

## Synthesis of Cycloundecanone from Benzimidazole Methiodide Salt

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**Abstract:** The intra-molecular addition reaction of Grignard reagent with quaternary C=N bond of benzimidazole methiodide salt is reported, and a novel method for the synthesis of cycloundecanone is provided.

**Keywords:** Cycloundecanone, benzimidazole methiodide salt, synthesis.

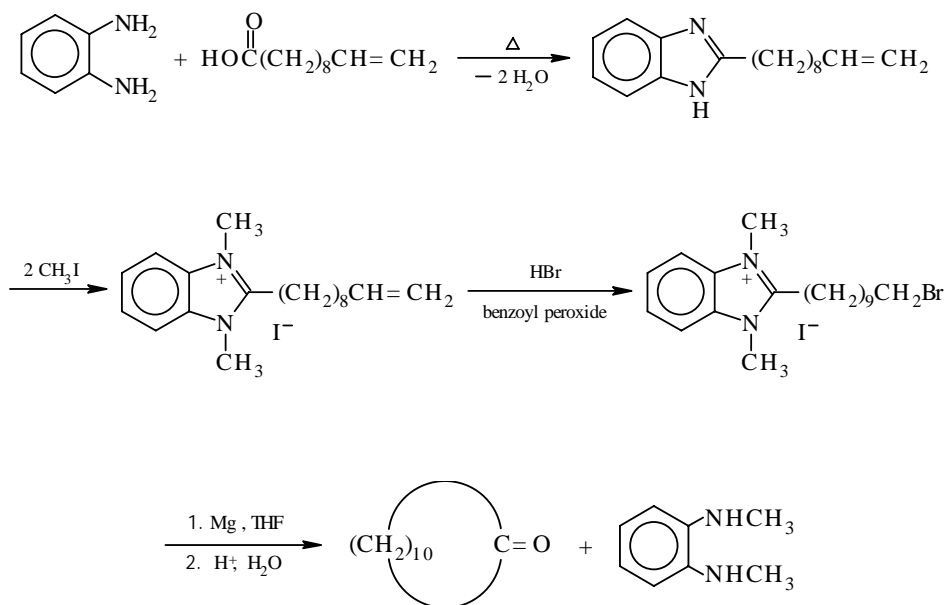
Cycloundecanone has been synthesized in several ways. Fawcett *et al.* prepared cyclo-undecanone by the reduction of 2-hydroxycycloundecanone<sup>1</sup>. Ruzicka *et al.* reported the synthesis of cycloundecanone by the pyrolysis of the thorium salt of dodecanedioic acid<sup>2</sup>. Schank and Eistert synthesized cycloundecanone by ring contraction of cyclododecanone<sup>3</sup>. Garbisch *et al.* improved the ring contraction reaction in over-all yields consistently ranging between 85 and 90%<sup>4</sup>. Garbisch's method gave higher yields and was less expensive and more expeditious than the previously published methods<sup>5</sup>.

We reported the addition-hydrolysis reaction of benzimidazole methiodide salts with Grignard reagents, and a novel synthetic method for ketones was provided<sup>6</sup>. In this paper, an intra-molecular addition reaction of Grignard reagent group with quaternary C=N bond of benzimidazolium iodide has been studied, a convenient and useful method for the synthesis of cycloundecanone is provided ( **Scheme 1** ).

Benzimidazolium iodide was prepared from 1,2-benzenediamine and 10-undecenoic acid *via* cyclization, quaterisation and radical anti-Markovnikov addition of HBr to C=C bond. The mechanism for the reaction of benzimidazolium iodide with Grignard reagents was discussed in our previous paper<sup>6</sup>. The reaction described in this paper can be reasonably explained by an intra-molecular addition reaction of Grignard reagent with quaternary C=N bond of benzimidazolium iodide and the formation of benzimidazolidine which can be hydrolyzed to give cycloundecanone in acidic solution ( **Scheme 2** ).

The formation of quaternary ammonium salt probably assists the addition reaction by increasing the polarity of C=N bond being attacked by Grignard reagent, because a free C=N bond does not successfully undergo a reaction with Grignard reagent. Further investigation of this kind reaction is being continued in our laboratory.

Scheme 1



## Experimental

### *Synthesis of benzimidazolium iodide*

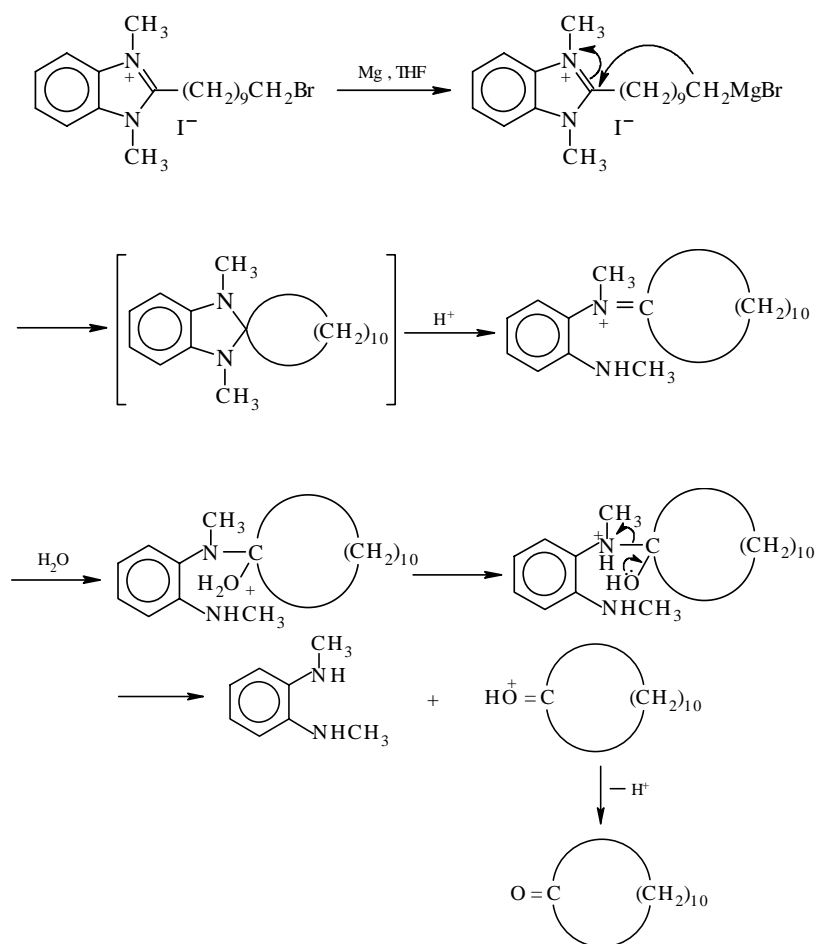
Benzimidazolium iodide was prepared according to our previous paper<sup>6</sup>.

### *Synthesis of cycloundecanone*

A 250 mL three necked round-bottomed flask, fitted with a tantalum wire Hershberg stirrer, a condenser, was arranged for use of a nitrogen atmosphere. Benzimidazolium iodide ( 2.5 g, 5 mmol), magnesium (0.4g, 15 mmol) and 20 mL of anhydrous tetrahydrofuran were placed in the flask. The flask was warmed in a water bath and a small crystal of iodine was added. After the reaction initiated, 2.5 g ( 5 mmol ) of benzimidazolium iodide and 150 mL of anhydrous tetrahydrofuran were added to the reaction mixture again. The mixture was stirred at 40-45°C for 24 h and then a 10% solution of hydrochloric acid was added slowly, the resulting mixture was heated at 40-50°C for 30 min with stirring. Tetrahydrofuran was removed and the residue was extracted with chloroform (3×30 mL). The combined organic extracts were washed with 5% sodium bicarbonate, dried over anhydrous magnesium sulfate and evaporated.

The residue was purified by chromatography on a silica gel column, using ethyl acetate as eluent, to give 0.9g (53.6%) of product as pale yellow oil, b.p.109-110°C/0.93KPa. The product solidified on cooling and melted at 15-16°C (lit<sup>4</sup>. b.p. 109-110°C/0.93KPa, m.p.16°C). The spectral properties of the compound were in agreement with those previously reported<sup>5</sup>.

Scheme 2



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