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Synthesis of 3-acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole

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Abstract 3-Acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole was prepared through successive *o*-methyl benzoylation and acetylation of *N*-ethylcarbazole in one pot. The overall yield was 85.6% and the structure was confirmed by ^{1}H-NMR and ^{13}C-NMR. A preliminary investigation had also been carried out on the mechanism of the *o*-methyl benzoylation of *N*-ethylcarbazole.

Keywords 3-Acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole · Acylation · Aluminum chloride

Introduction

Carbazole and its derivatives had been widely used in optical materials for their huge conjugated systems and active intramolecular electron transfer [1, 2]. Recently, with the further research of two-photon chemistry, more and more people focused their research on the synthesis of new carbazole derivatives with longer conjugated chain, which was in favor of larger two-photon absorption cross-section and stronger two-photon property [3].

Herein, 3-acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole, a new carbazole derivative with special D–π–D structure, was synthesized through two successive different acylation of *N*-ethylcarbazole, as sketched in Scheme 1. In this product, the N atom of carbazole was linked with an alkyl chain to increase the electron

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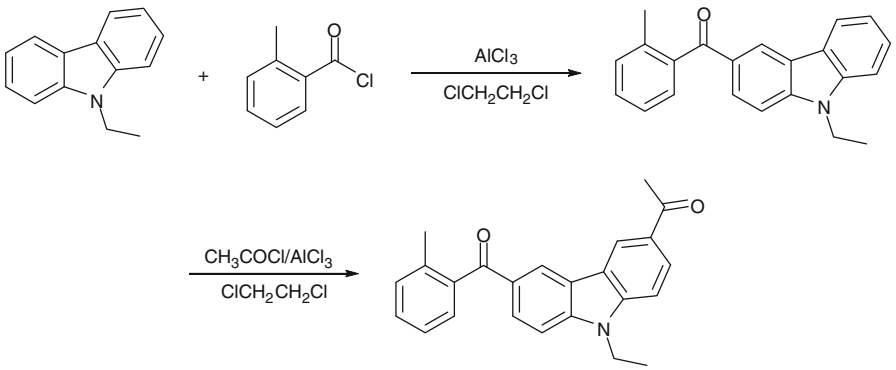


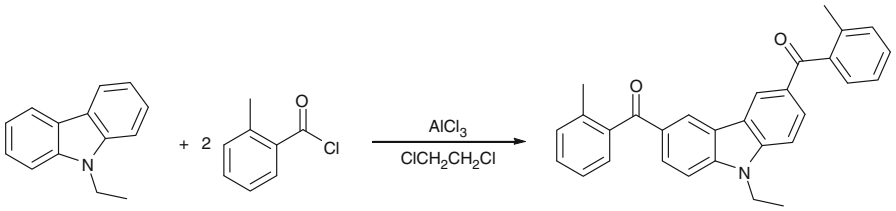
Scheme 1 The synthetic route of 3-acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole

donating ability of the conjugated system, and conjugated acyl groups were introduced to carbazole to extend the conjugated chain, thus, the two-photon absorption cross-section and the two-photon property were further enlarged.

The two different groups introduced to *N*-ethylcarbazole by two successive acylation were *o*-methyl benzoyl and acetyl, so the control of the *o*-methyl benzoylation to monoacyl substitution, which was frequently accompanied by diacylation (as sketched in Scheme 2), was crucial for the successful synthesis of product. To synthesize similar compounds, the purification of the product by column chromatography on silica gel was always needed [4]. In this paper, we found that, surprisingly, the dosage of catalyst aluminum chloride could change the distribution of the products to a large extent.

According to the mechanism of Friedel–Crafts acylation [5], the complex comprised of catalyst aluminum chloride and the acylation product must be broken down by the addition of water after the reaction. And the aluminum chloride in the formed complex could no longer catalyze acylation. So, in acylation reactions, theoretically, the dosage of aluminum chloride should be at least equimolar to the raw material, and, actually, it was 10–50% in excess of the equimolar dosage in many cases [6, 7].

However, in our case, there was no need to use an equimolar catalyst dosage to *N*-ethylcarbazole to maintain high conversion in the *o*-methyl benzoylation. The results showed that the conversion could reach more than 90% at 0–5 °C,



Scheme 2 The subsidiary reaction of the 3-acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole synthesis

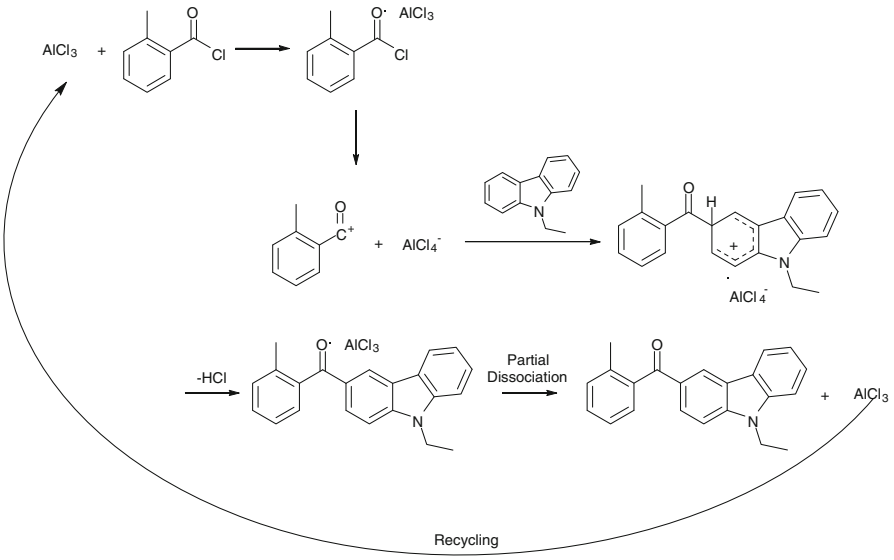


Fig. 1 The mechanism of the *o*-methyl benzoylation of *N*-ethylcarbazole

even when the molar ratio between aluminum chloride and *N*-ethylcarbazole was only 0.7. It was demonstrated that part of the complex-formed forehead was dissociated, and the aluminum chloride that departed from the complex could be reused in the acylation catalysis. Based on the findings, we supposed the mechanism of the *o*-methyl benzoylation of *N*-ethylcarbazole as shown in Fig. 1. The catalyst aluminum chloride and *o*-methyl benzoyl chloride formed a complex to weaken the C–Cl bond, and then formed *o*-methyl benzoyl carbocation, which attacked *N*-ethylcarbazole to form aromatic carbocation. Then, a molecule of HCl was eliminated from the aromatic carbocation to form a complex comprised of aluminum chloride and the acylation product. The complex could be partially dissociated to the aluminum chloride, which formed a new complex with another molecule of *o*-methyl benzoyl chloride and repeated the process described above.

Furthermore, when the dosage of aluminum chloride was less equimolar than that of *N*-ethylcarbazole, the diacylation was, to a large extent, restrained, which meant that the *o*-methyl benzoylation reaction was successfully controlled in the monoacyl substitution stage. In other words, the aluminum chloride released from the partial dissociation of the complex made it unnecessary to use a larger catalyst dosage to ensure the complete conversion of *N*-ethylcarbazole and, as a consequence, the diacylation was avoided.

For the second step of two successive acylations progressed in one pot, the released aluminum chloride in *o*-methyl benzoylation could be used in a subsequent acetylation, and an additional 0.5 equimolar to the *N*-ethylcarbazole produced the acetylation high yield.

Experimental

All reagents were commercially obtained without further purification. The melting point was recorded on a WSR-I capillary melting point apparatus and was uncorrected. ^{1}H-NMR and ^{13}C-NMR data were recorded on a Bruker 400 MHz spectrometer operating near 400 (^{1}H) or 100 (^{13}C) MHz in $CDCl_3$ solutions and TMS was used as the internal standard.

To a well-stirred reaction vessel, which was kept in an ice water bath to maintain a temperature of 0–5 °C, was added aluminum chloride (4.6 g, 0.035 mol), *N*-ethylcarbazole (9.75 g, 0.05 mol) and dichloroethane (65 mL). To the content, the solution of *o*-methyl benzoyl chloride (6.5 mL, 0.05 mol) and dichloroethane (15 mL) was added dropwise over 0.5 h. Upon completion of the addition, the mixture was kept at 0–5 °C for an additional 0.5 h. Then, the ice water bath was removed and warmed slowly to room temperature. A mixture of aluminum chloride (3.4 g, 0.025 mol) and acetyl chloride (4.5 mL, 0.06 mol) was added and the content was kept at this temperature for another 0.5 h. Then, the mixture was poured into water. After the phase separation, the organic layer was successively washed with saturated sodium carbonate solution and water to neutralization and dried over Na_2SO_4. Then, the solvent was completely evaporated under reduced pressure and the residue was extracted with acetone (3 × 20 mL). The combined acetone solution was cooled in the refrigerator to maintain a temperature of 0 °C and kept for 12 h and, thereupon, 3-acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole was crystallized as a white solid (15.2 g, 85.6% yield), mp. 162.1–163.2 °C.

3-Acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole: ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 1.46–1.50 (t, 3H, –CH_2–CH_3), 2.35 (s, 3H, –CH_3), 2.70 (s, 3H, –CO–CH_3), 4.41–4.43 (q, 2H, –CH_2–), 7.29–7.48 (m, 6H, Ar–H), 8.09–8.11 (m, 1H, Ar–H), 8.14–8.17 (m, 1H, Ar–H), 8.54–8.55 (m, 1H, Ar–H), 8.68–8.69 (m, 1H, Ar–H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 13.81 (–CH_2–CH_3), 19.83 (–CH_3), 26.69 (–CO–CH_3), 38.16 (–CH_2–), 108.69 (–Ar), 108.82 (–Ar), 122.08 (–Ar), 122.90 (–Ar), 122.93 (–Ar), 124.21 (–Ar), 125.30 (–Ar), 127.07 (–Ar), 127.97 (–Ar), 128.63 (–Ar), 129.71 (–Ar), 129.83 (–Ar), 129.93 (–Ar), 130.89 (–Ar), 136.16 (–Ar), 139.48 (–Ar), 143.37 (–Ar), 143.53 (–Ar), 197.50 (Ar–CO–Ar), 198.17 (–CO–CH_3).

Conclusion

3-Acetyl-6-(*o*-methyl benzoyl)-*N*-ethylcarbazole was prepared in 85.6% yield through two successive different acylations of *N*-ethylcarbazole. In the *o*-methyl benzoylation of *N*-ethylcarbazole, less than *N*-ethylcarbazole molar dosage of aluminum chloride was enough to obtain high conversion, and which was effective to restrain the multi-acylation. The total molar dosage of aluminum chloride of two successive acylations was reduced to 1.2 times that of *N*-ethylcarbazole for the recycling of aluminum chloride in *o*-methyl benzoylation and the two successive acylations in one pot.

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