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# FACILE PROCEDURE FOR THE SYNTHESIS OF 3-ACETYL-9-ETHYLCARBAZOLE AND CORRESPONDING FUNCTIONALIZED BIS-β-DIKETONE COMPOUNDS

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Acetylation-substituted N-ethylcarbazole at the 3-position was synthesized in 80% yield using  $ZnCl_2$  as catalyst, and its corresponding functionalized bis- $\beta$ -diketone compounds 2a and 2b were prepared by Claisen condensation with acceptable yields. Lanthanide complexes with the two compounds could be used as potential luminescent materials.

Keywords: Bis-β-diketone; carbazole; Claisen condensation; Friedel-Crafts acetylation

In recent years, substituted carbazoles have attracted considerable attention because of their wide use in biological research and luminescent materials. Carbazole derivatives constitute the structural framework of several naturally occurring alkaloids with a broad spectrum of biological activities.<sup>[1]</sup> It is also well known that carbazole compounds exhibit good hole-transporting properties and that their rare-earth complexes can create free carriers in the visible region through the photocarrier generation process.<sup>[2]</sup> Therefore, carbazole-containing compounds have been extensively studied for applications in electroluminescent (EL) devices.<sup>[3]</sup> The  $\beta$ -diketone ligand shows strong absorption within a wide wavelength range for its  $\pi \rightarrow \pi$  transition and consequently has been targeted for its ability to sensitize the luminescence of the lanthanide(III) ions.<sup>[4]</sup>

For the purpose of exploring novel efficient chelating ligands that can coordinate with lanthanide(III) ions, the target compounds of carbazole-functionalized bis- $\beta$ -diketone, methyl 6-(9-ethylcarbazole-3-yl)-oxoacetyl-2-pyridinecarboxylate (**2a**), and 1,1'-(2,6-bispyridyl)-bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (**2b**) have been prepared via the Claisen condensation, after the 3-position Friedel–Crafts acetylation of N-ethylcarbazole (Scheme 1). The synthesis presented was efficient and started from readily available and inexpensive substrates.

The first key step involved in the synthesis is the Friedel–Crafts acetylation of N-ethylcarbazole with acetyl chloride catalyzed by ZnCl<sub>2</sub>. Carbazoles undergo facile electrophilic addition at the 3- and 6-positions, and conditions have been established

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Scheme 1. Synthetic route of carbazole functionalized bis-β-diketones.

for obtaining the mono- and disubstituted products.<sup>[5]</sup> In particular, 3-position acetylcarbazoles were used as the common synthon for the synthesis of complicated carbazole-containing compounds. In the conventional method, the Friedel–Crafts acetylation of N-alkylcarbazole catalyzed by AlCl<sub>3</sub> has been reported to give a mixture of 3- and 3,6-diacetyl derivatives,<sup>[6]</sup> together with large amounts of tarry products resulting from the high Lewis acidity of AlCl<sub>3</sub>. Compared with several recent highly efficient catalysts for monoacetylation of N-alkylcarbazoles, as reported by Nagarajan,<sup>[7]</sup> herein we selected ZnCl<sub>2</sub> as the catalyst of acetylation because of its easily available and mild Lewis acidity. The workup of the reaction was convenient, and the yield is remarkable high. The results of Friedel–Crafts acetylation of 9-ethylcarbazole using different catalysts are given in Table 1.

The reaction was performed by addition of a little excess acetyl chloride to a stirred solution of 9-ethylcarbazole with a 120 mol% of ZnCl<sub>2</sub> for 6 h. Examination of thin-layer chromatography (TLC) showed that 3-acetyl-9-ethylcarbazole (1) was the main product during the acetylation; meanwhile, minimal tarry products were formed. The reaction was run at room temperature, because when it was higher than 30°C, the solvent  $CH_2Cl_2$  would suffer alkylation with the aromatic ring of carbazole structure.

As shown in Scheme 1, two bis- $\beta$ -diketone compounds (**2a** and **2b**) were prepared via Claisen condensation with the catalyst of sodium. The sodium was selected as the catalyst because of readily accessible and facile operation. The subsequent workups were easily carried out, and the yields are about 75%. Besides the acceptable

Catalyst	Time (h)	Temperature (°C)	Molar ratio (%) <sup>a</sup>	Yield (%) <sup>b</sup>
AlCl <sub>3</sub>	6	-5	120	45
PPh <sub>3</sub> , HClO <sub>4</sub>	4	20	20	59 (61) <sup>c</sup>
$ZnCl_2$	6	20	120	80

Table 1. Yields of 3-acetyl-9-ethylcarbazole with different catalysts

<sup>a</sup>Molar amount ratio of catalyst and N-ethylcarbazole.

<sup>b</sup>The yield is based on isolation by column chromatography, and 3-acetyl-9-ethylcarbazole was characterized by FT-IR and <sup>1</sup>H NMR.

<sup>c</sup>Yield reported in the literature.<sup>[7a]</sup>



Figure 1. Tautomeric interconversion of  $\beta$ -diketone.

yields of Claisen condensation, the reactions were accompanied by many side reactions, such as Aldol condensation. The products can be purified by recrystallization from appropriate mixed solvents.

Two different products (2a and 2b) have been synthesized with different molar ratios of compound 1 and dimethyl 2,6-pyridinedicarboxylate (1:1 for 2a and 2:1 for 2b). The bis- $\beta$ -diketone compounds have theoretical tautomeric equilibrium between the keto-isomer and enol-isomer (see Fig. 1); the factual existent form can be confirmed on the basis of the compound characterization data. First, the Fourier transform–infrared (FT-IR) spectra show a broad band of medium intensity centered at about 3430 cm<sup>-1</sup>, which can be assigned as  $\nu$ (C–OH) of enol-isomer of the compounds. For the <sup>1</sup>H NMR, the superlow field of ca.16.50 ppm can be assigned as the OH proton of enol-isomer, according to the relative integral areas of the OH proton and olefin proton of  $\beta$ -diketone unit, the proportion of enol-isomer is approximate 100%. It obviously shows that the solid bis- $\beta$ -diketone compounds exist in the form of enol-isomer at room temperature.

In conclusion, we have developed a facile, efficient method for the synthesis of 3-acetyl-9-ethylcarbazole with acetyl chloride catalyzed by  $ZnCl_2$ , and the final bis- $\beta$ diketone products were successfully prepared by Claisen condensation with satisfactory yields. The compounds 2a and 2b can coordinate with Eu(III) and Tb(III) ions, generating novel luminescent tris( $\beta$ -diketonates) lanthanide complexes. The investigations of photoluminescence properties of the complexes show that the Eu(III) and Tb(III) ions can produce a strong intense emission via sensitization by the bis- $\beta$ diketone ligands. The emission spectra of the Eu(III) complexes exhibit two sharp characteristic emission peaks at about 596 and 618 nm corresponding to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  (magnetic dipole transition) and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  (electric dipole transition), respectively. The hypersensitive  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition has the most intense and narrow bandwidths, pointing to a highly polarizable chemical environment around the central Eu(III) ion. The emission spectra of the Tb(III) complexes consist of four main lines at approximately 495 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ), 548 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ), 587 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ ), and 625 nm  $({}^{5}D_{4} \rightarrow {}^{7}F_{3})$ , and we can see that the emission band  $({}^{5}D_{4} \rightarrow {}^{7}F_{5})$  is obviously stronger than the other emission bands and has extremely narrow bandwidths. In a word, the lanthanide complexes that used compounds 2a and 2b as the ligands have a very good luminescent performance and could be candidates for efficient luminescent materials.

#### EXPERIMENTAL

Dimethyl 2,6-pyridinedicarboxylate and 9-ethylcarbazole were synthesized respectively as described in the literature.<sup>[8,9]</sup> The solvents were dried and redistilled

prior to usage. Melting points were observed on an XR-4 apparatus (thermometer uncorrected). FT-IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region using a Nicolet Nexus 670 FT-IR spectrophotometer with KBr plates. <sup>1</sup>H NMR spectra were measured with a Bruker 400-MHz nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as internal reference. Elemental analyses were carried out by a Perkin-Elmer 2400 elemental analyzer. Chromatographic separations were performed on silica gel (100–200 mesh).

#### Synthesis of 3-Acetyl-9-ethylcarbazole (1)

To a solution of 9-ethylcarbazole (4.0 g, 20.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), anhydrous ZnCl<sub>2</sub> (3.4 g, 25.0 mmol) was added quickly, and the mixture was stirred at room temperature; meanwhile, a solution of acetyl chloride (1.80 mL, 24.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added dropwise. The reaction mixture was incubated and stirred at ambient temperature for about 6 h. Then cooled water (100 mL) was added to the mixture and extracted with  $CH_2Cl_2$  (3 × 20 mL). The mixture was dried on anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using a mixture of ethyl acetate-petroleum ether (1:9) as eluent. The crude product was recrystallized from 95%ethanol to give white needles of compound 1 (3.9 g, 80%). Mp 114-116°C (literature.<sup>[6]</sup> 115°C); IR (cm<sup>-1</sup>): 3042, 2966, 1660, 1622, 1591, 1493, 1436, 1353, 1327, 1245, 1158, 748; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 (d, 1H, J=1.2 Hz, PhH), 8.11–8.16 (m, 2H, J = 4.0 Hz, J = 2.4 Hz, PhH), 7.26–7.54 (m, 4H, J = 4.0 Hz, PhH), 4.33–4.39 (q, 2H, J=7.2 Hz, CH<sub>2</sub>), 2.73 (s, 3H, OCH<sub>3</sub>), 1.42–1.46 (t, 3H, J = 7.2 Hz, CH<sub>3</sub>). Anal. calcd. for C<sub>16</sub>H<sub>15</sub>NO: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.32; H, 6.39; N, 5.74.

### Synthesis of Methyl 6-(9-Ethylcarbazole-3-yl)-oxoacetyl-2-pyridinecarboxylate (2a)

A suspension of freshly cut sodium (0.09 g, 4.0 mmol) in anhydrous toluene (20 mL) was placed in a three-necked flask. The mixture was heated up to 120°C and stirred vigorously until the sodium was molten and scattered, and then dimethyl 2,6-pyridinedicarboxylate (0.78 g, 4.0 mmol) was added into the mixture. Meanwhile, a solution of 3-acetyl-9-ethylcarbazole (0.95 g, 4.0 mmol) in toluene (15 mL) was added dropwise. The reaction mixture was incubated and stirred at 120°C for about 6 h until the brown-yellow sodium salt precipitated. The sodium salt was collected by filtration, washed thoroughly with petroleum ether, and dried. The dried solid was added to dilute hydrochloric acid, and the resulting precipitate was collected by filtration. The crude product was purified by recrystallization from methanol and tetrahydrofuran (1:1) to give the compound 2a as a pale brown powder (1.22 g, 76%). Mp 96–98°C; IR (cm<sup>-1</sup>): 3437, 3047, 2973, 1727, 1592, 1471, 1384, 1232, 1204, 1133, 773, 544; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  16.50 (s, 1H, C=C-OH), 8.06-8.94 (m, 3H, PyH), 7.46-7.67 (m, 7H, PhH), 7.25 (s, 1H, -CH=), 4.41  $(q, 2H, J = 6.8 \text{ Hz}, CH_2), 3.94 (s, 3H, OCH_3), 1.29 (t, 3H, J = 6.8 \text{ Hz}, CH_3).$  Anal. calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: C, 71.99; H, 5.03; N, 7.00. Found: C, 72.24; H, 5.12; N, 6.88.

## Synthesis of 1,1'-(2,6-Bis-pyridyl)-bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (2b)

The reaction procedure was the same as that of **2a** except for the half amount of dimethyl 2,6-pyridinedicarboxylate (0.38 g, 1.9 mmol). After filtration and acidization, the dried crude products were purified by recrystallization from methanol and chloroform (2:1), and the brownish yellow of compound **2b** was obtained (0.85 g, 74%). Mp 113–115°C; IR (cm<sup>-1</sup>): 3432, 3051, 2975, 1708, 1593, 1492, 1472, 1448, 1383, 1346, 1233, 796, 749, 545; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  16.95 (s, 1H, OH), 16.82 (s, 1H, OH), 7.93–8.95 (m, 3H, PyH), 7.25–7.52 (m, 16H, PhH, CH), 4.36–4.39 (q, 4H, J = 7.2 Hz, CH<sub>2</sub>), 1.27–1.47 (t, 6H, J = 7.2 Hz, CH<sub>3</sub>). Anal. calcd. for C<sub>39</sub>H<sub>31</sub>N<sub>3</sub>O<sub>4</sub>: C, 77.34; H, 5.16; N, 6.94. Found: C, 77.50; H, 5.02; N, 6.87.

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