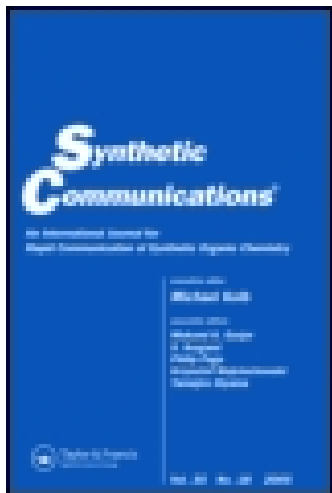


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### Reduction of Aromatic $\alpha$ -Halo Ketones with Metallic Bismuth

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## REDUCTION OF AROMATIC $\alpha$ -HALO KETONES WITH METALLIC BISMUTH

Ping-Da Ren,\* Qi-Hui Jin and Zi-Peng Yao

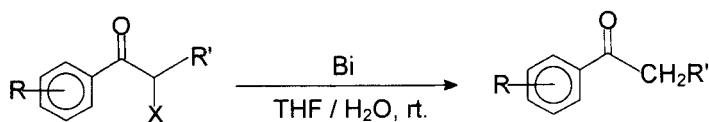
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**ABSTRACT:** Aromatic  $\alpha$ -bromo ketones and  $\alpha$ -iodio ketones can be reduced by bismuth prepared from  $\text{NaBH}_4$  and  $\text{BiCl}_3$  in water to their parent ketones in high yields, but aromatic  $\alpha$ -chloro ketones should be added to sodium iodide first.

Activated metal powders developed by Rieke *et al.* have been prepared by the reduction of a metal halide with group I element (Li, Na, K) in an ether or tetrahydrofuran and have been employed in organic synthesis.<sup>1</sup> Recently, we reported a Barbier Type Reaction promoted by *in situ* formed active metal bismuth from  $\text{NaBH}_4$  and  $\text{BiCl}_3$  in aqueous media,<sup>2</sup> we discovered that the black metal bismuth powder generated by our procedure is in a very finely divided state and of high reactivity. In this communication, we would like to report a facile method for dehalogenation of aromatic  $\alpha$ -halo ketones with the active metal bismuth prepared from the combination of  $\text{NaBH}_4$  and  $\text{BiCl}_3$ . (Scheme 1)

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\* To whom correspondence should be addressed.

**Scheme 1**

Conversion of  $\alpha$ -halo ketones into the parent ketones is a reaction that is sometimes used in synthesis,<sup>3</sup> and several new reagents have been introduced for this transformation.<sup>4</sup> The application of metal bismuth in organic synthesis has recently attracted much attention due to its potentiality as a reductant for various synthetic purposes.<sup>5</sup> Now it was found that the active metal bismuth was a mild and convenient reagent for dehalogenation of  $\alpha$ -halo ketones.

The results are summarized in **Table 1**. We found that  $\alpha$ -iodio ketones were reduced easiest, and  $\alpha$ -chloro ketones were hardly reduced at room temperature. In addition, when there is a group beside halogen (Entry 9, 10), more bismuth (1.2 amounts) should be added, otherwise the substrates won't be all reduced.

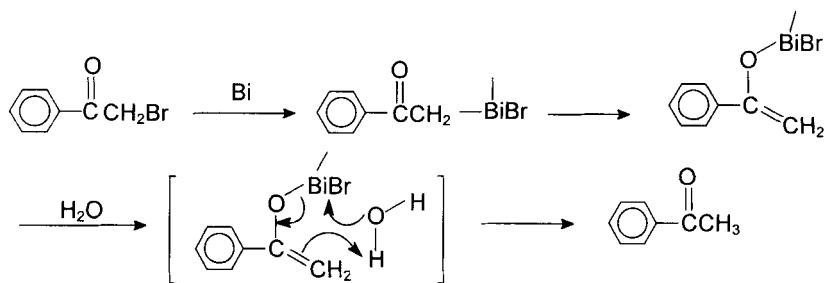
The mechanism of the reaction has not been studied yet. We suggested that the  $\alpha$ -halo ketones initially reacted with bismuth, tautomerized to its enolate form, then H<sub>2</sub>O made these enolates into ketones. (**Scheme 2**)

Although there were several methods available to the dehalogenation of  $\alpha$ -halo ketones, we believed our method was a useful addition to them in view of the mild conditions, simple manipulation and the high yields.

**Table 1** Reaction of  $\alpha$ -halo ketones to ketones

Entry <sup>a</sup>	X	R	R'	Yield of ketone (%) <sup>b</sup>
1	Br	H	H	96.0
2	Br	<i>p</i> -CH <sub>3</sub>	H	87.9
3	Br	<i>p</i> -Cl	H	93.4
4	Br	<i>p</i> -Br	H	92.5
5	Br	<i>p</i> -OCH <sub>3</sub>	H	92.9
6	Br	<i>p</i> -NO <sub>2</sub>	H	88.0
7	Br	<i>m</i> -NO <sub>2</sub>	H	90.9
8	I	H	H	94.2
9	Br	H	CH <sub>3</sub>	91.9
10	Br	<i>p</i> -CH <sub>3</sub>	CH <sub>3</sub>	94.6
11	Cl	H	H	90.0
12	Cl	<i>p</i> -F	H	82.1
13	Cl	<i>p</i> -Cl	H	85.8
14	Cl	<i>p</i> -Br	H	98.0
15	Cl	<i>p</i> -OCH <sub>3</sub>	H	93.3

- a. All reaction were carried out on a 2.0 mmol scale; mol ratio of substrates / BiCl<sub>3</sub> / NaBH<sub>4</sub>: 2.0 / 2.0 / 6.0 ( Entry 1 ~ 8 ); 2.0 / 2.4 / 6.0 ( Entry 9 ~ 10 ); substrate / NaI / BiCl<sub>3</sub> / NaBH<sub>4</sub>: 2.0 / 2.2 / 2.0 / 6.0 ( Entry 11 ~ 15 ).
- b. All yields refer to isolated products. All physical data including IR & NMR spectra were consistent with the literature data.

**Scheme 2**

### ***General procedure***

To a water solution of bismuth trichloride ( 2.0mmol ),  $\text{NaBH}_4$  ( 6.0mmol ) was added in portions in ice-water bath, poured out the water, then added substrate ( 2.0mmol ) and solution of THF /  $\text{H}_2\text{O}$  ( 4 / 1 ) 15ml. The mixture was stirred for 4 hours at room temperature then filtrated. The filtrate was extracted with ether ( 20ml  $\times$  3 ), the combined extracts was washed with brine then dried with anhydrous sodium sulfate. After the evaporation of ether, the crude residue was purified by flash column chromatograhly.

For entry 11 ~ 15, to a solution of  $\alpha$ -halo ketones ( 2.0mmol ) in acetone ( 3 ml ) is added a solution of sodium iodide ( 2.2 mmol ) dissolved in acetone ( 3 ml ), and the mixture was stirred for 15 min. at room temperature, then the metallic bismuth ( 2.0 mmol ) ( prepared as above ),  $\text{H}_2\text{O}$  ( 3 ml ) and acetone ( 6 ml ) was added orderly.

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