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Synthesis of nitrogenated scaffolds derived from fluorene by a modified Ullmann type reaction

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ABSTRACT

Two novel aromatic molecules were synthesized via a modified Ullmann coupling starting from a known compound 2,7-diiodofluorenone with carbazole derivatives. These compounds were obtained in very good yields. Due to their fluorophore components, like fluorenone and carbazole, they could be applied as scaffolds for the development of organic materials like dendrimers and polymers.

Introduction

Novel nitrogenated aromatic compounds derived from 2,7-diiodofluorenone were obtained using a modified Ullmann coupling protocol. These new molecules are interesting structures which combine fluorenone and carbazole moieties, two promising scaffolds for the synthesis of macromolecules in the development of organic materials with optoelectronic properties as hole transporting or nonlinear optical processes.

Organic substances exhibiting significant nonlinear optical effects have been the subject of intense academic and industrial research.[1] In particular, semiconducting materials showing efficient optoelectronic and modulable self-organization properties have been extensively investigated during the past two decades due to their use as electroactive components in photovoltaic cells,[2] light-emitting diodes (OLEDs),[3] or field-effects transistors.[4] 9-Fluorenone is a molecular scaffold that shows important applications in material sciences as optical materials,[5] organic dyes,[6] plastic additives, biomedical materials,[7] organic solar cells,[8] OLEDs,[9] etc. Moreover, the electrochemical properties of fluorenone can be dramatically modified through functionalization at positions 2 and 7.[10]

On the other hand, the production of hole transporting materials is an important and challenging field in the design of new OLEDs. Arylamines and various triphenylamines derivatives have been employed with these objectives and played a major role in the improvement of organic electronics.[11] The combination of the optoelectronic properties of fluorenone with aromatic nitrogenated derivatives can be accomplished when using 2,7-dihalofluorenones as starting materials.

There is a tendency among chemists to discover new candidates but ignoring the difficulties in their preparation. The synthesis of complex target structures is an accomplishment from the chemical point of view but they are real progress in material development only if they could be achieved in a practical and scalable way. Therefore, our interest is the production of new optoelectronic properties through a simple synthesis of novel organic materials.[12] Herein, we describe the preparation of two new compounds derived from 2,7-bis-amine fluorenones that could be used as dendrons and led to a new class of hole transporting materials. The aryl amine substituents chosen were carbazole derivatives and the C–N chemical bonds were built by a modified Ullmann reaction protocol even though a previous report[13] discourages this method for the functionalization of 2,7-halofluorenones.

Results and discussion

Low cost and easily available fluorene **1** was used as starting material. Electrophilic iodination of **1** afforded 2,7-diiodofluorene **2**, which was subsequently oxidized to 2,7-diiodofluorenone **3** in 85% overall yield (Scheme 1).[14]

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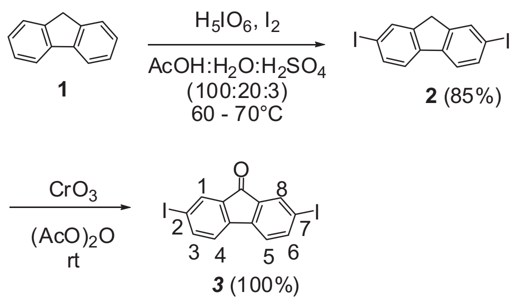
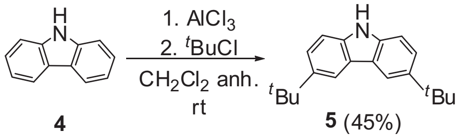
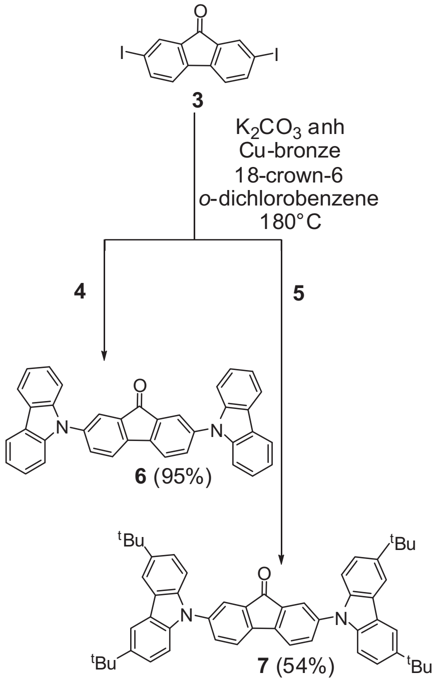


Scheme 1. Synthesis of 2,7-diiodofluorenone **3**.



Scheme 2. Synthesis of 3,6-di-*tert*-butyl carbazole **5**.



Scheme 3. Synthesis of 2,7-disubstituted fluorenones **6** and **7**.[26]

Carbazole is a heterocyclic system with known hole transporting capability[11a,15] that conferred interesting optical and electrochemical properties when this moiety is either the outer layer or the backbone of dendritic scaffolds.[16] For this reason, we decided to use carbazole **4** and 3,6-di-*tert*-butyl carbazole **5** to functionalized positions 2 and 7 of fluorenone **3**. Di-*tert*-butyl carbazole **5** was obtained by the Friedel–Crafts reaction of **4** and *tert*-butyl chloride in moderate yield (Scheme 2).[17]

One of the most extended methods to form a C–N chemical bonding between diarylamines and haloaryl derivatives is the Buchwald–Hartwig procedure. Buchwald and co-workers[18] and Hartwig and co-workers[19] have developed palladium mediated methods for C(aryl)–O and C(aryl)–N bond formations. The success of their research, led to a vast array of applications of this Pd-catalyzed procedure, providing an entry to a wide variety of aromatic amine structures. The possibility to tune the reaction conditions allows access to target molecules that incorporate an aryl amine motif, although this methodology still exhibits significant limitations. For example, certain functional groups such as free NH or OH are not adequate and may cause side reactions, Pd-based methods are sensitive to moisture and oxygen and large scale applications of this type of chemistry is restrictive because of the cost of the metal catalysts and ligands. On the other hand, many of the drawbacks of the classical Ullmann reaction (high reaction temperatures, long reaction times, high metal loadings, and narrow scope) have been successfully overcome through the development of improved catalytic versions of this grand old chemistry. The 'renaissance' of this methodology is now known as the 'modified Ullmann reaction'.[20]

Both approaches could be found reported in the literature in order to prepare 2,7-diamino fluorene derivatives.[21–23] Selection between these two methods has to take into account the known sensitivity of position 9 in fluorenones toward strong bases.[13,24] In our case, evidences of this behavior were found when **3** and bis-arylamines were submitted to Ullmann conditions. The ^{1}H NMR spectra demonstrated the presence of acidic protons and the corresponding carboxylic carbons in the ^{13}C NMR spectra. The formation of these carboxylic acid derivatives is consistent with other reports regarding fluorenones reactivity when treated with potassium hydroxide, giving mainly substituted biphenyl 2-carboxylic acids.[24a] Surprisingly to our delight, even though the reaction between **3** and bis-arylamines was unsuccessful, carbazole derivatives afforded the expected Ullmann products in high yields without detection of any carboxylic byproducts or decomposition ones.

Molecules **6** and **7** were assembled by coupling carbazoles **4** and **5** with diiodofluorenone **3** by a modified Ullmann reaction[25] without using Pd catalyzed conditions (Scheme 3).

To the best of our knowledge, there are no reports in the literature describing the synthesis of 2,7-diamino fluorenone derivatives from 2,7-dihalo fluorenone in these conditions. In previous literature reports these types of systems could only be obtained using more expensive and laborious palladium catalyzed aminations.[5a,b,7,27]

Conclusions

In summary, we describe a simple and efficient preparation of two novel aromatic compounds with a fluorenone core in good yields. Products **6** and **7** were obtained applying the modified Ullmann reaction between **3** and carbazoles **4** and **5**. The strategy for the C–N bond formation between the fluorenone core and carbazole systems open a myriad of possibilities to combine the nonlinear optical properties of fluorenone and the photoconductor and hole transporting properties of carbazole moieties. By modification of the positions 3 and 6 of carbazole new structures could be obtained by this simple and known Ullmann coupling reaction. These new molecules have a potential application in the development of novel electroactive organic dendrimers and polymers.

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Supplementary data

Supplementary data (experimental procedures, characterization data and copies of ^{1}H and ^{13}C NMR spectra (1D and 2D), FT-IR spectra and mass spectra of all compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.11.133. These data include MOL files and InChiKeys of the most important compounds described in this article.

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