

## **SODIUM BISMUTHATE OXIDATION OF ALCOHOLS**

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### **ABSTRACT**

Sodium bismuthate in an acid medium reacts with primary and secondary aliphatic alcohols and benzylic alcohols under mild conditions to give the corresponding carbonyl compounds in moderate to high yields. Sodium bismuthate can be applied advantageously for the oxidation of benzylic alcohols.

### **INTRODUCTION**

In 1950 Rigby first discovered the synthetic potential of sodium bismuthate in organic oxidations when he demonstrated the cleavage of vicinal diols and the conversion of acyloins to  $\alpha$ -diketones in high yield (Rigby, 1950). In spite of Rigby's work and more recent studies by a number of groups on the oxidation of phenols with sodium bismuthate (Adderly and Hewgill, 1968; Kon and Mcneilis, 1976), bismuth reagents are seldom used in organic synthesis. Considering the high oxidation potential of bismuth(V) compounds (Burstein and Wright, 1969) and to widen the application of sodium bismuthate, it was decided to explore the oxidation of alcohols with this reagent.

### **EXPERIMENTAL**

**Materials:** All chemicals used were reagent grade products. The alcohols were purified and dried by the usual methods (Perrin et al, 1966).

The following procedure for the oxidation of benzyl alcohol is representative. In a 100 ml round bottomed flask with a magnetic bar were added 0.1 g (0.01 mol) of benzyl alcohol, 15 ml of glacial acetic acid and 1.79 g (0.01 mol) of sodium bismuthate. The reaction mixture was permitted to stir at room temperature for 3 days; bismuth in the resul-

ting solution was removed by precipitation with 5–6 ml of 3.33 M phosphoric acid. The crude product was treated with an excess of a saturated solution of 2,4-dinitrophenyl - hydrazine in sulfuric acid and alcohol and kept in refrigerator for ca 24h. The precipitated 2,4-dinitrophenyl - hydrazone (DNP) was filtered off, dried, weighed, recrystallized from acetic acid and weighed again.

The melting points determined are uncorrected.

## RESULTS AND DISCUSSION

The oxidation of various alcohols with sodium bismuthate is shown in Table. It was found that sodium bismuthate in acetic acid oxidizes alcohols to corresponding carbonyl compounds:

Table

Oxidation of alcohols to carbonyl compounds using sodium bismuthate under heterogeneous conditions

Alcohol <sup>a</sup>	Product	Reaction time <sup>b</sup>	mp of 2,4-DNP(C°)		Yield (%)
			found	reported	
1- Butanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	6	122	123	46
1- Pentanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHO	6	96	98	40
2- Phenylethanol	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHO	6	119	121	39
2- Propanol	(CH <sub>3</sub> ) <sub>2</sub> CO	7	127	126	36
Cyclohexanol	Cyclohexanone	6	161	162	45
Benzyl alcohol	C <sub>6</sub> H <sub>5</sub> CHO	3	235	237	80
m-Nitrobenzyl alcohol	m-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	4	290	292	77
p-Nitrobenzyl alcohol	p-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	4	319	320	82

a: The molar ratio of sodium bismuthate: alcohol was 1:1

b: Reaction time in days at room temperature



(R: H, alkyl  
or phenyl)

The reactions were typically run by mixing equimolar amounts of sodium bismuthate and alcohol in glacial acetic acid and stirring the heterogeneous mixture in a stoppered flask until the orange colour of the sodium bismuthate had dissipated. However, the addition of more than 1 molar equivalent of oxidant does not improve the yields.

The percentage conversions to carbonyl compounds were estimated by preparing their 2,4-dinitrophenylhydrazone derivatives. As it is seen from Table primary and secondary alcohols afford moderate yields of carbonyl compounds. Acetone obtained in the oxidation of 2-propanol was lost in part during workup due to its high volatility. Benzylic alcohols are smoothly oxidized to give the corresponding aldehydes. Initially it was found that benzyl alcohol was oxidized under the reaction conditions in 6h to benzaldehyde in 37% yield. When the reaction time prolonged to 24h, 48h, and 72h the yields of isolated benzaldehydes were 55%, 75%, and 80% respectively. The presence of electron-withdrawing group in the aromatic ring has little influence on the oxidation rate. Thus, p-nitrobenzyl and m-nitrobenzyl alcohols are almost quantitatively oxidized to aldehydes. Despite the long reaction times the heterogeneous nature of the reaction and the mild, room temperature conditions offer advantages over more traditional reagents, lead tetraacetate and sodium periodate. The long reaction times can possibly be attributed to the fact that the concentration of bismuthate ions in acetic acid solution of the alcohol is low, most of the sodium bismuthate during the reaction being present as a solid, whereas sodium periodate and lead tetraacetate are completely dissolved.

The formation of aldehydes and ketones from the corresponding alcohols may be understood as being due to loss of a hydrogen atom or loss of a proton from the carbinol carbon atom. When sodium bismuthate is employed as a suspension in a nonpolar solvent in the oxidation of phenols radical coupling products, typical of one-electron oxidation, predominate (Kon and Mcneilis, 1975). However, sodium bismuthate oxidation of phenols carried out in a medium containing acetic acid normally yields two-electron oxidation products. The action of sodium bismuthate in acetic acid towards phenols resembles that of leadtetraacetate. Analogously, in the reaction between alcohols and sodium bismuthate in a medium containing acetic acid a two-electron oxidation might be expected.

#### REFERENCES

- ADDERLY, C.J.R. and HEWGILL, F.R., 1968, *J. Chem. Soc. C*, 2770-4.  
BURSTEIN, G.T., 1969, *Nature (London)*, 221, 169-70.  
KON, E. and MCNEILIS, E., 1975, *J. Org. Chem.*, 40, 1515-7; 1976, *J. Org. Chem.*, 41, 1646-8.  
PERRIN, D.D., ARMAREGO, W.L. and PERRIN, D.R., 1966, *Purification of Organic Compounds*, Pergamon Press, Oxford.  
RIGBY, W. 1950, *J. Chem. Soc.*, 1907-13.