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Synthesis of a Novel β-Diketone Containing Carbazole and 2,5-Diphenyl-1,3,4-oxadiazole Fragments*

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Abstract—A novel β-diketone containing carbazole and 2,5-diphenyl-1,3,4-oxadiazole fragments as hole- and electron-transporting functional groups, respectively, was synthesized via efficient and convenient procedure. The product attracts interest from the viewpoint of its potential applications as optoelectronic material.

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β-Diketones are very important and familiar ligands in coordination chemistry due to their strong coordination ability, high stability, and extraordinary optical, electronic, and magnetic properties of their complexes. Synthesis and application of β-diketones have long attracted great interest in chemistry, material science, physics, and biochemistry. In the recent years, a great deal of metal ion (e.g., Eu^{3+}, Tb^{3+}, Sm^{3+}, Ir^{3+}) complexes derived from various β-diketones have been used as optoelectronic materials such as light-emitting materials in organic light-emitting diodes [1–4], memory materials in organic electrical memory devices [5, 6], etc. It has been confirmed that carbazole fragment is an excellent hole-transporting group [4, 7–10] and that 2,5-diphenyl-1,3,4-oxadiazole group is an excellent electron-transporting group [11, 12]; their derivatives had been widely used in optoelectronic devices [7–12], mainly due to their beneficial effect on the device performance via enhancement of charge conductivity. Apart from derivatives containing either carbazole or 2,5-diphenyl-1,3,4-oxadiazole group, organic molecules comprising both these are also very important materials in optoelectronic devices; for example, they were used as host [13] and light-emitting materials [14] in organic light-emitting diodes. The syntheses of β-diketones containing only carbazole [9] or 2,5-diphenyl-1,3,4-oxadiazole [15] fragment and their complexes have already been reported, whereas β-diketones containing both carbazole and 2,5-diphenyl-1,3,4-oxadiazole fragments still remain unknown, though such β-diketones should be very important and promising for use in optoelectronic materials.

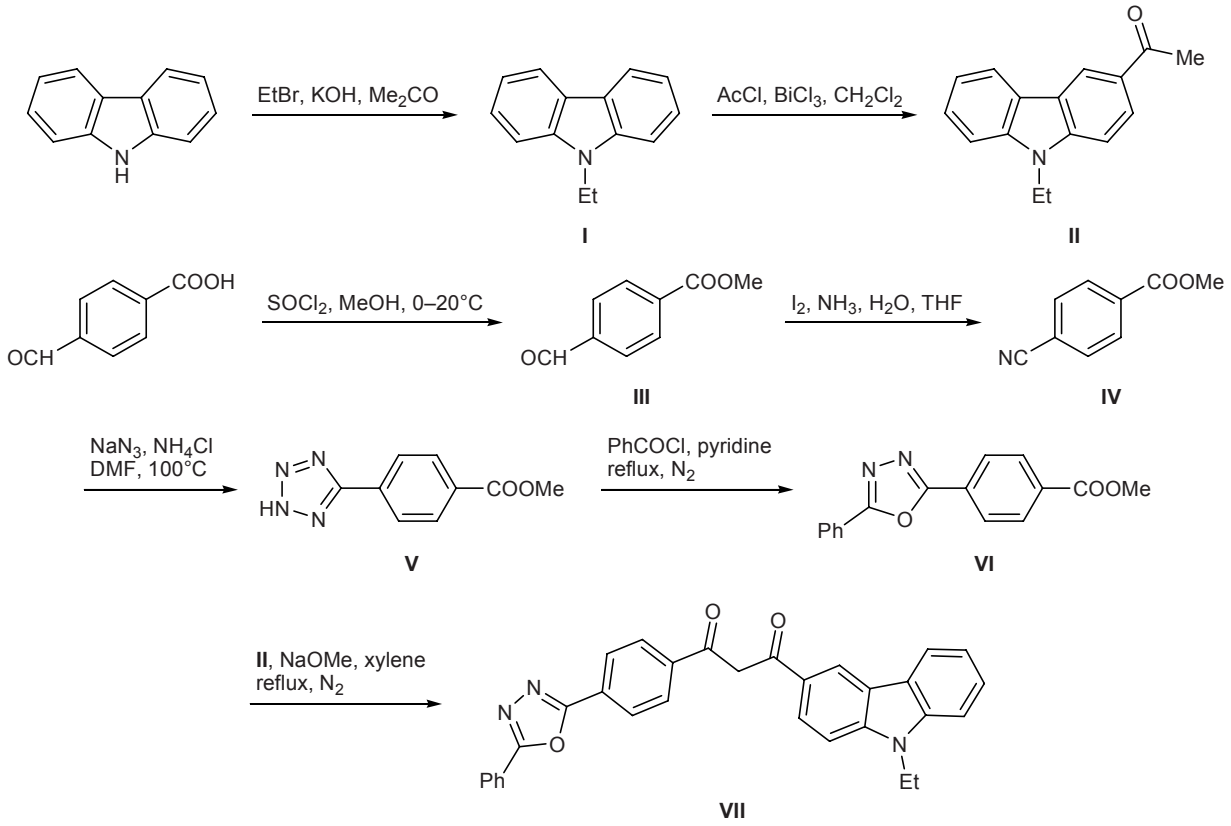
Generally, syntheses of β-diketones via traditional Claisen condensation of appropriate ketones and esters are not difficult; however, required initial ketones and esters are sometimes difficultly accessible. In the present article we describe an effective and convenient synthesis of β-diketone containing both carbazole and 2,5-diphenyl-1,3,4-oxadiazole fragments (Scheme 1).

3-Acetyl-9-ethylcarbazole (**II**) necessary for the subsequent Claisen condensation was synthesized in two steps starting from carbazole. Initially, 9-ethylcarbazole (**I**) was prepared according to the procedure described in [16]. The Friedel–Crafts acylation is commonly catalyzed by Lewis acids, in particular by $AlCl_3$. However, this Lewis acid turned out to be inappropriate in the acylation of 9-ethylcarbazole, for mixtures of 3-acetyl and 3,6-diacetyl derivatives were formed with large amounts of tarry products. Therefore, we used $BiCl_3$ as catalyst instead of $AlCl_3$ [17]. In addition, the procedure reported in [17] was modified so that a larger amount of $BiCl_3$ was applied and acetic anhydride was replaced by more reactive acetyl chloride. As a result, we succeeded in raising the yield of **II** from 60 to 81%.

Methyl 4-(5-phenyl-1,3,4-oxadiazol-2-yl)benzoate (**VI**) was previously synthesized under microwave irradiation [18]. Although microwave-assisted synthesis is rapid and efficient, the reaction is difficult to control due to tremendous energy transferred to the reactants in a very short time; furthermore, microwave-assisted syntheses are difficult to perform on enlarged scale. Taking into account the above stated, we tried to synthesize the required ester following conventional chemical approaches, i.e., from the corresponding acid

* The text was submitted by the authors in English.

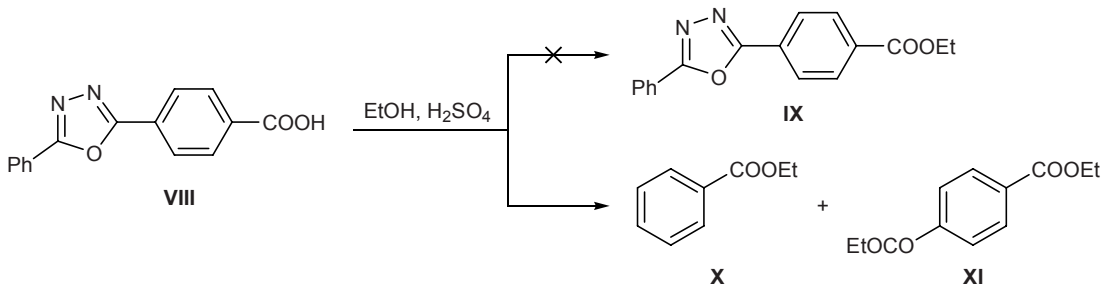
Scheme 1.



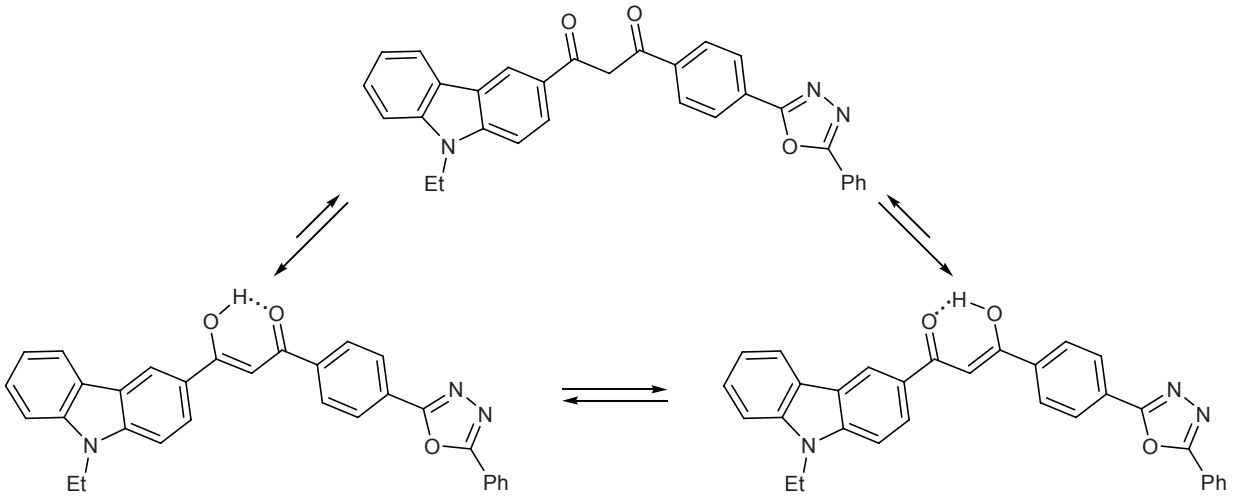
and alcohol. 4-(5-Phenyl-1,3,4-oxadiazol-2-yl)benzoic acid (**VIII**) can be prepared as described in [19]. However, we failed to obtain ester **IX** by esterification of acid **VIII** with ethanol as shown in Scheme 2; instead, the products were ethyl benzoate (**X**) and diethyl terephthalate (**XI**) which were formed as a result of alcoholysis of the 1,3,4-oxadiazole fragment. Therefore, we developed a new synthetic route to ester **VI** (Scheme 1). Methyl 4-formylbenzoate (**III**) was synthesized by a modified procedure [20]. Replacement of commonly used ethanol by methanol having a lower boiling point facilitated removal of excess alcohol under reduced pressure at room temperature. Compound **III** was then treated with a nearly equimolar amount of iodine and excess ammonia in aqueous tetrahydrofuran to obtain nitrile **IV**. The subsequent reaction of **IV** with sodium azide and ammonium chloride in dimethylformamide at 100°C gave 5-substituted tetrazole **V**, and the latter was converted into oxadiazole **VI** by the action of benzoyl chloride in anhydrous pyridine under nitrogen. Finally, Claisen condensation of ketone **II** with 1.5 equiv of ester **VI** in the presence of freshly prepared sodium methoxide as catalyst afforded the desired β-diketone **VII** possessing both carbazole and 2,5-diphenyl-1,3,4-oxadiazole fragments (Scheme 1).

All intermediate products and β-diketone **VII** were characterized by elemental analyses and ^{1}H NMR and

Scheme 2.



Scheme 3.



IR spectra. It should be noted that the ^{1}H NMR and IR spectra of compound **VII** were not fully consistent with the diketone structure. Presumably, it exists as enol tautomers stabilized by intramolecular hydrogen bonds [21] as shown in Scheme 3.

EXPERIMENTAL

All reagents were obtained from commercial sources and were used without additional purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh). Yields refer to the isolated pure compounds. The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ on a Varian Mercury VX300 spectrometer (300 MHz) using TMS as internal standard. The IR spectra were recorded in KBr on a Shimadzu FTIR-8201PC spectrometer. Elemental analysis was performed on a VarioEL III analyzer. The melting points were determined from the differential scanning calorimetry (DSC) curves which were obtained on a Netzsch DSC 200 analyzer on heating at a rate of 10 deg/min in static air.

9-Ethyl-9*H*-carbazole (I). A mixture of 14.00 g (250 mmol) of potassium hydroxide in 80 ml of acetone was stirred for 20 min, 6.60 g (40 mmol) of carbazole was added, and the mixture was stirred for 40 min. A solution of 6.54 g (60 mmol) of ethyl bromide in 20 ml of acetone was then added dropwise with stirring, and the mixture was stirred for 10 h, slowly poured into 1 l of water under stirring, and left to stand for several hours. The crude product was collected on a vacuum filter, washed with water, recrystallized from ethanol, and dried in a vacuum oven. Yield 7.0 g (91%), colorless needles, mp 68.6°C. IR spectrum, ν, cm^{-1}: 3047, 2929, 2854, 1597, 1484, 1467, 1453, 1384, 1326, 1229, 1150, 1128, 1081, 1055, 1018, 752, 722, 615. ^{1}H NMR spectrum, δ, ppm: 1.45 t (3H, CH_3, J = 7.2 Hz), 4.42 q (2H, CH_2, J = 7.2 Hz), 7.24–7.30 m (2H, H_{arom}), 7.44–7.54 m (4H, H_{arom}), 8.15 d (2H, H_{arom}, J = 8.1 Hz). Found, %: C 85.75; H 6.59; N 7.22. $C_{14}H_{13}N$. Calculated, %: C 86.12; H 6.71; N 7.17.

1-(9-Ethyl-9*H*-carbazol-3-yl)ethanone (II). Dry 9-ethylcarbazole (**I**), 7.80 g (40 mmol), was mixed with 100 ml of anhydrous methylene chloride, 20.50 g (65 mmol) of $BiCl_3$ was added under stirring, a mixture of 7.85 g (~7.0 ml, 100 mmol) of acetyl chloride in 10 ml of anhydrous methylene chloride was added dropwise, and the mixture was stirred for 2 h at room temperature with a mechanical stirrer. Concentrated hydrochloric acid, 50 ml, and water, 30 ml, were added, and the mixture was stirred until the brown precipitate dissolved completely. The mixture was then extracted with methylene chloride (3×50 ml), the combined extracts were dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using methylene chloride as eluent. The product was additionally recrystallized from ethanol. Yield 7.70 g (81%), colorless or pale yellow needles, mp 114.5°C. IR spectrum, ν, cm^{-1}: 3059, 2930, 1660, 1591, 1440, 1384, 1353, 1244, 1157, 748. ^{1}H NMR spectrum, δ, ppm: 1.49 t (3H, CH_3, J = 7.2 Hz), 2.78 s (3H, $COCH_3$), 4.43 q (2H, CH_2, J = 7.2 Hz), 7.29–7.39 m (1H, H_{arom}), 7.46–7.56 m (3H, H_{arom}), 8.15–8.21 m (2H, H_{arom}), 8.78 d (1H, H_{arom}, J = 1.5 Hz). Found, %: C 80.78; H 6.41; N 5.94. $C_{16}H_{15}NO$. Calculated, %: C 80.98; H 6.37; N 5.90.

Methyl 4-formylbenzoate (III). A mixture of 7.50 g (50 mmol) of dry 4-formylbenzoic acid and 150 ml of anhydrous methanol was cooled to 0°C, and 30 ml of thionyl chloride was added dropwise under stirring. The mixture was stirred for 10 h at room temperature, filtered, and evaporated, and the residue was slowly poured into 500 ml of water. The product was collected on a vacuum filter, washed with water, and dried in a vacuum oven. Yield 7.65 g (93%), pale yellow solid, mp 52.7°C (DSC). IR spectrum, ν, cm^{-1}: 3421, 3019, 2958, 2887, 2846, 1952, 1726, 1706, 1682, 1612, 1577, 1503, 1437, 1391, 1285, 1202, 1110, 1057, 1014, 958, 853, 809, 758, 686. ^1H NMR spectrum, δ, ppm: 3.97 s (3H, CH_3), 7.96 d (2H, H_{arom}, J = 7.8 Hz), 8.20 d (2H, H_{arom}, J = 7.8 Hz), 10.11 s (1H, CHO). Found, %: C 65.68; H 4.97. $C_9H_8O_3$. Calculated, %: C 65.85; H 4.91.

Methyl 4-cyanobenzoate (IV). Iodine, 11.18 g (44 mmol), was added under stirring to a mixture of 6.56 g (40 mmol) of methyl 4-formylbenzoate (**III**), 40 ml of tetrahydrofuran, and 30 ml of 28% aqueous ammonia. The mixture was stirred for 4 h at room temperature, a 0.1 M solution of $Na_2S_2O_3$ was added dropwise until the dark brown color disappeared, and the mixture was extracted with methylene chloride (3×50 ml). The extracts were combined and dried over anhydrous Na_2SO_4, the solvent was distilled off, and the residue was recrystallized from methanol. Yield 5.45 g (85%), pale yellow needles, mp 67.0°C (DSC). IR spectrum, ν, cm^{-1}: 3421, 3103, 3073, 3055, 3030, 3008, 2956, 2849, 2228, 1948, 1825, 1720, 109, 1565, 1441, 1405, 1317, 1277, 1196, 1104, 1017, 961, 866, 834, 764, 691, 546. ^1H NMR spectrum, δ, ppm: 3.97 s (3H, CH_3), 7.75 d (2H, H_{arom}, J = 7.8 Hz), 8.14 d (2H, H_{arom}, J = 9.0 Hz). Found, %: C 67.15; H 4.43; N 8.60. $C_9H_7NO_2$. Calculated, %: C 67.07; H 4.38; N 8.69.

Methyl 4-(2*H*-tetrazol-5-yl)benzoate (V). Sodium azide, 3.9 g (60 mmol), and ammonium chloride, 3.21 g (60 mmol) were added under stirring to a solution of 6.44 g (40 mmol) of methyl 4-cyanobenzoate (**IV**) in 50 ml of *N*,*N*-dimemylformamide, and the mixture was stirred for 24 h at 100°C. The mixture was cooled, poured into 500 ml of water, and acidified to pH ~1.0 with concentrated hydrochloric acid, and the precipitate was filtered off, washed with water, and dried in a vacuum oven. Yield 6.15 g (75%), white solid, mp 225.7°C (DSC). IR spectrum, ν, cm^{-1}: 3357, 3156, 3099, 3067, 2956, 2868, 2797, 1714, 1686, 1564, 1433, 1288, 1189, 1111, 1062, 997, 958, 863, 829, 783, 735, 706. ^1H NMR spectrum, δ, ppm: 3.97 s (3H, CH_3), 4.43 s (1H, NH), 8.10–8.20 m (4H, H_{arom}). Found, %: C 52.65; H 4.23; N 27.68. $C_9H_8N_4O_2$. Calculated, %: C 52.94; H 3.95; N 27.44.

Methyl 4-(5-phenyl-1,3,4-oxadiazol-2-yl)benzoate (VI). Benzoyl chloride, 4.64 g (33 mmol), was added dropwise under stirring to a solution of 6.12 g (30 mmol) of methyl 4-(2*H*-tetrazol-5-yl)benzoate (**V**) in 50 ml of anhydrous pyridine, and the mixture was stirred for 4 h on heating under reflux in a nitrogen atmosphere. The mixture was cooled and poured into 500 ml of water, and the precipitate was filtered off, washed with water, and recrystallized from ethanol. Yield 7.08 g (84%), pale yellow solid, mp 169.2°C. IR spectrum, ν, cm^{-1}: 3059, 3000, 2948, 1717, 1611, 1582, 1548, 1485, 1451, 1433, 1414, 1277, 1108, 1073, 964, 865, 779, 716, 689. ^1H NMR spectrum, δ, ppm: 3.99 s (3H, CH_3), 7.56–7.58 m (3H, H_{arom}), 8.16–8.26 m (6H, H_{arom}). Found, %: C 68.44; H 4.21; N 9.78. $C_{16}H_{12}N_2O_3$. Calculated, %: C 68.56; H 4.32; N 9.99.

1-(9-Ethyl-9*H*-carbazol-3-yl)-3-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]propane-1,3-dione (VII). Freshly prepared sodium methoxide, 1.08 g (20 mmol), was added to a mixture of 2.37 g (10 mmol) of dry ketone **II** and 4.20 g (15 mmol) of methyl 4-(5-phenyl-1,3,4-oxadiazol-2-yl)benzoate (**VI**) in 50 ml of anhydrous xylene, and the mixture was heated for 12 h under reflux while stirring in a nitrogen atmosphere. The mixture was cooled, acidified with hydrochloric acid, and extracted with xylene (3× 50 ml). The extracts were combined and dried over anhydrous Na_2SO_4, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using a mixture of petroleum ether (bp 60–90°C), chloroform, and ethyl acetate (1:2:1, by volume) as eluent. Yield 2.73 g (56%), yellow solid, mp 248.0°C. IR spectrum, ν, cm^{-1}: 3043, 2984, 2936, 1626, 1587, 1548, 1487, 1470, 1448, 1384, 1330, 1231, 1209, 1122, 1069, 1048, 781, 753, 727, 709, 690. ^1H NMR spectrum, δ, ppm: 1.50 t (3H, CH_3, J = 3.6 Hz), 4.44 q (2H, CH_2, J = 3.6 Hz), 7.08 s (1H, =CH, enol), 7.23–7.60 m (7H, H_{arom}), 8.17–8.30 m (8H, H_{arom}), 8.84 s (1H, H_{arom}); signals from the enol OH protons were not detected due to fast exchange. Found, %: C 76.82; H 4.64; N 8.40. $C_{31}H_{23}N_3O_3$. Calculated, %: C 76.69; H 4.77; N 8.65.

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