The $CeCl_3 \cdot 7H_2O/NaI/SiO_2$ System as an Efficient Promoter for the Friedel–Crafts Reaction of Indoles to Nitroalkenes under Solvent-Free Conditions

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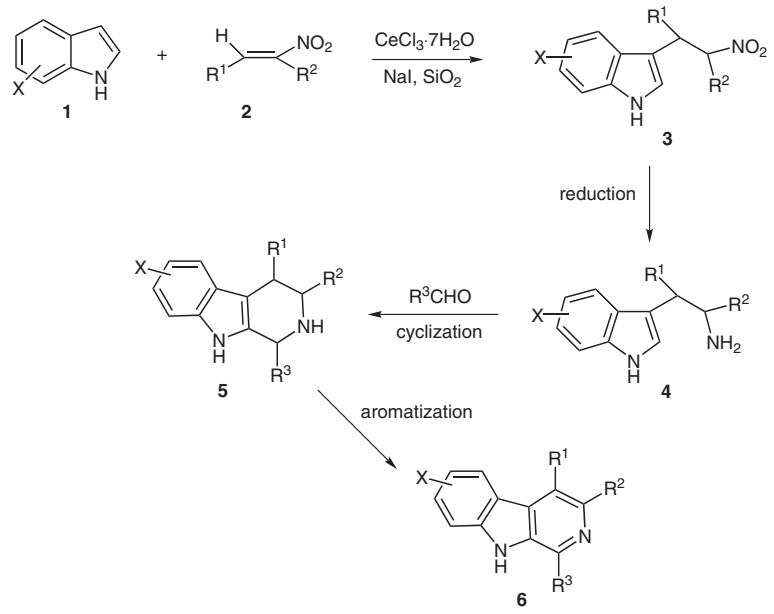
Abstract: The cheap, nontoxic and easy-to-handle $CeCl_3 \cdot 7H_2O/NaI$ Lewis acid promoter is optimal with regard to economic and ecological consideration and allows for useful applications in the synthesis of heterocyclic polyfunctionalized molecules. The procedure becomes efficient if the reaction is carried out under solvent-free conditions and on the surface of $CeCl_3 \cdot 7H_2O/NaI$ supported on silica gel. The simplicity of our method, especially that no precautions need to be taken to exclude moisture or oxygen from the reaction system, permit us to perform the Friedel–Crafts-type conjugate addition of indoles to nitroalkenes. The success of the reaction is independent of the type of indole or nitroalkene used, and provides 3-(2-nitroethyl)indolyl derivatives which are useful building blocks for the synthesis of various types of 3-(2-aminoethyl)indolyl derivatives. These can be subsequently transformed to the β-carbolines with different substituents.

Key words: addition reactions, alkaloids, heterocycles, indoles, lanthanides, Lewis acids, natural products



Scheme 1

Introduction

The Friedel–Crafts reaction is one of the most important reactions in organic synthesis, in that it provides an useful method for the direct introduction of a functional group onto heterocycles or aromatic compounds.[1] Among these, the formation of 3-substituted indoles in good yield from indole is quite a powerful tool for the synthesis of heterocycles that contain this moiety, a structure which is broadly found in a large number of natural products[2] and biologically active substances.[3] The plethora of ingenious methods developed for Lewis acid promoted conjugate addition of indoles to electron-poor alkenes is a clear testimony to their paramount importance. However, most of these procedures are associated with serious disadvantages involving strictly anhydrous conditions. To solve these problems, several lanthanoid triflates have been applied in the Friedel–Crafts-type conjugate addition of indoles in water.[4] Unfortunately, these Lewis acid catalyzed reactions[5] in water with triflates generally require a certain amount of organic solvents such as THF and ethanol

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mixable with water to dissolve organic substrates. In this way the reaction is promoted efficiently, but it is not optimal with regard to economic and ecological considerations. Their use should be minimized as far as possible or even avoided altogether. The best solvent from this point of view therefore is, without a doubt, no solvent at all.[6]

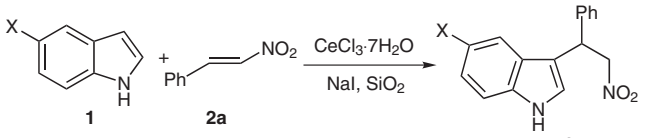
Recently, there has been a great development in reactions that can be carried out in the absence of solvent,[7] and the area of growth includes reactions on supported inorganic reagents.[8] Thus, due to the current challenge for developing solvent-free and environmentally benign synthetic system, and extending our interest in the applications of cerium trichloride for various organic transformations,[9] we have focused our attention on the use of a $CeCl_3 \cdot 7H_2O$/NaI system supported on SiO_2 in the Friedel–Crafts reactions.[10] Although SiO_2 was originally introduced only as a support that not only facilitated the work-up of the reaction mixture, it was found to also enhance the rate constant of the reaction. This fact, together the acceleration effect caused by addition of NaI to $CeCl_3 \cdot 7H_2O$, make our system optimal with regard to suppress the tendency of electron-rich heteroaromatic rings such as indoles to polymerize under acid-catalyzed conditions. Thus, useful applications in bond forming reactions in solvent-free conditions for the preparation of heterocyclic polyfunctionlized molecules have been realized.[11] The treatment of indoles with α,β-disubstituted nitroalkenes in the presence of our $CeCl_3 \cdot 7H_2O$/NaI system supported on SiO_2 gives the corresponding β-indolyl nitroalkanes.[12]

It is known that nitroalkenes are one of the strongest Michael acceptors[13] providing as common pathway to nitroalkanes,[14] which could serve as stock compounds for the corresponding amino compounds. Thus, our system is a useful addition to the synthetic toolbox of indole chemistry,[15] and this Friedel–Crafts-type conjugate addition can be exploited in the synthesis of different pyrido[3,4-*b*]indoles and β-carbolines (Scheme 1). The product **3** obtained by reaction promoted by our $CeCl_3 \cdot 7H_2O$/NaI/SiO_2 combination is converted to tryptamine derivative **4** by reduction. Conversion of this compound into the tetrahydro-β-carboline **5** proceeds under Pictet–Spengler conditions. Finally, the aromatization by palladium-on-carbon treatment gives the fully aromatic β-carbolines **6** with different substituents. These heterocycles are of interest to the pharmaceutical industry due to their numerous reported biological activities.[16] Herein, we describe a reliable, scalable synthesis of methyl 9H-β-carbolines-4-carboxylate without requiring protection of the nitrogen.

Scope and Limitations

The Friedel–Crafts-type conjugate addition was optimized using indole (**1a**) and *trans*-β-nitrostyrene (**2a**) as the test substrates (Table 1, entry 1). The substitution on the indole nucleus occured exclusively at the 3-position giving β-indolyl nitroalkanes in good yields, and N-alkylation products were not observed. By screening the various conditions, we observed that an equimolar ratio of the reagents was necessary, and in optimizing the reaction conditions we found that 0.3 equivalent of $CeCl_3 \cdot 7H_2O$ and 0.3 equivalent of NaI supported on SiO_2 (0.5 g/mmol of nitrolakene) were crucial in these reactions. When the same reactions were performed in their absence, no alkylation took place. The best results were obtained under solvent-free conditions, and taken together, these data allow important advances in chemical processes to minimize waste, a demanding challenge for synthetic chemists when atom-economy and green chemistry are considered.

Table 1 Friedel–Crafts-Type Conjugate Addition of Indoles **1** with *trans*-β-Nitrostyrene (**2a**)[a]

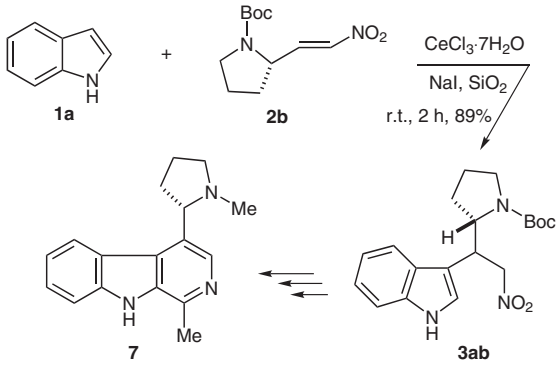


Entry	Indole	X	Time (h)	Product[a]	Yield (%)[b]
1	**1a**	H	8	**3aa**	96
2	**1b**	OMe	4	**3ba**	92
3	**1c**	CN	18	**3ca**	85
12	**1d**	OH	24	**3da**	74

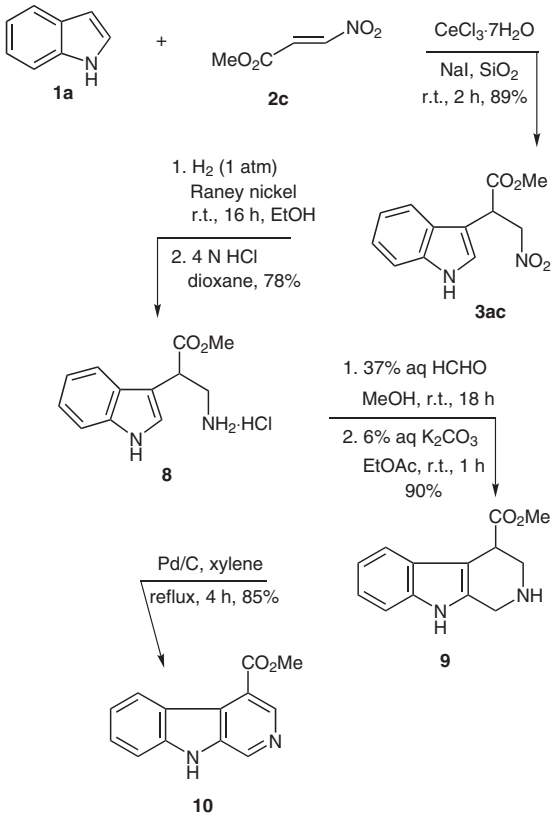
[a] All products were identified by their IR, NMR and GC/MS spectra.
[b] Yields of products isolated by column chromatography.

The reaction proceeded in good yields even in the case of poorly reactive indoles (Table 1, entry 3). The rate was accelerated when an electron-donating group was present on the indole nucleus (Table 1, entry 2) and, interestingly, in the case of an indole derivative containing an hydroxyl group (**1d**). It is known that a direct Lewis acid promoted reaction of hydroxy indole substrates is generally problematic and normally results in low yield due to the interaction of the indolyl hydroxyl group with the Lewis acid catalyst.[17] Analogously, the utilization of commercially available basic alumina as solid catalyst[18] gave low yield of the corresponding adduct **3da**, because the free hydroxy group present in the benzene ring of the indole is preferentially deprotonated by the basic catalyst, leading to a consistent acidity and hence reduction of the pyrrole nucleus. With our system, this problem with hydroxy indoles is much reduced. The presence of electron-withdrawing groups in the pyrrole ring reduces the overall nucleophilicity, and indole substrates with a methoxycarbonyl or a benzenesulfonyl group on the pyrrole moiety do not give the corresponding Friedel–Crafts adducts. Thus, our Friedel–Crafts-type conjugate addition of indoles under solvent-free conditions was also efficient with α- or β-substituted enones. The reaction did not work for α,β-unsaturated sulfones and nitriles. The corresponding esters are less reactive, and in the case of α,β-unsaturated aldehydes, the reaction suffered from regiochemical restriction caused by competing 1,2- and 1,4-addition.

With nitroalkenes substituted in the α- or β-position, the reaction proceeded with good yields, and the synthetic potential of this system was applied to promote the synthesis of 3-(2-nitroethyl)indolyl derivative **3ab** (Scheme 2).[19] This can be converted, in several steps,[20] into the β-carboline ring of (–)-(*S*)-brevicolline, the major alkaloid of the plant *Carex brevicollis*, which is biologically important for its phototoxic effect against bacteria and fungi. The chiral nitroalkene synthon **2b** was obtained starting from the natural amino acid (*S*)-proline.[21] These findings suggest a suitable route to the synthesis of carbolines starting from an easy and convenient method of making tryptamines by Friedel–Crafts-type conjugate addition of indoles to nitroalkenes.



Scheme 2



Scheme 3

We have been interested in evaluating the general utility of our silica gel supported $CeCl_3 \cdot 7H_2O$/NaI combination by synthesizing methyl 9*H*-β-carboline-4-carboxylate (**10**). The method reported in literature requires N-protection,[22] whereas our linear approach involves introduction of the 4-substituent in the first synthetic step (Scheme 3). The product **3ac** obtained by the reaction of indole (**1a**) to the readily available *trans*-β-nitroacrylate (**2c**) promoted by $CeCl_3 \cdot 7H_2O$/NaI/SiO_2 under solvent-free conditions was converted into the tryptamine derivative **8** by hydrogenation in the presence of Raney nickel in ethanol. The corresponding 3-(2-aminoethyl)-1*H*-indole is part of an important class of compounds frequently used as building blocks in the construction of numerous indole alkaloids. Unfortunately, these are not stable; thus, compound **8** was isolated as its stable hydrochloride by treating with aqueous 4 N HCl in dioxane. This was directly used without purification in the next step. However, its treatment with formaldehyde under protic conditions followed by Pictet–Spengler cyclization of the imine[23] afforded a modest yield of the 4-substituted 1,2,3,4-tetrahydro-β-carboline **9**. On the other hand, preparation of the compound **9** proceeded in good yield when a 37% formalin solution was added to the hydrochloride of **8** in methanol, followed by the conversion into the free base. Finally, aromatization with palladium-on-carbon afforded the fully aromatic β-carboline **10** with a substituent at the 4-position.

In conclusion, we have achieved a practical and highly efficient method for the preparation of 2-indolyl-1-nitroalkane derivatives in good yields by using $CeCl_3 \cdot 7H_2O$/NaI/SiO_2 as a 'friendly' Lewis acid promoter. The simplicity of this approach provides facile access to the synthesis of 4-substituted β-carbolines, and the use of solvent-free conditions reduces the harmful effects of organic solvents on the environment.

Most solvents and reagents were used without purification unless otherwise mentioned. Solvents (EtOAc and hexane) for chromatography were distilled. Anhyd xylene was prepared by distillation from Na under N_2 and used immediately. All air- or moisture-sensitive reactions were carried out in flame-dried glassware under N_2. All the products obtained were characterized by IR, GC/MS, ^{1}H and ^{13}C NMR spectroscopy. The compounds **3**[12] are all known and their structures were consistent with their published physical data. ^{1}H NMR (200 MHz) spectra were recorded in $CDCl_3$ with residual signals of solvent as an internal standard. ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ and chemical shifts are reported relative to the center line of the triplet at 77.00 ppm for $CDCl_3$. Mass spectra were recorded on a Hewlett-Packard 5988 gas chromatography with a mass-selective detector MSD HP 5790 MS, utilizing electron ionization (EI) at an ionizing energy of 70 eV. Microanalyses were performed with a EA1108 CHNS-D Fisons Instruments. IR spectra were recorded on PerkinElmer FTIR Paragon 500 spectrometer on NaCl plates. Only the characteristic peaks are quoted. Analytical GC was performed with a capillary fused silica column (0.32 mm × 25 cm), stationary phase OV1 (film thickness 0.40–0.45 μm). Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a Baker silica gel (230–400 mesh) column using an EtOAc in hexanes as eluent.

Analytical TLC was performed using precoated glass-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet, Von's reagent, $KMnO_4$, or I_2 stain.

3-(1-Methoxycarbonyl-2-nitroethyl)-1*H*-indole (3ac)

Silica gel (5 g) was added to a mixture of $CeCl_3 \cdot 7H_2O$ (11.2 g, 3 mmol) and NaI (0.134 g, 3 mmol) in MeCN (100 mL), and the mixture was stirred overnight at r.t. The MeCN was removed by rotary evaporation and the resulting mixture was stored in a bottle at r.t. To the $CeCl_3 \cdot 7H_2O$/NaI combination supported on silica gel (4.5 g) prepared as above was added indole (**1a**; 0.9 g, 7.63 mmol) and *trans*-β-nitroacrylate (**2c**;[24] 1.0 g, 7.63 mmol). The mixture was stirred at r.t. for 4 h by using a mechanical stirrer. After addition of Et_2O (250 mL), the mixture was passed through a short pad of Celite and the filtrate was concentrate under reduced pressure. The crude was purified by chromatography on a silica gel column (eluent: EtOAc in hexanes, 30:70) to give the adduct **3ac** (1.62 g, 86%) as an oil.

IR (neat): 3406, 3030, 1745, 1552, 1376 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.70 (s, 3 H), 4.65–4.87 (m, 2 H), 5.10–5.20 (m, 1 H), 7.02–7.19 (m, 3 H), 7.38–7.42 (m, 1 H), 7.86 (d, *J* = 8.5 Hz, 1 H), 8.30 (br s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 40.1, 52.9, 75.4, 112.0, 120.5, 123.9, 124.4, 125.8, 136.7, 172.7.

MS (EI): *m*/*z* = 248 [M^+], 201, 160, 143 (100), 142, 115, 73, 62.

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 58.01; H, 4.80; N, 11.23.

Methyl 3-Amino-2-(1*H*-3-indolyl)propionate Hydrochloride (8·HCl)

A vigorously stirred mixture of 3-(2-nitroethyl)indolyl derivative **3ac** (1.57 g, 6.33 mmol), EtOH (325 mL), and Raney Ni (9.15 g) was hydrogenated at atmospheric pressure for 16 h. The Ni was then removed by filtration over Celite and washed with hot EtOH (850 mL). Evaporation of the filtrate under vacuum afforded a syrup that was treated with 1 equiv of 4 N HCl in dioxane. The product (1.25 g, 78%) was filtered, after which it was sufficiently pure for further use.

^1H NMR (D_2O): δ = 3.35–3.67 (m, 5 H), 4.35 (t, *J* = 7.50 Hz, 1 H), 4.75 (s, 3 H), 6.75–7.16 (m, 2 H), 7.34 (s, 1 H), 7.38–7.50 (m, 1 H), 8.00 (br s, 1 H, NH).

Methyl 1,2,3,4-Tetrahydro-1*H*-β-carboline-4-carboxylate (9)

A mixture of **8** (1.10 g, 4.35 mmol) and 37% formalin (0.45 g, 5.25 mmol) in MeOH (100 mL) was stirred at r.t. for 18 h. The mixture was diluted with Et_2O (350 mL), and the resulting crystals were collected by filtration and dried to give **9**·HCl as colorless needles. The HCl salt was converted into the free base by treatment with aq 6% K_2CO_3 (38 mL) in EtOAc (125 mL). The resulting mixture was stirred at r.t. for 1 h; then the organic layer was dried ($MgSO_4$), and the solvent was evaporated under vacuum. The residue was chromatographed on silica gel by eluting with hexanes–EtOAc–EtOH (6:3:1) to give **9**; yield: 1.0 g (90%); mp 162–164 °C (EtOH).

IR (Nujol): 3402, 1730, 1463, 1424 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.26 (br s, 1 H, NH), 3.05 (dd, *J* = 13.73, 4.56 Hz, 1 H,), 3.60 (dd, *J* = 13.75, 2.16 Hz, 1 H), 3.72 (s, 3 H), 3.78–3.87 (m, 1 H), 4.01–4.12 (m, 2 H), 7.10–1.20 (m, 2 H), 7.34–7.42 (m, 1 H), 7.65–7.71 (m, 1 H), 8.10 (br s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 39.3, 46.6, 52.7, 53.4, 104.8, 112.2, 121.3, 122.9, 123.5, 124.9, 140.6, 142.3, 175.2.

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.81; H, 6.09; N, 12.23.

Methyl 9*H*-β-Carboline-4-carboxylate (10)

The pure tetrahydro-β-carboline **9** (0.90 g, 3.9 mmol) was dissolved in anhyd xylene (120 mL), and 10% Pd/C catalyst (0.60 g) was added. The mixture was heated under reflux with vigorous stirring for 4 h until no starting material remained, as indicated by TLC using toluene–EtOH (9:2) as eluent. The catalyst was removed by filtration over Celite and washed with EtOAc (5 × 50 mL). Evaporation of the filtrate gave a residue which was purified by chromatography on silica gel (eluent, hexanes–EtOAc–EtOH, 6:3:1) to afford the crystalline β-carboline **10**; yield: 0.762 g (85%); mp 192–195 °C (EtOH).

IR (Nujol): 3380, 1730 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 4.10 (s, 3 H), 7.23–7.36 (m, 1 H), 7.60–7.71 (m, 2 H), 8.75–8.82 (m, 2 H), 9.12 (s, 1 H), 12.90 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 50.9, 112.8, 120.7, 121.0, 125.8, 127.3, 130.3, 136.2, 137.8.

MS (EI): *m*/*z* = 226 ([M^+], 100%), 195, 167, 140, 113.

Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 68.98; H, 4.38; N, 12.36.

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