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The application of *N*,*N*′-dibromo-*N*,*N*′-1,2-ethanediylbis-(*p*-toluenesulphonamide) as a powerful reagent for the oxidation of primary and secondary alcohols to aldehydes and ketones

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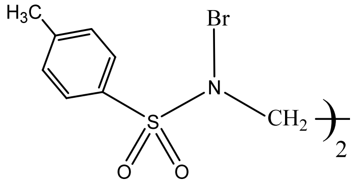
Abstract—Aliphatic and benzylic alcohols are readily oxidized to aldehydes and ketones in good yields under mild conditions by *N*,*N*′-dibromo-*N*,*N*′-1,2-ethanediylbis(*p*-toluenesulphonamide) [BNBTS].

The selective oxidation of primary and secondary alcohols to aldehydes and ketones in organic chemistry is very important and can be achieved by many reagents,[1] that can be used, either in an isolated form[2] or generated 'in situ'.[3] One of the classic reagents is *N*-chlorosuccinimide which is used for the oxidation of alcohols.[4] Other oxidizing agents are polymer-supported hypobromite which oxidizes secondary alcohols to ketones,[5] and polymer-supported iodate which oxidizes catechols to quinones.[6] *N*-Chloronylon 6,6 is used for the oxidation of alcohols[7] and sulphides.[8]

These oxidizing agents are relatively expensive and difficult to prepare, therefore it was decided to study the application of *N*,*N*′-dibromo-*N*,*N*′-1,2-ethanediylbis(*p*-toluenesulphonamide) [BNBTS],[9] which is relatively easy to make. We now report a convenient method for conversion of alcohols to aldehydes and ketones using BNBTS (Fig. 1).

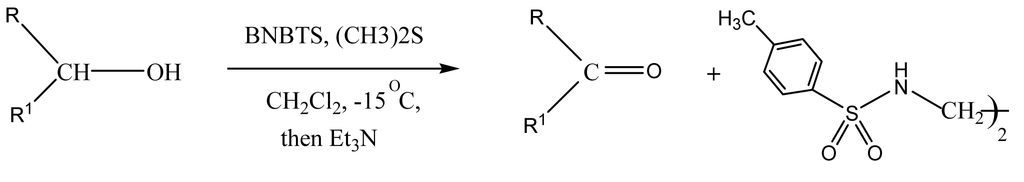
Primary and secondary alcohols were found to be oxidized to aldehydes and ketones using BNBTS/dimethyl sulfide without overoxidation to carboxylic acids (Scheme 1).

The results of the conversion of various alcohols to aldehydes and ketones are presented in Table 1.



1 BNBTS

Figure 1.



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R, R^1= alkyl, H

Scheme 1.

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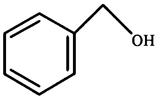
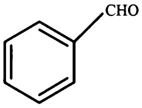
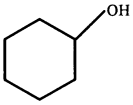
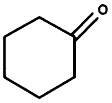
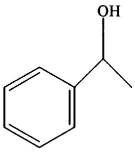
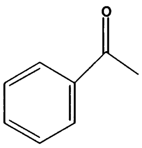
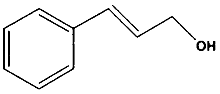
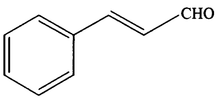
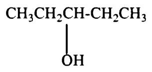
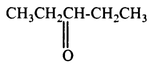
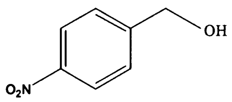
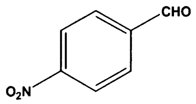
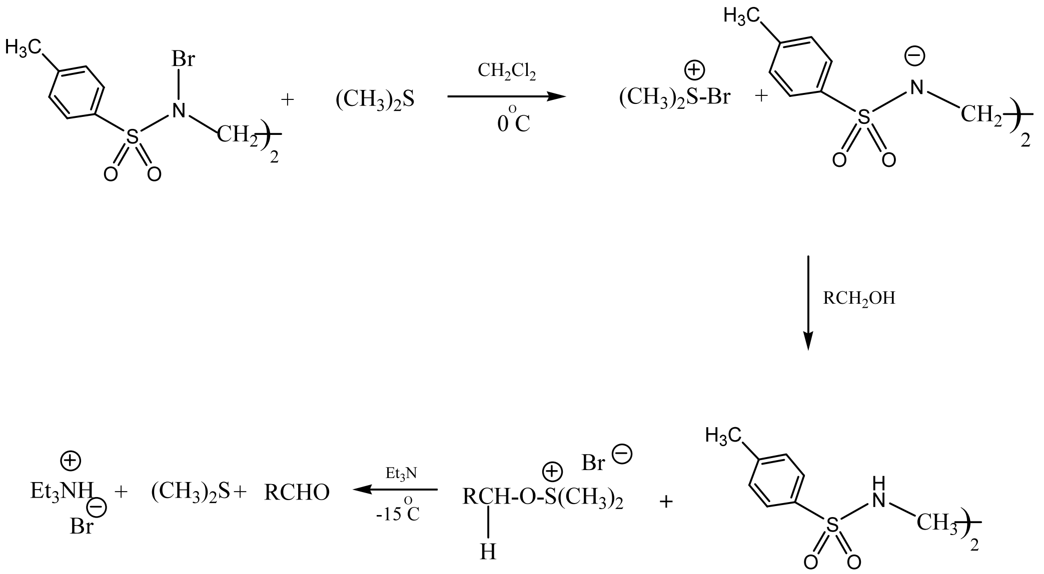
Table 1. Oxidation with BNBTS

Entry	Substrate	Product[a]	Yield (%)
1			95
2			90
3			90
4			89
5	 $\mathrm{CH_3CH_2\underset{\displaystyle OH}{\underset{\vert}{C}}H\text{-}CH_2CH_3}$	 $\mathrm{CH_3CH_2\underset{\displaystyle O}{\underset{\Vert}{C}}H\text{-}CH_2CH_3}$	90
6			95

[a]Products were characterized by their physical properties, comparison with authentic samples, and by spectroscopic methods.



Scheme 2.

Since BNBTS contain two bromine atoms which are attached to nitrogen atoms it is very possible that this reagent releases Br^+ in situ which can act as an electrophilic species.[9] Therefore the following mechanism can be suggested for the conversion of alcohols to aldehydes and ketones (Scheme 2).

The advantages of BNBTS are as fellows:

1. The preparation of BNBTS is easy.
2. BNBTS is stable in atmospheric conditions for two months.
3. After complete of reaction and evaporation of CH_2Cl_2, the sulphonamide is recovered and can be reused many times without decreasing the yield.

IR and NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a 90 MHz Jeol FT NMR spectrometer, respectively.

General procedure for oxidation of alcohols with *N*,*N′*-dibromo-*N*,*N′*-1,2-ethanediylbis (*p*-tolouenesulphonamide). The cool dimethyl sulphide (2 ml) was added dropwise to a magnetically stirred solution of BNBTS (5 mmol) in dry CH_2Cl_2 (30 ml) at about 0°C under nitrogen in a round bottom is flask (250 ml) equipped with a reflux condenser and a calcium chloride guard tube. It was cooled to −15°C. The alcohol (5 mmol) in CH_2Cl_2 (10 ml) was added dropwise to the mixture, and stirred for 3 h under the same conditions. Then triethylamine (5 ml) in CH_2Cl_2 (5 ml) was added dropwise to the mixture, which was then allowed to reach room temperature. The solution was poured into distilled water (10 ml). The insoluble sulphonamide **2** was removed by filtration and washed with cold methylene chloride (10 ml). The organic layer was separated from the aqueous layer. Removal of the solvent under reduced pressure gave the crude product. The product being dissolved in ether and the ether solution washed, dried and concentrated.

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