenient conditions and more simpler work-up, but also the time of reactions reduce to just a few minutes in the comparison with BNBTS [*N,N'*-dibromo-*N,N'*-1,2-ethanediybis(*p*-toluene sulfonamide)] (**Scheme-II**, Table-1). So in this present method, the application of *N*-bromo sulfonamides, BNBS as a green, rapid and selective oxidation reagent for the transformation of a wide rang of alcohols into the corresponding carbonyl compounds has been investigated (**Scheme-II**).



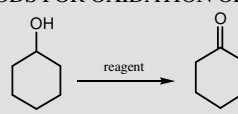
Scheme-II

The results of the oxidation of aliphatic (cyclic and acyclic), aromatic (with electron-withdrawing and electron-releasing groups), to the corresponding carbonyl compounds in the presence of BNBS under solvent free conditions are presented in Table-1. The reaction proceeds in good yields within short times (Table-1).

Side reactions such as oxidations of carbon-hydrogen bonds, overoxidation of aldehydes and bromination of aromatic rings, were not observed. On the basis of our investigations, in comparison with the presence of solvent (CH_2Cl_2), the oxidation of alcohols to the corresponding carbonyl compounds with BNBS under solvent-free conditions were the more simple work up and more rapid²⁵.

As shown in Table-2, the advantages or the characteristic aspects of the described method in this communication in comparison with other previously *N*-halo reported reagents for the oxidation of cyclohexanol are: (i) The reaction has been occurred in a very short time^{24,26-29}. (ii) There is no need to use a co-reagent such as heavy metals^{24,26-29}, therefore has good economic and environmental viewpoints. (iii) This method proceeds under neutral conditions without having any assistance of acids or bases²⁴. (iv) The reactions occur at room temperature^{24,29}. (v) The need for solvent is avoided^{24,26-29}. The other advantages of BNBS are, the low cost, no moisture sensitivity and no special efforts require for preparation (Table-2).

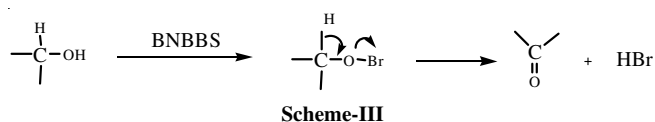
TABLE-2
COMPARISON OF THE ACTIVITY OF THIS PROCEDURE WITH
VARIOUS METHODS FOR OXIDATION OF CYCLOHEXANOL



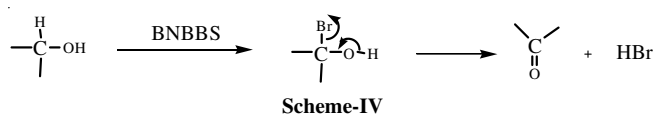
Entry	Catalyst	Condition	Time	Yield (%)	Ref
1	BNBBS	Solvent-free, rt	5.0 min	90	This work
2	BNBTS	CH ₂ Cl ₂ , (CH ₃) ₂ S, Et ₃ N, -15 °C	3.0 h	90	25
3	DABCO-Br ₂	CH ₂ Cl ₂ , rt	3.5 h	84	26
4	NCS, TEMPO, TBACl*	CH ₂ Cl ₂ , rt	–	–	27
5	Bis(quinuclidine) bromine, AgBF ₄	CH ₂ Cl ₂ , rt	0.5 h	102	28
6	NBS, Bu ₄ NI	Acetonitrile, m.w. (150 W)	–	N.R.	30
7	NBS, Co	Acetonitrile, reflux	1.5 h	80	29

*Reaction with cyclohexanol has not been reported.
rt = Room temperature.

The mechanism of the oxidation has not been clearly established, although two interpretations have been advanced. While it is generally accepted that a "positive" halogen is the attacking species in polar media, the site of attack may be open to question. It has been suggested that the primary or secondary alcohol forms a hypobromite³⁰ which readily loses hydrogen bromide to form the carbonyl product (**Scheme-III**).



An alternate mechanism has been suggested³⁰ in which it is proposed that oxidation proceeds through halogen substitution of a hydrogen on the carbon atom bearing the -OH group, with rapid loss of hydrogen halide (**Scheme-IV**). Here, the rate-determining step is the cleavage of the C-H bond to form the halo intermediate.



Conclusion

The friendly environmental advantages of this method are: (i) The lower toxicity and the decrease of the amount of solvent allow the increase of the safety and lower costs. (ii) *N,N'*-Dibromo-*N,N'*-1,2-ethanediyldis(benzene sulfonamide) (BNBBS) is a recyclable, inexpensive, non-metallic, low toxic and corrosive, air and water stable oxidant. (iii) The procedure is simple and allows for very rapid and selective oxidation of

alcohols to carbonyl compound under very mild, neutral and solvent-free condition. (iv) After the complication of reaction, the reagent was converted to *N,N'*-1,2-ethanediyldis(benzene sulfonamide) (**1**), which can be isolated, brominated and reused as oxidation reagent for many times without decreasing the yield. (v) No need to use supports such as alumina, zeolite, or silica for reaching very clean product.

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