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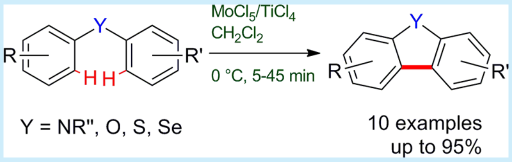
Versatile Oxidative Approach to Carbazoles and Related Compounds Using $MoCl_5$

Simon Trosien, Philipp Böttger, and Siegfried R. Waldvogel*

Institute of Organic Chemistry, Duesbergweg 10-14, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

Ⓢ *Supporting Information*

ABSTRACT: The unique oxidizing power of molybdenum pentachloride provides an easy to perform, versatile, and high yielding method to construct carbazoles and the corresponding dibenzo analogues of thiophene, furan, and selenophene. The coupling reaction tolerates a variety of functional groups. The synthesis is highly modular. By this approach a precursor for the naturally occurring carbazole koenigicine was prepared.



The synthesis and application of carbazoles, dibenzothiophenes, and dibenzofurans has experienced significant attention in the past decades. A variety of bioactive natural products contain carbazole[1] and the dibenzofuran skeleton[2] and provide important pharmacological features. A large number of biologically active compounds involve dibenzothiophene moieties.[3] Furthermore, carbazoles[4] and dibenzothiophenes are important building blocks for functional materials as luminescent polymers,[5] photovoltaic devices,[6] or transition metal complexes.[7]

For the construction of carbazoles, a plethora of synthetic methods are known.[1] Direct oxidative cyclization reactions starting from diarylamines are feasible by an electrocyclization reaction induced photochemically[8] or thermally.[9] The absence of leaving functionalities makes this approach attractive and was first reported using palladium(II) acetate in the oxidative coupling process.[10] Despite the moderate yields and the limited scope of this transformation, the originally reported protocol is still the best procedure for this kind of cyclization reaction. Because of the high costs and toxicity of the palladium salt, catalytic versions have been developed. The first versatile palladium catalysis using cupric acetate as an oxidant was reported by Knölker and co-workers.[11] Other groups applied alternative oxidizers, e.g. benzoquinone,[12] *tert*-butyl hydroperoxide,[13] molecular oxygen,[14a] or air.[14b−e] Although this method provides a wide range of substrates, only the formation of 9*H*-carbazoles is viable, whereas *N*-functionalized carbazoles are not accessible.[14a]

For intramolecular C,C bond formation of diaryl sulfides to form dibenzothiophenes, only the photoinduced electrocyclization followed by oxidation using iodine is known.[15] When appropriate leaving functionalities are involved, the cyclization can be accomplished by standard palladium catalysis.[16] In addition, several methods for the arylation of sulfides/sulfoxides are known wherein cationic species are generated,[17] or an aromatic moiety of dibenzothiophenes is constructed.[18]

Analogous to the carbazole preparation, the synthetic approaches to dibenzofurans from the corresponding diaryl ether are known: Employing a 2-fold C,H activation[10,14a,b] by directed *ortho* metalation and subsequent cyclization,[19] by photocyclization with rearomatization in the presence of iodine,[15,20] and by transition metal catalyzed cyclization[21] with leaving functionalities.[22−24] Furthermore, a cyclization can be accomplished by palladium migration.[25] Other synthetic routes involve the formation of the C,O bond.[26]

Despite the current repertoire for synthesizing carbazoles, dibenzothiophenes, and dibenzofurans, each method exhibits its limitation. Therefore, new methods for the versatile preparation of these heterocycles are highly desired.

Molybdenum pentachloride is a powerful oxidizer with Lewis acidic properties.[27] A variety of labile functionalities as amides, iodo groups, or acetals are tolerated in the process of the coupling reaction.[28] The performance of the reagent is influenced by use of additives, e.g. Lewis acids such as $TiCl_4$, because a preorientation of the substrate is caused[29] and side reactions are avoided by trapping hydrogen chloride.[30] During the reaction, molybdenum salts are coordinated on the substrates, which leads to unusual consecutive redox reactions[31] and controls the stereoselectivity.[32] $MoCl_5$ compared to hypervalent iodo reagents was found to exhibit superior performance.[33]

Herein, we report a modular synthesis of carbazoles, dibenzofurans, dibenzothiophenes, and dibenzoselenophenes involving an intramolecular oxidative coupling step using a $MoCl_5$/$TiCl_4$ reagent mixture.

Diarylamines serve as precursors for the carbazoles and are easily accessible by a 2-fold Buchwald−Hartwig amination.[34] Starting with an amine and an aryl halide (see Supporting Information (SI)) using the effective catalytic system $Pd(dba)_2$/JohnPhos/NaO^{t}Bu, the symmetric intermediates were obtained in 63−87% yield (Scheme 1). If an aryl chloride and an aryl bromide are present, the unsymmetrically substituted diarylamines are selectively formed under the same conditions as described above (Scheme 1, method a).[35] Alternatively, sequential addition of different aryl halides can be carried out (method b). If the arene is equipped with both, chlorine and

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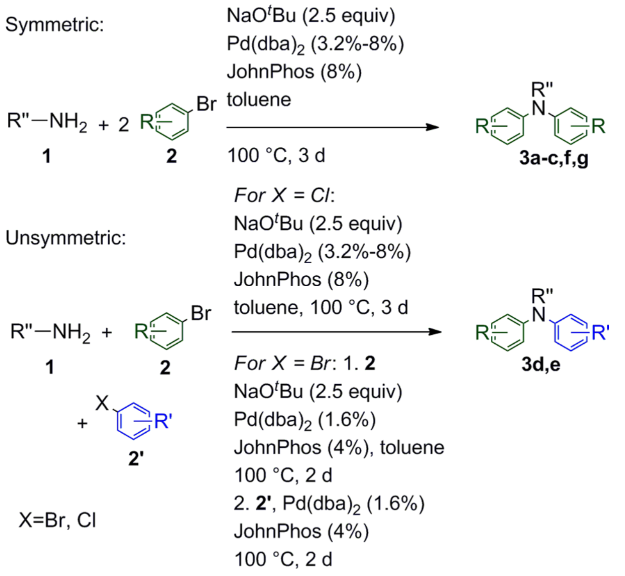
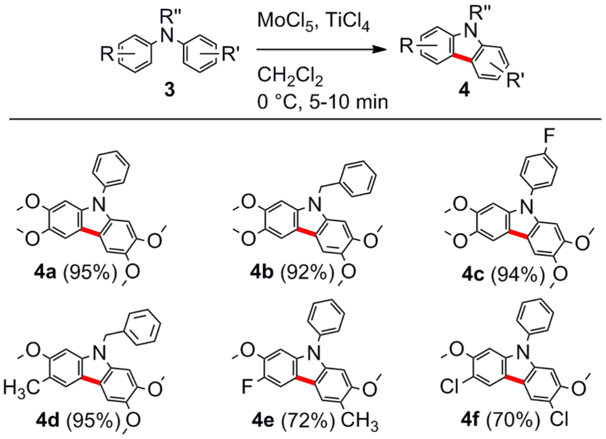
Scheme 1. Synthesis of the Starting Materials



bromine as the leaving functionality, the bromine is clearly preferred in the amination process and chlorinated aryl amines can be selectively constructed (see SI).

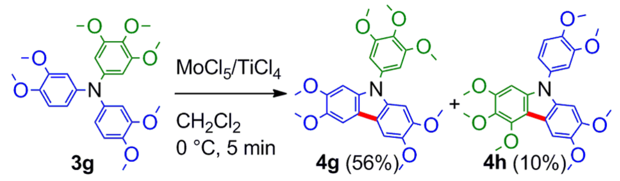
Scheme 2. Synthesis of Various Carbazoles (Newly Formed Bonds in Bold and Red)



The oxidative cyclization of diarylamines to the corresponding carbazoles is very efficiently performed by the MoCl$_5$/TiCl$_4$ mixture (Scheme 2). Because of the high oxidative power of the reagent and the electron-rich nature of the substrates, the reaction is complete within a few minutes. In general, tetramethoxylated substrates are preferred for the coupling reaction and can be coupled in excellent isolated yields (**4a**−**c**). If the positions 3 and 6 of the carbazoles are different substituted, two methoxy groups are sufficient for the cyclization in very good yields (**4e**, **4f**). If these atoms are unsubstituted, these positions are too reactive and side reactions such as intermolecular coupling processes and chlorination predominate. This cannot be avoided by low temperature or high dilution. Consequently, di-(3-methoxyphenyl)phenylamine is not transformable to the corresponding carbazole. Fluorine (**4c**, **4e**) and even chlorine (**4f**) substituents on the aromatic core are compatible with the reaction conditions. Chlorine moieties are suitable leaving groups for subsequent transition metal catalysis. Carbazole **4f** exhibits two chlorine functionalities and is a very useful building block for polymer synthesis.[36] The substitution pattern of the arene moiety in position 9 of the carbazoles is highly adjustable and tolerates electron-rich (**4g**) and electron-poor (**4c**) substituents. Even benzyl groups at the heterocyclic nitrogen persist during the coupling process, and **4b** and **4d** can be cyclized in excellent yields (Scheme 2). Additionally, methyl groups in position 3 are tolerated (**4d**, **4e**), which are important moieties in various natural products.[1]

Because of a statistic advantage and a higher electron density the coupling of trimethoxylated arenes might be favored over that of dimethoxylated arenes. Despite these facts, amine **3g** cyclizes preferentially at the dimethoxylated arene moieties when being treated with the MoCl$_5$/TiCl$_4$ mixture (Scheme 3).

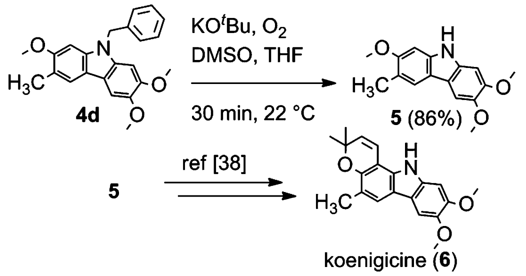
Scheme 3. Regioselective Coupling Reaction



Therefore, a 56% yield of the tetramethoxylated carbazole **4g** is isolated, whereas only 10% of the pentamethoxycarbazole **4h** is obtained. This can be attributed to the sterical repulsion between a methoxy group in position 4 and C,H in position 5.

The benzyl group of derivative **4d** can easily be cleaved off using KO^{t}Bu/oxygen in DMSO/THF to yield carbazole **5** (Scheme 4).[37] This molecule can easily be transformed to the naturally occurring pyranocarbazole koenigicine (**6**) described by Kapil and co-workers (Scheme 4).[38]

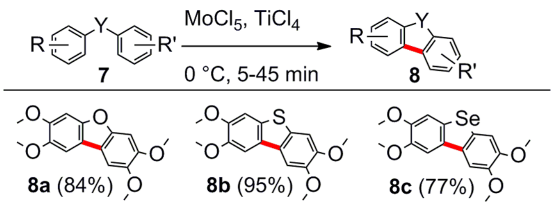
Scheme 4. Synthesis of Koenigicine (6)



The oxidative coupling reaction is not limited to the generation of carbazoles, but is also capable of the formation of dibenzofurans **8a**, dibenzothiophenes **8b**, and dibenzoselenophenes **8c** in very good to excellent yields (Scheme 5).

The starting materials for these compounds are synthesized by copper-catalyzed Ullmann-type reactions (see SI).

Scheme 5. Synthesis of 9-Oxa-, Thia-, and Selenafluorenes



To demonstrate that the reactions are not a Nazarov-type reaction,[39] we confirmed that the formation of compounds **4a** and **8b** is not feasible with $TiCl_4$ as the sole reagent (entries 4, 9).

The unique performance of the $MoCl_5/TiCl_4$ mixture is underlined by comparison with different oxidizing conditions (Table 1). The combination with the $TiCl_4$ is superior in all cases (entries 1, 7). Neither ferric chloride (entry 5) nor $Pd(OAc)_2$/HOAc (2 equiv of palladium salt, entry 6) is capable of accomplishing this transformation as effectively as the $MoCl_5/TiCl_4$ mixture (entry 3). The use of molybdenum pentachloride as the sole reagent leads to significantly more byproducts resulting in a lower amount of the desired product (entries 2 and 8).

Table 1. Comparison of Coupling Conditions and Oxidizing Mixtures

entry	reagents	reaction conditions	product	yield
1	**$MoCl_5/TiCl_4$**	**0 °C, 10 min**	**4e**	**72%**
2	$MoCl_5$	0 °C, 10 min	**4e**	55%
3	**$MoCl_5/TiCl_4$**	**0 °C, 5 min**	**4a**	**95%**
4	$TiCl_4$	0 °C, 5 min	**4a**	0%[a]
5	$FeCl_3$	0 °C, 5 min	**4a**	<30%[a]
6	$Pd(OAc)_2$/HOAc	100 °C, 1 h	**4a**	0%[a]
7	**$MoCl_5/TiCl_4$**	**0 °C, 20 min**	**8b**	**95%**
8	$MoCl_5$	0 °C, 20 min	**8b**	91%
9	$TiCl_4$	0 °C, 20 min	**8b**	0%[a]

[a] Determined by GC analysis.

In summary, the oxidative coupling reaction using $MoCl_5/TiCl_4$ provides a novel synthetic access to 9-heterofluorenes in very good to excellent yields. Because of the power of the reagent mixture, the transformations are completed at 0 °C within a few minutes. The syntheses are easy to perform and absolutely reliable. A large number of functional groups endure the coupling conditions, e.g. benzyl groups, chloro, fluoro, and methyl substituents. This approach is an inexpensive alternative to oxidative coupling using palladium acetate, provides better yields, and is capable of synthesizing N-substituted carbazoles. This method offers new perspectives for the synthesis of complex carbazole alkaloids and building blocks for functional materials. This approach is an inexpensive alternative to oxidative coupling using palladium acetate, provides better yields, and is capable of synthesizing *N*-substituted carbazoles. This method offers new perspectives for the synthesis of complex carbazole alkaloids and building blocks for functional materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and analytical data for all isolated intermediates and products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: waldvogel@uni-mainz.de.

Notes

The authors declare no competing financial interest.

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