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Marwa M. Aborways, Wesley J. Moran

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## Dual oxidation/bromination of alkylbenzenes

Marwa M. Aborways<sup>a</sup> and Wesley J. Moran<sup>a\*</sup>Received 00th January 20xx,  
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Abstract:

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In the presence of sodium bromide and Oxone, a range of alkylbenzene derivatives are brominated and/or oxidized with up to four C-H bonds being functionalized.

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**In the presence of sodium bromide and Oxone, a range of alkylbenzene derivatives are brominated and/or oxidized with up to four C-H bonds being functionalized.**

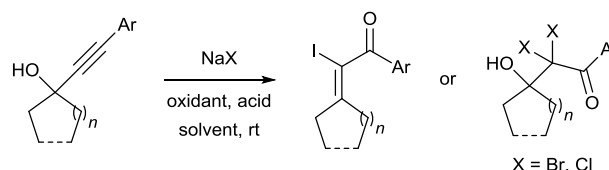
The development of new methods for the functionalization of simple inexpensive aromatic compounds is an important area of investigation. In particular, developing conditions that do not require the use of expensive, toxic or difficult to handle compounds is a worthwhile endeavor. For example, the halogenation of arenes is a ubiquitous chemical transformation for which there are many published procedures, however the use of elemental halogen or reagents such as *N*-halosuccinimide are often required.<sup>1,2</sup> These reactants have disadvantages such as toxicity, corrosiveness, ease-of-use, relative high cost, low atom efficiency or supply issues.

We previously reported the use of sodium halides, in the presence of an oxidant, as electrophilic halogenating agents for the conversion of propargyl alcohols to  $\alpha$ -iodoenones,  $\alpha,\alpha$ -dibromoketones and  $\alpha,\alpha$ -dichloroketones.<sup>3</sup> We wished to extend this concept to the functionalization of simple alkylbenzenes. We envisaged that halogenation of the aromatic ring would occur with concomitant oxidation of the benzylic methylene to a ketone (Fig. 1).

We started our study with ethylbenzene **1** using our previously published conditions of sodium bromide with Oxone in the presence of trichloroacetic acid dissolved in a mixture of acetonitrile and water (Table 1).<sup>3a</sup> Performing the reaction at room temperature in the dark led to very low conversion to  $\alpha$ -bromoketone **3** (entry 1). Repeating the reaction in the light also led to low conversion of the starting material (entry 2). Heating the reaction mixture at 50 °C in the dark led to higher conversion and a mixture of products **2** and

**3** (entry 3). However, when the reaction was repeated at 50 °C in the light conversion increased significantly and ketone **3** was isolated in 65% yield (entry 4). At this point, the requirement for the acid was evaluated and it was found that its removal led to no detriment in yield (entry 5). Small amounts of the *ortho*- and *meta*-bromination products were evident in the crude reaction mixtures but these could be removed by recrystallization. Lowering the number of equivalents of sodium bromide and oxidant led to lower yield.

## Previous work: alkynyl group functionalization



## This work: aryl and/or alkyl group functionalization

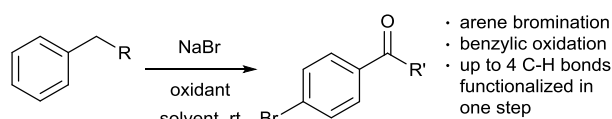


Fig. 1 Previous study of oxidative halogenation and this work

Table 1 Investigation of reaction conditions

Entry	Temperature (°C)	Conditions	Yield (%) <sup>a</sup>
1	20	in the dark	<5 ( <b>3</b> )
2	20	in the light	6 ( <b>3</b> )
3	50	in the dark	13 ( <b>2</b> ), 16 ( <b>3</b> )
4	50	in the light	65 ( <b>3</b> )
5	50	in the light	65 ( <b>3</b> ) <sup>b</sup>

<sup>a</sup> Yield of isolated compound. <sup>b</sup> No Cl<sub>3</sub>CCO<sub>2</sub>H added.

<sup>a</sup> Department of Chemistry, University of Huddersfield, Huddersfield HD1 3DH, UK.  
E-mail: w.j.moran@hud.ac.uk

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