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Synthesis of 2-hetaryl substituted indoles via palladium-catalysed reductive *N*-heterocyclisation

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Abstract

An improved synthesis of a family of polidendate ligands embodying indole subunit(s) was performed, via a nitrene insertion as a key step, starting from easily accessible *o*-nitrostyryl precursors. This transformation was efficiently achieved through the agency of CO in the presence of Pd(2,4,6-trimethylbenzoate)$_2$ as catalyst and 3,4,7,8-tetramethyl-1,10-phenanthroline as co-ligand.

Keywords: Synthesis; 2-Hetaryl substituted indoles; Reductive *N*-heterocyclisation; Palladium catalyst

1. Introduction

The investigation of the chemistry of indoles has been, and continues to be, one of the most studied fields of heterocyclic chemistry. This ring system is of utmost importance because it is present in the essential amino acid, tryptophan, and is embodied in a wide variety of naturally occurring compounds (e.g., alkaloids, antibiotics) having relevant physiological activity [1,2]. Since the first synthesis by Fischer, an impressive number of reports and reviews concerning the preparation of indoles has appeared in the literature. Moreover, nucleophilic cyclisation onto Pd(II)-complexed alkenes as well as intramolecular Heck reactions have found quite wide use in the construction of indoles (for reviews on synthesis of heteroaromatic compounds mediated by transition metals, see Refs. [3–6]). Over the past two decades nitroarenes have emerged as powerful precursors used for the transition-metal catalysed regiocontrolled entry into a number of *N*-heterocycles via nitrene insertion as the key synthetic step [7–15].

In conjunction with our long-standing interest in this field, it was envisioned that this methodology might be ideally incorporated in the synthesis of indole-containing *N*-ligands according to the strategy outlined in retrosynthetic format depicted in Scheme 1.

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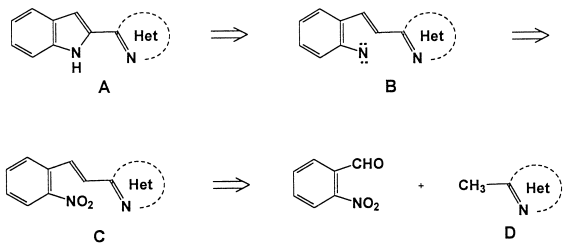


Scheme 1.

The viability and efficiency of this methodology not only depends on the availability of the precursors but also on their steric and electronic features, nature and amount of catalyst, external ligands, solvent, temperature and presence of molecular sieves. Product studies suggest that, through the agency of carbon monoxide, several competing reactions are involved in the fate of the nitrenoid intermediate leading to amines (reduction) or carbonylated compounds.

We herein report that in the presence of catalytic Pd(2,4,6-trimethylbenzoate)$_2$ [Pd(TMB)$_2$] and 3,4,7,8-tetramethyl-1,10-phenanthroline (TMPhen) as π-acceptor *N,N*-ligand under CO pressure we are able to 'tailor' the catalytic cycle in such a way that we can selectively perform the nitrene insertion without suffering from the above side-reactions.

Accordingly, the vinyl double bond of *o*-nitrostyryl precursor **C** (Scheme 1) would participate in a Pd(II)-catalysed reductive *N*-heterocyclisation (5-*endo*-trig ring closure) resulting in good to high yields of indole **A**. Because a variety of **C** is readily available from activated methyl azines or azoles **D**, the use of this catalytic system provide a very convenient and general method for an improved access to a library of polidentate ligands embodying indole subunit(s). These ligands can act either as anionic polidentate ligands after deprotonation of the (non-coordinating) N–H indole nitrogen or as neutral ligands.

2. Results and discussion

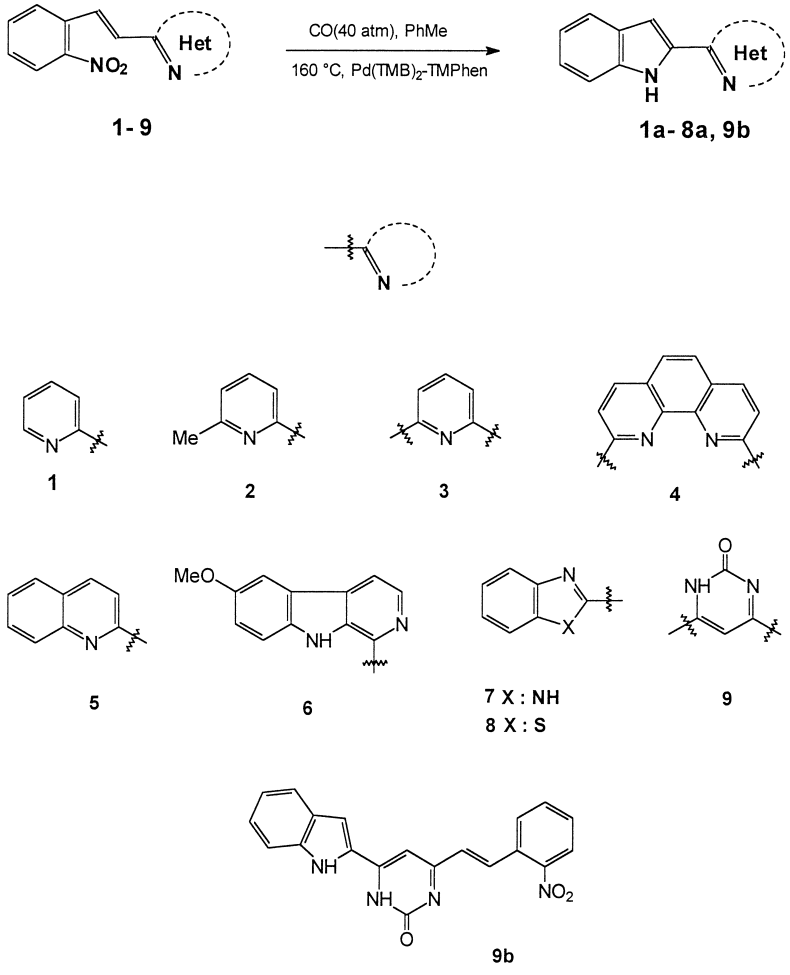
It is well known that Me groups at the α- and γ-position of azines (i.e., 2-methyl pyridine; 2,6-dimethyl pyridine; 2,9-dimethyl-1,10-phenanthroline; 2-methyl quinoline, etc.) as well as at the 2-position of 1,3-benzazoles (i.e., 2-methyl-1*H*-benzimidazole; 2-methyl-1*H*-benzothiazole) undergo alkylidenation (mainly styrylation) on treatment with aldehydes in the presence of condensing agents [16].

The required intermediates **1**–**9** were readily prepared in 68–88% range yield by treating 2-nitro benzaldehyde with the Me-derivatives **D** in refluxing acetic anhydride for 5–10 h under N_2 [17]. In the case of **9** [arising from the commercially available 4,6-dimethyl-2(1*H*)-pyrimidinone)], the intermediate *o*-acetyl pyrimidine derivative was hydrolysed with aq. NaOH.

Our initial studies were carried out with **1** as *o*-nitrostyryl model and a number of variations in nature of catalyst, ligand, solvent and reaction conditions was also explored. Although the results were reaction-dependent, low yields ($< 40\%$), messy reactions, and long reaction times were uniformly observed. The presence of a pendent nitrogen donor in **1**–**9** appeared to adversely affect the required nitrene insertion by reducing the selectivity and/or the conversion, thus a fine tuning of reaction conditions was needed. Most likely, the 6-membered heterocycles, being π-deficient, are excellent π-acceptors and the π-deficient 1,3-azoles are much poorer π-acceptors and better π-donors [18]. The best compromise between selectivity and conversion was displayed by Pd(TMB)$_2$ modified

by the presence of the rigid bidentate ligand TMPhen which, under 40 atm (4053 kPa) of CO at 160°C in dry toluene [in 20:2:1 molar ratio of **1**/TMPhen/$Pd(TMB)_2$], effected a 100% conversion of **1** after 6 h, producing a 95% isolated yield of **1a**. Unless stated otherwise, these optimised conditions were applied throughout giving the corresponding indoles in 56–95% isolated yield (at 85–100% conversion).

One exception to the applicability of this procedure was observed that being the reaction of (*E*,*E*)-4,6-bis[2-(2-nitrophenyl)ethenyl]-2(1*H*)-pyrimidinone **9**. The expected reaction to **9a** stalled at the intermediate monoindolyl derivative **9b** (75%) even though the reductive carbonylation was carried out at a higher CO pressure and for a longer reaction time. The structures of the precursors and the final products were confirmed by ^{1}H NMR, elemental analyses and/or HRMS. The data of known compounds were consistent with those reported in the literature.



The synthetic methodology presented here stems from the reductive cyclisation of a 2-nitrostyrene, a reaction that is conveniently formulated proceeding via a nitrene intermediate [19–22], which could be generated from the nitroarene by deoxygenation with carbon monoxide. Most accounts on this reaction in the presence of transition metal-complexes likely implicate the involvement of a

metal-complexed nitrene (e.g., imido complex Ar–N=ML_n) rather than a *free* nitrene intermediate [23–27]. Judging from the large bond dissociation energy (BDE) for a H–C (sp^2) bond ($\sim$108 kcal/mol) [28], it is likely that the products **1a**–**8a** and **9b** actually arise from the addition of a C=C bond to electrophilic nitrene followed by rearrangement (e.g., valence isomerisation and/or sigmatropic shift) [29]. The occasional formation of traces of amines ($<5\%$) as byproducts lends support to the proposed intermediacy of nitrenes, which can also concurrently abstract hydrogen from the solvent or from adventitious water before the ring closure [30]. The formal insertion of a nitrene (or nitrenoid) into a C–H bond, has been made the key step in several systematic routes to both five- and six-membered nitrogen heterocycles [31]. The methods currently available include: (i) pyrolysis of nitroarenes in the presence of iron (II) oxalate [32], (ii) pyrolysis or photolysis of azidoarenes [33,34], (iii) deoxygenation (via nitrosoarenes) of nitroarenes induced by $(EtO)_3P$ [35,36] or $(TMSO)_3P$ [37]. Of these possibilities, the use of P(III)-based reagents appeared to offer remarkable advantage over the photolytic or pyrolytic methods in terms of either yields or accessibility of starting materials (nitro- vs. azido compounds). Our method avoids side reactions such as the formation of dimers or phosphonic amides encountered with the use of $P(OR)_3$ [36] and, in addition, avoids large amounts of these reagents (stench!) usually employed as solvents and their subsequent removal by high-vacuum distillation.

In conclusion, the straightforward method described in this paper allows for an expedient entry to polidendate indole-containing ligands in two steps starting from commercially available materials and it could find application in high-throughput screening of ligands as additives and modifiers in organic reactions mediated by transition metals.

3. Experimental

All m.p.s are uncorrected. ^{1}H NMR spectra were recorded on a Bruker WP 80SJ spectrometer with $CDCl_3$ as solvent (unless stated otherwise) and TMS as internal standard; chemical shifts are reported in δ(ppm) and coupling constants J in Hz. EIMS and HRMS were performed on a VG7070EQ instrument. $Pd(TMB)_2$ [38,39] and compound **1** [40] were prepared according to procedures in the literature. TMPhen was purchased from Aldrich. Toluene was freshly distilled from sodium under N_2.

*3.1. Alkylidenation of Me-azoles and Me-azines to **1**–**9***

Following the general procedure of Shaw and Wagstaff [17], 2.0 mmol of heterocyclic base and 2.0 mmol of 2-nitrobenzaldehyde were mixed in 5 ml of Ac_2O and heated at reflux with stirring under nitrogen for 5–10 h during which time the suspended solids dissolved (TLC check). The mixture was evaporated in vacuo and the resultant dark-yellow solid was purified by crystallisation from ethanol to give the required styryl compound. For **3**, **4** and **9**, 4.0 mmol of 2-nitrobenzaldehyde were used.

*3.2. Reductive carbonylation of compounds (**1**–**9**)*

A 100-ml glass autoclave liner was charged with 0.25 mmol of $Pd(TMB)_2$, 0.5 mmol of TMPhen and 5 mmol of styrylderivative and 20 ml of dry toluene. After removal of air from the autoclave (three freeze–pump–thaw cycles and nitrogen refill) was finally pressured to 40 atm (4053 kPa) of carbon monoxide at room temperature with magnetical stirring, placed in a 160°C oil bath and held at this temperature for 6 h. After cooling and venting, the autoclave was opened and the content diluted

with 20 ml of dichloromethane and evaporated at reduced pressure. Subsequent silica gel chromatography of the residue led to the isolation of the pure compounds **1a**–**8a** and **9b.** All reactions involving the use of carbon monoxide were carried out in a fume cupboard with an appropriate detector to warn of any exposure.

3.3. Characterisation of the products

*3.3.1. (E)-2[2-(2-nitrophenyl)ethenyl]-6-methylpyridine (**2**)*

(88% yield from 2,6-dimethyl pyridine); m.p. 88°C (dec.) (EtOH); ^{1}H NMR 8.21 (dd, 1H, $J = 8.2$, 3.2), 8.11 (d, 1H, $J = 14.5$), 7.23 (d, 1H, $J = 14.5$), 7.88–7.33 (m, 6H), 2.61 (s, 3H); EI MS m/z 240 ($M^{+\cdot}$, 25%), 223 (100), 193 (60). Calcd. for $C_{14}H_{12}N_2O_2$(240.26): C 69.97, H 5.04, N 11.66; found: C 69.81, H 5.15, N 11.73.

*3.3.2. (E,E)-2,6-bis-[2-(2-nitrophenyl)ethenyl]-pyridine (**3**)*

(76% yield from 2,6-dimethyl pyridine); m.p. 137°C (EtOH); ^{1}H NMR 8.19 (dd, 2H, $J = 8.4$, 3.1), 8.16 (d, 2H, $J = 14.3$), 7.28 (d, 2H, $J = 14.3$), 8.04–7.32 (m, 9H); EI MS m/z 373 ($M^{+\cdot}$, 25%), 311 (100), 265 (60). Calcd. for $C_{21}H_{15}N_3O_4$(373.36): C 67.54, H 4.05, N 11.26; found: C 67.58, H 4.09, N 11.18.

*3.3.3. (E,E)-2,9-bis-[2-(2-nitrophenyl)ethenyl]-1,10-phenanthroline (**4**)*

(78% yield from 2,9-dimethyl-1,10-phenanthroline); m.p. 198°C (dec). (EtOH); ^{1}H NMR 8.22 (dd, 1H, $J = 8.3$, 3.3), 8.11 (d, 1H, $J = 14.6$), 7.48 (d, 1H, $J = 14.6$), 8.44–7.31 (6H, m); EI MS m/z 474 ($M^{+\cdot}$, 55%), 353 (64), 428 (60), 382 (100). Calcd. for $C_{28}H_{18}N_4O_4$(474.48): C 70.87, H 3.83, N 11.81; found C 70.82, H 3.85, N 11.78.

*3.3.4. (E)-2[2-(2-nitrophenyl)ethenyl]-quinoline (**5**)*

(82% yield from 2-methyl quinoline); m.p. 96°C (EtOH); ^{1}H NMR 8.25 (dd, 1H, $J = 8.2$, 3.1), 7.98 (d, 1H, $J = 13.6$), 7.46 (d, 1H, $J = 13.6$), 7.98–7.51 (m, 9H); EI MS m/z 276 ($M^{+\cdot}$, 55%), 259 (60), 232 (100). Calcd. for $C_{17}H_{12}N_2O_2$(276.29): C 73.9, H 4.38, N 10.14; found C 73.94, H 4.31, N 10.20.

*3.3.5. (E)-1[2-(2-nitrophenyl)ethenyl]-7-methoxy-9H-pyrido-[3,4-b]-indole (**6**)*

(65% yield from 7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*] indole); m.p. 205°C (EtOH); ^{1}H NMR 11.95 (s, 1H), 8.38 (d, 1 H, $J = 13.1$), 8.22 (dd, 1H, $J = 8.4$, 3.1), 7.25 (d, 1H, $J = 13.1$), 8.05–7.41 (m, 8H), 3.88 (s, 3H); EI MS m/z 345 ($M^{+\cdot}$, 57%), 328 (100), 298 (22). Calcd. for $C_{20}H_{15}N_3O_3$(345.35): C 69.56, H 4.38, N 12.17; found C 69.61, H 4.21, N 12.10.

*3.3.6. (E)-2[2-(2-nitrophenyl)ethenyl]-1H-benzimidazole (**7**)*

(81% yield from 2-methyl-1*H*-benzimidazole); m.p. 225°C (EtOH); ^{1}H NMR 11.91 (s, 1H), 8.24 (dd, 1H, $J = 8.2$, 3.3), 8.11 (d, 1H, $J = 12.9$), 7.45 (d, 1H, $J = 12.9$), 8.33–8.21 (m, 7H); EI MS m/z 265 ($M^{+\cdot}$, 35%), 219 (50), 117 (100). Calcd. for $C_{15}H_{11}N_3O_2$(265.27): C 67.92, H 4.18, N 15.84; found C 67.88, H 4.11, N 15.91.

*3.3.7. (E)-2[2-(2-nitrophenyl)ethenyl]-1H-benzothiazole (**8**)*

(78% yield from 2-methyl-1*H*-benzothiazole); m.p. 128°C (EtOH); ^{1}H NMR 8.21 (dd, 1H, $J = 8.3$, 3.1), 8.01 (d, 1H, $J = 12.4$), 7.35 (d, 1H, $J = 12.4$), 8.15–7.2 (m, 7H); EI MS m/z 282

($M^{+\cdot}$, 48%), 265 (100), 236 (32). Calcd. for $C_{15}H_{10}N_2O_2S$(265.27): C 63.82, H 3.57, N 9.92; found C 63.8, H 3.66, N 9.83.

*3.3.8. (E,E)-4,6-bis[2-(2-nitrophenyl)ethenyl]-2(1H)-pyrimidinone (**9**)*

(68% yield from 4,6-dimethyl-2(1*H*)-pyrimidinone); m.p. 176°C (EtOH); ^{1}H NMR 11.5 (s, 1H), 8.21 (d, 1H, $J = 14.6$, 8.18 (dd, 1H, $J = 8.1, 3.3$), 7.13 (d, 1H, $J = 14.6$), 7.91–7.38 (m, 9H), 4.57 (s, 1H); EI MS *m/z* 390 ($M^{+\cdot}$, 75%), 344 (100), 373 (80). Calcd. for $C_{20}H_{14}N_4O_5$(265.27): C 61.52, H 3.62, N 14.36; found C 61.55, H 3.71, N 14.44.

*3.3.9. 2-(2-pyridinyl)-1H-indole (**1a**)*

(95% yield, 100% conversion); m.p. 153°C (hexane–toluene) (lit. [41]: 154°C); ^{1}H NMR (DMSO-d_6) 11.62 (s, 1H), 8.62 (dd, 1H, $J = 5; 2$), 7.97 (dt, 1H, $J = 8, 2$), 7.84 (1H, dt, $J = 8.2$), 7.70–6.90 (m, 6H); EI MS 194 ($M^{+\cdot}$, 100%), 167 (13), 140 (71), 139 (8).

*3.3.10. 2-(1H-indol-2-yl)-6-methyl pyridine (**2a**)*

(87% yield, 100% conv.); m.p. 112°C (EtOH); ^{1}H NMR 10.77 (s, 1H), 7.78–7.03 (m, 8H), 2.62 (s, 3 H); EI MS 208 ($M^{+\cdot}$, 55%), 117 (100), 116 (65). Calcd. for $C_{14}H_{12}N_2$(208.26): C 80.74, H 5.81, N 13.45; found C 80.66, H 5.91, N 13.51.

*3.3.11. 2,6-bis-(1H-indol-2-yl)-pyridine (**3a**)*

(56% yield, 85% conv.); m.p. 255°C (EtOH) (lit. [42]: 258°C); ^{1}H NMR 10.65 (s, 2H), 7.80–7.63 (m, 4H), 7.52 (d, 2H, $J = 7.5$), 7.35–7.02 (m, 7H); EI MS 309 ($M^{+\cdot}$, 55%), 107 (100). Calcd. for $C_{21}H_{15}N_3$(309.37): C 81.53, H 4.88, N 13.58; found C 81.55, H 4.91, N 13.62.

*3.3.12. 2,9-bis-[2-(1H-indol-2-yl)]-1,10-phenanthroline (**4a**)*

(65% yield, 90% conv.); m.p. 211°C (EtOH); ^{1}H NMR 10.8 (s, 1H), 8.44–7.31 (m, 8H); EI MS 410 ($M^{+\cdot}$, 28%), 116 (100), 117(54). Calcd. for $C_{28}H_{18}N_4$(410.47): C 81.93, H 4.42, N 13.65; found C 81.97, H 4.30, N 13.61.

*3.3.13. 2-(1H-indol-2-yl)-quinoline (**5a**)*

(76% yield, 95% conv.); m.p. 176°C (EtOH); ^{1}H NMR 9.81 (s, 1H), 8.38–7.19 (m, 11H); EI MS 244 ($M^{+\cdot}$, 65%), 129 (100), 117 (53). Calcd. for $C_{17}H_{12}N_2$(244.30): C 83.58, H 4.95, N 11.47; found C 83.60, H 4.81, N 11.49.

*3.3.14. 1-(1H-indol-2-yl)-7-methoxy-9H-pyrido-[3,4-b]-indole (**6a**)*

(58% yield, 90% conv.); ^{1}H NMR 11.96 (s, 1H), 11.54 (s, 1H), 8.75–6.79 (m, 10H), 3.81 (s, 3H); EI MS 313 ($M^{+\cdot}$, 75%), 282 (100), 117 (31). HR MS calcd. for $C_{20}H_{15}N_3O$ 313.1262; found: 313.1270.

*3.3.15. 2-(1H-indol-2-yl)-1H-benzimidazole (**7a**)*

(81% yield, 95% conv.); ^{1}H NMR 12.73 (s, 1H), 11.92 (s, 1H), 8.19–6.87 (m, 9H); EI MS 233 ($M^{+\cdot}$, 45%), 117 (100). HR MS calcd. for $C_{15}H_{11}N_3$ 233.0952; found 233.0955.

*3.3.16. 2-(1H-indol-2-yl)-1H-benzothiazole (**8a**)*

(83% yield, 100% conv.); ^{1}H NMR (DMSO-d_6) 12.21 (s, 1H), 8.18–6.81 (m, 9H); EI MS 250 ($M^{+\cdot}$, 5%), 135 (100), 117 (82). HR MS calcd. for $C_{15}H_{10}N_2S$ 250.0564; found 250.0569.

*3.3.17. 4-[(1H-indol-2-yl)]-6-[2-(2-nitrophenyl)-ethenyl]-2(1H) pyrimidinone (**9b**)*

(75% yield, 100% conv.); ^{1}H NMR 11.98 (s, 1H), 8.21 (dd, 1H, $J = 8.3$, 3.3), 7.97 (d, 1H, $J = 14.9$), 7.23 (d, 1H, $J = 14.9$), 7.71–7.08 (m, 9H), 3.48 (s, 1H); EI MS 358 ($M^{+\cdot}$, 65%), 341 (100), 311 (83), 283 (64). HR MS calcd. for $C_{20}H_{14}N_4O_3$ 358.1065; found 358.1071.

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