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Synthesis of Symmetric Diketones from Imidazolinium Salt and Bis-Grignard Reagents

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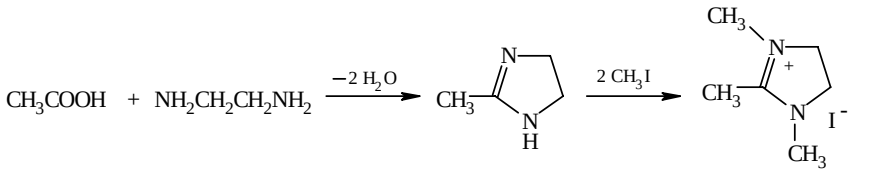
Abstract: The reaction of 2-substituted imidazolinium salt with bis-Grignard reagents is reported and a new method for the synthesis of symmetric diketones from carboxylic acids and bis-Grignard reagents is provided.

Keywords: Diketones, imidazolinium salt, bis-Grignard reagents, synthesis.

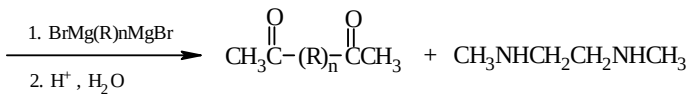
In our earlier paper, we reported a convenient method for the synthesis of symmetric diketones from benzimidazolium salts and bis-Grignard reagents[1]. The yields of product obtained by the reported method are better then that of the former methods[2, 3]. However the method suffers from dramatic expensive material, such as *o*-phenyldiamine, which makes it not to be useful for large-scale preparation.

In order to overcome this disadvantage and find a new method which can be utilized in industry, we have explored a method to prepare symmetric diketones, based on the study on the reaction of imidazolinium salt with bis-Grignard reagents (**Scheme1**).

Scheme 1



1 **2**



3 – 6

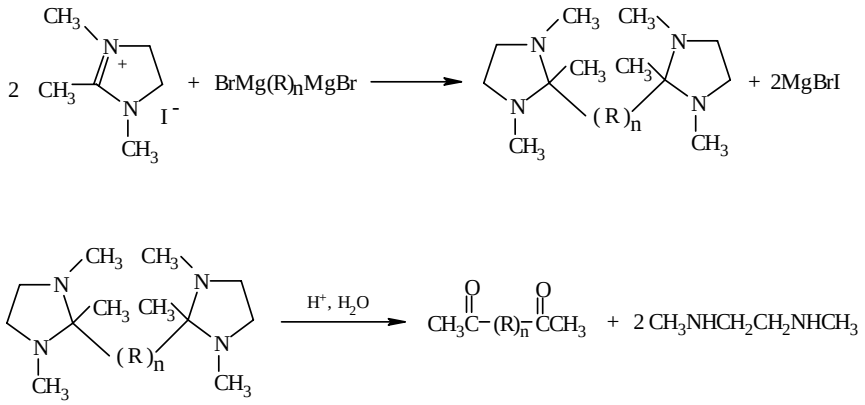
3 R=CH_2 n=3 **4** R=CH_2 n=4 **5** R=CH_2 n=5 **6** R=C_6H_4 n=1

2-Methylimidazoline **1**, easily obtained from acetic acid and ethylenediamine, was treated with CH_3I to afford 1,2,3-trimethylimidazolium **2** in high yield. Compound **2** was reacted with bis-Grignard reagents, then hydrolized with aqueous solution of oxalic acid,

the symmetric diketions **3~6** were prepared. This method can be used not only for the preparation of aliphatic diketones but also for aromatic diketones and it is not reported in literature. A variety of imidazolines can be prepared by using different carboxylic acid instead of acetic acid for obtaining other useful symmetric diketones. The reactions proceeded under simpler and in general moderate reaction conditions and gave good yields.

The mechanism for the reaction of benzimidazolium salts with bi-Grignard reagents was discussed in our earlier paper[1]. The reaction of imidazolinium salt with bis-Grignard reagent can be reasonably explained by the addition reaction of bis-Grignard reagent with imidazolinium salt and the formation of bis-imidazolidine which can be hydrolyzed to give diketone in acidic solution (**Scheme 2**).

Scheme 2



Experimental

Apparatus and reagents

Melting points were taken on a model X4 melting point apparatus uncorrected. Reagents were purified by standard methods.

*Synthesis of 2-methylimidazoline **1***

2-Methylimidazoline **1** was prepared from acetic acid and ethylenediamine according to the methods described in literature[4], m.p. 106-107℃ (Lit.[5] m.p.105℃), yield 85%.

*Synthesis of 1, 2, 3-trimethylimidazolinium salt **2***

1, 2, 3-Trimethylimidazolinium salt **2** was prepared by addition of CH_3I (0.3mol) to compound **1**(0.1mol) in 75mL DMF and 0.1mol K_2CO_3. The mixture was refluxed with stirring for 6 hours. Then KI was filtered off and the filtrate was distilled under reduced

pressure to remove DMF. The residue was yellow crude product, which was recrystallized from ethyl acetate to give white needle crystals. Yield 87 %, m.p. 87-89℃; Anal.Calcd for $C_6H_{13}N_2I$: C, 30.00; H, 5.41; N 11.67. Found: C, 29.87; H, 5.33; N, 11.47.

Preparation of bis-Grignand reagent

Bis-Grigand reagents were prepared according to literature procedures[6, 7].

*General procedure for synthesis of symmetric diketones **3 – 6***

A solution of compound **2** (0.10mol) in dry THF(75 mL) was added dropwise to a stirred solution of bis-Grignard reagent (0.05mol) in THF(50mL) under nitrogen. The reaction mixture was heated under reflux for 20 h, then cooled to room temperature, treated with a saturated aqueous solution of oxalic acid until to pH 5~6, and THF was evaporated. The residue was extracted with ether or benzene (3×50mL), and the extracts were dried over $MgSO_4$. Removal of solvents gave the crude product, which was recrystallized from acetone-petroleum ether (1:9) to afford pure product. The results are given in **Table 1** and **Table 2**.

Table 1 The physical properties of compounds **3** – **6**

Comp.	R	n	Color and state	m.p.(℃)	Yield(%)
3	CH_2	3	white solid	31-32(32-33)[8]	65
4	CH_2	4	white solid	43-44(44)[9]	68
5	CH_2	5	white solid	45-46(46)[10]	70
6	C_6H_4	1	white solid	113-114(114)[11]	58

Table 2 The IR and elementary analysis of compounds **3** – **6**

Comp.	IR (ν /cm^{-1})	Elementary analysis (%) / found (calcd.)	
		C	H
3	1700	65.78 (65.63)	9.45 (9.37)
4	1705	67.67 (67.60)	9.89 (9.86)
5	1716	69.33 (69.23)	10.27 (10.26)
6	1680	74.38 (74.08)	6.13 (6.17)

Acknowledgments

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