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# An Improved Method for the Halogenation of 2(3H)-Benzoxazolones

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## *ABSTRACT*

*An improved method for the mono-, di- and trihalogenation of 2(3H)-benzoxazolones by means of hydrochloric or hydrobromic acid and hydrogen peroxide in acetic acid media is described. The simple procedure, higher yields and purity, and shorter reaction time are the advantages of the method.*

## INTRODUCTION

6-chloro- and 6-bromo-2(3H)-benzoxazolones are valuable intermediates for the synthesis of compounds with wide practical application, e.g. the insecticide 'phosalone',[1] and 5-halogeno-2-aminophenols,[2,3] intermediates for metal complex dyes. 4,5,6-Trichloro-2(3H)-benzoxazolone is included in the composition of a large number of pesticides.[4,5] An improved method of halogenation of the readily available 2(3H)-benzoxazolones is proposed in this present paper. This method leads to higher yields and purity of the corresponding products and the reaction time required is shorter compared to known methods.

## RESULTS AND DISCUSSION

According to methods reported in the literature, the halogenation of 2(3H)-benzoxazolone to 6-bromo- and 6-chloro-2(3H)-benzoxazolone with bromine or gaseous chlorine can be carried out in an organic solvent

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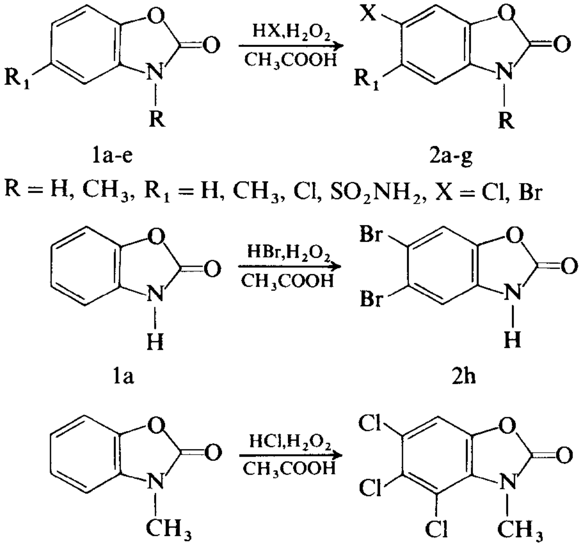
medium.[6,7] Chlorination in a dry organic solvent can also be performed with sulfuryl chloride.[3] The use of organic solvents has some disadvantages, e.g. toxicity and solvent recovery procedures. Additionally, the use of gaseous chlorine requires special equipment for the control of this reagent since the use of it in excess leads to the formation of a mixture of 4,6-dichloro- and 4,5,6-trichloro-2(3H)-benzoxazolones.[6] The halogenation process is often lengthy, from 2–3 to 24 h, and low purity products requiring additional purification are obtained with yields not exceeding 80–90%.

The chlorination of 2(3H)-benzoxazolone with alkali and alkali earth hypochlorites, or with chlorine ions and inorganic peroxides in the presence of mineral acids has been patented.[7] This procedure is applicable to the formation of chloro derivatives only, the process duration is at least 5 h, the purity of the 6-chloro-2(3H)-benzoxazolone is 80–90% and yields are in the region of 80–84%. Whilst this method has advantages over previously described chlorination techniques, the approach described in this present paper offers further advantages.

We describe here a method for the halogenation in acetic acid medium of 2(3H)-benzoxazolone and its 3-, 5- or 6-substituted derivatives, using hydrochloric or hydrobromic acid and hydrogen peroxide as an oxidant in the presence of a catalyst (Scheme 1). Halogenation is carried out by the



1a R = R$_1$ = H; 1b R = H, R$_1$ = Cl; 1c R = H, R$_1$ = CH$_3$; 1d R = H, R$_1$ = SO$_2$NH$_2$; 1e R = CH$_3$, R$_1$ = H; 2a R = R$_1$ = H, X = Cl; 2b R = H, R$_1$ = X = Cl; 2c R = H, R$_1$ = CH$_3$, X = Cl; 2d R = H, R$_1$ = SO$_2$NH$_2$, X = Cl; 2f R = R$_1$ = H, X = Br, 2g R = H, R$_1$ = Cl, X = Br.

**Scheme 1**

**TABLE 1**
Yields, Melting Points and Analytical Data of Compounds **2a**–**2i**

| *Starting materials* | | *Reaction product* | *Yield (%)* | *Melting points (°C) (lit. values)* | *Analysis %N calcd/found* |
|---|---|---|---|---|---|
| *Compound* | *HX* | | | | |
| **1a** | HCl | **2a** | 98 | 197–198 (190·5–191[3]) | 8·26–8·30 |
| **1b** | HCl | **2b** | 97 | 201–202 (196–197[8]) | 6·87/7·04 |
| **1c** | HCl | **2c** | 95 | 196–197 (182–184[9]) | 7·63/7·50 |
| **1d** | HCl | **2d** | 96 | 193–194 — | 11·27/11·48 |
| **1e** | HCl | **2e** | 95 | 106–107 (102–103[10]) | 7·63/7·77 |
| **1a** | HBr | **2f** | 96 | 193–194 (190–191[11]) | 6·54/6·46 |
| **1b** | HBr | **2g** | 95 | 213–215 (202[12]) | 5·64/5·63 |
| **1a** | HBr | **2h** | 96 | 255–257 — | 4·81/4·75 |
| **1e** | HCl | **2i** | 95 | 172–173 — | 5·57–5·33 |

Compounds **2d**, **2h** and **2i** are new compounds. Compounds **2a**, **2e**–**2i** were recrystallized from ethanol; compounds **2b** and **2d** from ethanol:water 2:1 and compound **2c** from chlorobenzene.

addition of hydrogen peroxide in some excess (5–10%) to an acetic acid solution of 2(3H)-benzoxazolone or a derivative thereof in the presence of a hydrohalogenic acid and a catalytic amount of $FeCl_3$, at a temperature not exceeding 80°C. The reaction is complete within 30–45 min. In order to obtain di- and trihalogenated derivatives, respectively, larger amounts of hydrohalogenic acid and hydrogen peroxide are used. The yields are almost quantitative (Table 1) and high purity (96–97%, by potentiometric titration) products are obtained.

To the best of our knowledge a 5,6-dibromo-2(3H)-benzoxazolone **2h** is thus obtained for the first time by direct halogenation procedures. Aromatic proton signals in the $^1$H-NMR spectra for both compound **2h** and for 5,6-dichloro-2(3H)-benzoxazolone **2b** obtained by chlorination of 5-chloro-2(3H)-benzoxazolone **1b**, are in accord with substitution in the 5- and 6-positions.

The short reaction time, almost quantitative yields, and the possibility of obtaining mono-, di- and trihalo derivatives thus offer an effective synthetic route for this practically important class of compounds.

## EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. $^1$H-NMR spectra were recorded on a Tesla BS-487, 80 MHz instrument in $CDCl_3$ and DMSO-$d_6$ with TMS as internal standard.

## General procedure for mono-, di- and trihalogenation of 2(3H)-benzoxazolones

The appropriate substituted or unsubstituted 2(3H)-benzoxazolone (0·1 M) was dissolved in glacial acetic acid (40 ml) and the solution stirred at 40–50°C. Hydrohalogenic acid (37% HCl or 40% HBr in amounts 0·23 M (22·7 g HCl or 46·5 g HBr) for monohalogenation, 0·42 M (41·4 g HCl or 85 g HBr) for dihalogenation or 0·66 M (61·5 g HCl or 133·5 g HBr) for trihalogenation was then added. Hydrogen peroxide (30% in amounts 0·128 M (14·5 g), 0·21 M (23·8 g) and 0·31 M (35·1 g) for mono-, di- and trihalogenation, respectively) was then slowly dropped into the reaction mixture with vigorous stirring, maintaining the temperature below 80°C. After completion of the addition of hydrogen peroxide the reaction mixture was heated on a steam bath at 80°C for 30–45 min. Subsequent cooling of the reaction mixture and dilution with water (two parts by volume) result in the formation of a precipitate. The product was filtered, washed with water and dried. Yields, melting points and analytical data are shown in Table 1.

$^1$H-NMR: **2b** (DMSO + $CDCl_3$) $\delta$ 6·95–7·25 (**2d**, 2H-Ar); 11·43 (s, NH-1H). **2h** (DMSO + $CDCl_3$) $\delta$ 7·15–7·32 (**2d**, 2H-Ar); 11·92 (s, NH-1H).

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