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# Reductive dehalogenation of halophenols in sulfite–bisulfate medium

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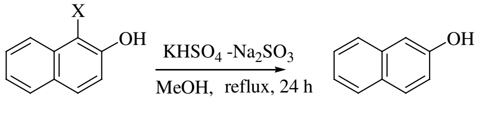
**Abstract**—The $KHSO_4$–$Na_2SO_3$ system is found to be simple and inexpensive for reductive elimination of halogens (Br, I) from the corresponding halophenols under reflux conditions in dry methanol. Under similar conditions the reaction is sluggish with chlorophenols.

## 1. Introduction

In recent years, the halogens on aromatic rings have been used as potential protecting or blocking groups in synthetic organic chemistry.[1,2] Aromatic halides are readily reduced by metal-catalyzed transfer hydrogenolysis.[3] The process of reductive elimination of halogens from aromatic rings is relatively quite a difficult task. There are reports of the use of Pd(II) salts, to give the corresponding dehalogenated compounds.[4] Generally, debrominations have been carried out in hydrobromic acid in the presence of a suitable bromine scavenger such as aniline or phenol or sodium sulfite.[2,5] Dehalogenation by direct hydrogenolysis has been accompanied by the reduction of double bonds in the case of unsaturated halides and the formation of amines in case of nitro halides. Dehalogenation of aromatic halides has been reported over palladium deposited on carbon[6] in the presence of a proton donor like limonene and *p*-menthene at 50–100 °C, but the nitrile group of *o*/*p*-chlorobenzonitrile was also reduced. Cortese and Heck[3] have achieved the dehalogenation of aromatic halides without affecting a nitrile group by employing triethylammonium formate/triarylphosphine catalyzed by palladium or palladium acetate at 50–100 °C. Nucleophilic reagents such as $LiEt_3BH$[7,8] and $2LiAlH(OCH_3)_3$–CuI[9] have been used in dehalogenation reactions. Tyrlik and Wolochowicz[10] have employed a $TiCl_3$/3THF–Mg system for easy reduction and dehydrohalogenation of organic halides under a nitrogen/argon atmosphere obtaining moderately low yields.

In earlier communications[11] we have reported dehalogenation in the presence of H-β zeolite catalyst and dehalonitration of halophenols in $HNO_3$.[12] Here, we wish to report our further findings of reductive dehalogenation of halophenols carried out in a bisulfate ($KHSO_4$)–sulfite ($Na_2SO_3$) medium.

The reductive deiodination of 1-iodo-2-naphthol, **1** was chosen as a model reaction and carried out as shown in Eq. 1 over a bed of $KHSO_4$ (5 mol equiv)–$Na_2SO_3$ (6 mol equiv) at reflux in dry methanol. The progress of the reaction was monitored by TLC analysis following the production of 2-naphthol, **2**.[11] The reaction was complete in 24 h and the product was isolated in 98% yield, showing the present system to be more efficient than the H-β zeolite-catalytic system,[11] wherein a 97% yield was achieved in a 48 h reaction. Under similar experimental conditions, 1-bromo-2-naphthol, **3** gave a 92% yield of **2**, while 1-chloro-2-naphthol was unchanged. The conversion of 1-iodo-2-naphthol was higher than its bromo analogue.[10]



(1)

**2**

**1**, X = I, 98%; **3**, X = Br, 92%

The same strategy was extended to 2,4,6-triiodophenol and 2,4,6-tribromophenol to obtain the corresponding 2,6-dihalophenol in moderate yields after 48 h (Eq. 2).

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*Keywords*: $KHSO_4$–$Na_2SO_3$; Debromination; Deiodination.

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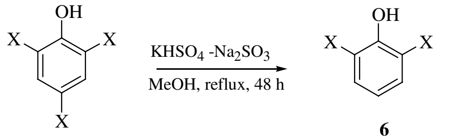
The present investigations revealed that the halonaphthols are more easily dehalogenated than halophenols. Presumably this could be due to the reduction of keto form of halonaphthol intermediates resulting in their dehalogenation. Lin and Roth[13] reported the debromination of *p*-bromophenol using $NaBH_4$ in the presence of a nickel catalyst and obtained less encouraging results.

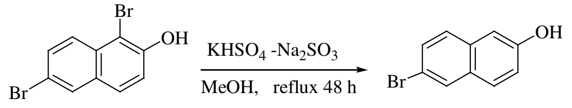


(2)

**4**, X = I, 57%
**5**, X = Br, 45%

**6**

6-Bromo-2-naphthol, **8** is an important starting material in synthetic and industrial chemistry[14] and is conventionally obtained by selective debromination of 1,6-dibromo-2-naphthol, **7** using hydrobromic acid.[15,16] Vona and Merker[17] reported the preparation of 6-bromo-2-naphthol in 45.5% yield by reacting 2-naphthol, pyridinium tribromide and excess tin in glacial acetic acid. We have successfully achieved the preparation of 6-bromo-2-naphthol **8** in 55% yield by selective debromination of 1,6-dibromo-2-naphthol, **7** using $KHSO_4$–$Na_2SO_3$ (Eq. 3).



(3)

**7**

**8** ( 55%)

Attempts to dehalogenate 2-$CH_3$, 2-$NO_2$ and 2-Cl derivatives of 4,6-dibromophenol, the 4-I, 4-Br derivatives of phenol and anisole and the 1-I and 1-Br derivatives of 2-methoxy naphthalene failed to give the desired products even after prolonged reflux in methanol.

## 2. General experimental procedure

### 2.1. Deiodination of 1-iodo-2-naphthol

A mixture of **1** (0.25 g, 0.926 mmol), $KHSO_4$ (0.6296 g, 5 mmol) and sodium sulfite (0.70 g, 6.0 mmol) was refluxed in dry methanol (20 mL). The reaction was monitored by TLC for formation of **2**. The reactant, 1-iodo-2-naphthol was fully converted to 2-naphthol in 24 h. The mixture was cooled and extracted with diethyl ether thrice with (3 × 20 mL) to recover the product. The extracts were collected and concentrated and the pure product **2** was isolated by column chromatography over silica gel (10% ethyl acetate in hexane) to obtain 2-naphthol (0.13 g, 98%), which showed satisfactory spectral data and mp 122–123 °C (lit.[18] 121–123 °C).

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