# Novel Synthesis of α-Diketones from Bisbenzimidazolium Salt and Grignard Reagents

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**The reaction of bisbenzimidazolium salt with Grignard reagents and a new synthetic method of α-diketones from bisbenzimidazolium salt and Grignard reagents are reported. The structures of all α-diketones are characterized by elemental analyses, infrared spectroscopy and $^1$H NMR spectroscopy. The influences of the various Grignard reagents on the yield of α-diketones and the mechanism are discussed, and a new convenient synthetic method for α-diketones is provided.**

**Keywords** α-Diketones, bis-benzimidazolium salt, synthesis, Grignard reagent

## Introduction

α-Diketones are very important compounds in organic syntheses.[1-7] An efficient preparation of α-diketones has long been of interest, and several important methods have been developed. There are many reports in the literature which describe the synthesis of α-diketones from oxidation of acylions with copper(Ⅱ) acetate[8] or bismuth[9] or lithium[10] or pyrophoric lead.[11] Carto *et al.*[12] prepared α-diketones from pyridinium chlorochromate oxidation of benzylketones and obtained a good yield. Mueller *et al.*[13] reported the synthesis of α-diketones from organometallic reagents and 1,4-dialkylpiperazine-2,3-diones. Seyferth *et al.*[14] developed a new method for the synthesis of α-diketones. In this method, *n*-, *sec*-, or *tert*-butyllithium was added to a CO-saturated solution of an ester, R′COOR in a solvent system of 4:4:1 (by volume) THF/$Et_2O$/pentane at −110℃, then the reaction mixture was treated with saturated aqueous $NH_4Cl$ to give α-diketones. Kagan *et al.*[15] synthesized α-diketones by the reaction of acid chlorides with $SmI_2$.

We have reported the reaction of 1, 2, 3-trisubstituted benzimidazolium salt with Grignard reagent, and novel synthetic methods for ketones and diketones have been provided.[16,17] In this paper, the addition reaction of bisbenzimidazolium salt with Grignard reagent and the hydrolysis reaction of bisbenzimidazolidine were studied. Bisbenzimidazole (**1**) and bisbenzimidazolium salt (**2**) were prepared from *o*-phenylenediamine and oxamide. 2,3-Butanedione (**3**), 3,4-hexadione (**4**), 4,5-octadione (**5**), dibenzoyl (**6**) were prepared by the addition-hydrolysis reaction of bisbenzimidazolium salt with Grignard reagents, and a new convenient and useful synthetic method of α-diketones was provided. The route for the synthesis of α-diketones was as follows (Scheme 1).

Compared with the synthetic methods described in literature, the method described in this paper employs more available starting materials, *o*-phenylenediamine, oxamide, needs a moderate reaction condition and gives a good yield. It has been found that the Grignard reagent of different substituted group has much effect on the yield of α-diketone, and the reason why the yield of α-diketone from aromatic Grignard reagent is lower is the steric hindrance of aryl group to which MgX group is attached. Bisbenzimidazolium salt is partially soluble in tetrahydrofuran, but it is insoluble in ether, so when tetrahydrofuran is used as solvent, the reaction is finished in short time with high yield. This method provides a

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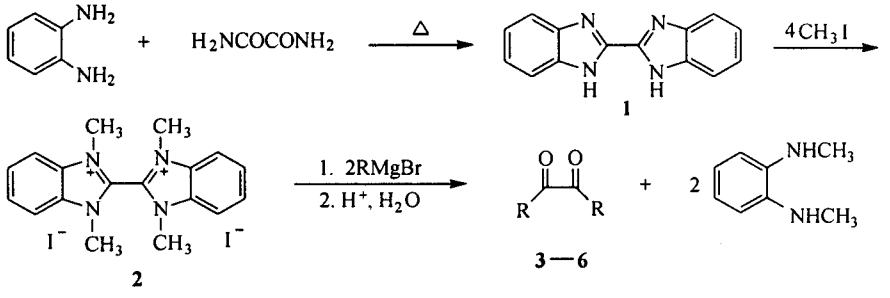
Received January 8, 2001; revised and accepted April 2, 2001.
Project supported by the National Natural Science Foundation of China (No. 29872032) and the Provincial Natural Science Foundation of Shaanxi Province.

useful synthetic method of α-diketones. It will play an important role in the syntheses of α-diketones and in the perfume industry.

**Scheme 1**




3, R = $CH_3$; 4, R = $CH_3CH_2$; 5, R = $CH_3(CH_2)_2$; 6, R = $C_6H_5$

## Experimental

Melting point was obtained on a model $X_4$ melting point apparatus and uncorrected. Microanalyses were performed by a PE-2400 CHN elemental analyzer. Infared spectra were measured with a Perkin Elmer-440 spectrometer (as KBr disc, values in $cm^{-1}$). $^1H$ NMR spectra were collected on a Brakter ARX-400 MHz spectrometer. $^1H$ chemical shifts (δ) were reported relative to tetramethylsilane (TMS). Bisbenzimidazole (**1**) was prepared from oxamide and *o*-diaminobenzene according to the literature.[18] Grignard reagents were prepared according to the literature.[19]

*Synthesis of* 1,1′, 3,3′-*tetramethyl*-2,2′-*bisbenzimidazolium salt* (**2**)

1, 1′, 3, 3′-Tetramethyl-2, 2′-bisbenzimidazolium salt (**2**) was prepared by literature procedures.[20] A solution of sodium (0.46 g, 0.02 mol) in ethanol was treated with 0.01 mol of bisbenzimidazole (**1**), 0.06 mol of iodomethane and 25.0 mol of benzene, then the mixture was refluxed for 18 h. The solvent was removed, the residue was recystallized from water-ethanol (1 : 1) to give bisbenzimidazolium (**2**), and the mp is over 300℃. Anal. $C_{18}H_{20}N_4I_2$. Calcd: C 33.73, H 4.02, N 13.65. Found: C 33.75, H 4.00, N 13.65.

*Synthesis of α-diketones* (**3**, **4**, **5** *and* **6**)

1, 1′, 3, 3′-Tetramethyl-2, 2′-bisbenzimidazolium salt (**2**, 0.02 mol) was added in small portions to a solution of Grignard reagent (0.06 mol) in tetrahydrofuran under nitrogen. The solution was stirred at reflux temperature for 16—18 h. After being left standing for half an hour, the mixture was treated with hydrochloric acid (10%) and stirred at 50—60℃ for 30 min. The solvent was removed and the mixture was distilled or extracted with ether, ethanol or benzene (5 × 30 mL). The residue was treated with 5% sodium hydroxide solution and *N*, *N*′-dimethyl-1,2-diaminobenzene was separated. The extracts were washed with 5% sodium bicarbonate and dried over anhydrous $MgSO_4$, and then distilled to give α-diketiones **3**, **4**, **5** and **6**).

Compound **3** as yellow liquid, yield 75%, bp 89—90℃ (lit.[21] 89—91℃). $\nu_{max}$ (KBr): 2980 ($CH_3$), 1710 (C = O). δ ($CDCl_3$): 2.31 (s, 6H, $CH_3$). Anal. $C_4H_6O_2$. Calcd: C 55.81, H 6.97. Found: C 55.84, H 6.96.

Compound **4** as yellow liquid, yield 73%, $n_D$ 1.4130 (lit.[22] 1.4157). $\nu_{max}$ (KBr): 2950, 1450, 1400, 1380(C—H), 1710(C = O), 1080, 880(C—C). δ($CDCl_3$): 1.04 (t, $J$ = 6.6 Hz, 6H, 2 × $CH_3$), 2.12(q, $J$ = 7.5 Hz, 4H, 2 × $CH_2$). Anal. $C_6H_{10}O_2$, Calcd: C 64.28, H 7.14. Found: C 64.27, H 7.16.

Compound **5** as yellow liquid, yield 69.0%, bp 94—96℃(lit.[21] 94—95℃). $\nu_{max}$(KBr): 2950 , 2850, 1460, 1395(C—H), 1710(C = O), 1110, 960, 860 (C—C). δ($CDCl_3$): 0.96 (t, $J$ = 8.3 Hz, 6H, 2 × $CH_3$), 1.25—2.05 (m, 4H, 2 × $CH_2$), 2.72 (t, $J$ = 6.7 Hz, 4H, 2 × $COCH_2$). Anal. $C_8H_{14}O_2$. Calcd: C, 69.56, H 7.25. Found: C 69.59, H 7.27.

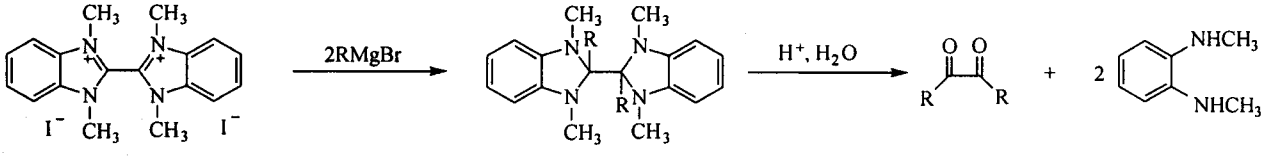
Compound **6** as white solid, yield 60.0%, mp 93—94℃ (lit.[23] 92—94℃). $\nu_{max}$(KBr): 1655(C=O), 1590, 1580, 790, 690, 680 ($C_6H_5$). δ($CDCl_3$): 7.20—7.90 (m, 10H, 2 × $C_6H_5$). Anal. $C_{14}H_{10}O_2$. Calcd: C 80.00, H 4.76. Found: C 79.97, H 4.78.

*N*, *N*′-Dimethyl-1,2-diaminobenzene was characterized, mp 34—35℃ (lit.[24] 34—35℃), $\nu_{max}$(KBr): 3300(N—H), 3010, 100, 1500, 735. Anal. $C_8H_{12}N_2$. Calcd: C 70.59, H 8.83, N 20.58. Found: C, 70.60, H 8.85, N 20.60.

## Results and discussion

The mechanism for the reaction of benzimidazolium salts with Grignard reagents was discussed in our earlier paper.[16] The reaction of bisbenzimidazolium salt with Grignard reagent can be reasonably explained by the formation of bisbenzimidazolidine which can be hydrolyzed to give α-diketone and *N*, *N*′-dimethyl-1,2-diaminobenzene in acidic solution.

The mechanism for the addition-hydrolysis reaction is as follows:




Further investigation of the mechanism of this kind reaction is being continued in our laboratory.

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(E0101083 JIANG, X.H.; DONG, L.J.)