Tetrahedron Letters 52 (2011) 411–414

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Regioselective synthesis of pyridoquinolones and pyridocoumarins via molecular iodine-mediated 6-*endo*-dig electrophilic cylization

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ARTICLE INFO

Article history:
Received 4 October 2010
Revised 10 November 2010
Accepted 12 November 2010
Available online 18 November 2010

Keywords:
Molecular iodine
Pyridoquinolone
Pyridocoumarin
Sonogashira coupling
6-*endo*-dig

ABSTRACT

Angular-pyridoquinolone and pyridocoumarin derivatives have been efficiently synthesized in 60–95% yields by molecular iodine-mediated cyclization of easily available starting materials, 6-(*N*-propargyl)amino quinolone and coumarin derivatives, in the presence of $NaHCO_3$. The reaction was carried out at room temperature.

Coumarins fused with heterocycles have received increasing attention due to their potential biological activities[1] and are common structural motifs in many natural products.[2] In particular, those coumarins fused to pyridines have been reported to possess antiallergic,[3] antidiabetic,[4] and analgesic[5] properties. On the other hand, quinolines and their derivatives occur in numerous natural products and many of them display interesting biological activities.[6] In particular, halogen-containing quinolines are of significant interest because the halogen atom sometimes plays a determinant role in the compound's bioactivity, and such compounds provide further scope for structural elaboration.[7] Nicolaides and co-workers[8] reported the synthesis of some angular pyridocoumarins from the reaction of 8- or 6-quinolinol with triphenylphosphine (PPh_3) and dimethylacetylenedicarboxylate (DMAD). Pyridocoumarin was synthesized in 14% yield by means of a Skraup reaction, carried out on 6-nitrocoumarin.[9] Recently, radical cyclization[10] has become a useful tool to the synthetic organic chemists for the construction of C–C bonds. The most useful mediator of radical cyclization is tributyltin hydride. Despite its widespread applicability, the problem of toxicity and the removal of even a trace of organotin residue from the product are frequently highlighted as reasons to avoid the tin reagents.[11,12] In our laboratory pyridocoumarin derivatives were synthesized by palladium-catalyzed intramolecular Heck reaction[13a,b] as well as organotinhydride-mediated radical cyclization reaction[13c] in excellent yields. On the other hand linear-pyridoquinoline derivatives have been synthesized by several methods[14–20] which are expensive as well as multistep reactions. However, to our knowledge angular-pyridoquinoline derivatives are not reported. In recent years, iodocyclization has emerged as an effective protocol in the preparation of a variety of heterocyclic and carbocyclic compounds.[21–26] This chemistry employs iodine that is cheap and easy to handle. The development of this methodology provides an efficient and mild reaction condition which allows easy isolation of the products from the reaction mixture. In continuation of our interest in the synthesis of nitrogen heterocycles[27] and electrophilic iodocyclization strategy[28] we have undertaken a study on the electrophilic cyclization of 6-(*N*-propargyl)amino quinolone and coumarin derivatives.

The precursors for the iodocyclization reaction, **3a**–**g** were obtained by a two-step approach. The preparation of **2a**,**b** was achieved by the reaction of **1a**,**b** with propargyl bromide in the presence of anhydrous K_2CO_3 and a catalytic amount of NaI in dry acetone under reflux condition, followed by standard Sonogashira coupling reaction[29] using *p*-substituted iodobenzenes. Other precursors **5a**,**b** were synthesized by the reaction of 6-amino quinolone **4a** and 6-amino coumarin **4b** with 1-bromo-2-butyne in the presence of anhydrous K_2CO_3 in dry acetone under refluxing condition and obtained as a 3:1 mixture of compounds **5a**,**b** and **6a**,**b**, respectively (Scheme 1).

When compound **3a**[30] was subjected to iodocyclization reaction in the presence of 3 equiv of I_2 and 3 equiv of $NaHCO_3$ in CH_3CN at room temperature for 13 h, the 6-*endo* cyclized dihydropyridoquinolone derivative **7a**[31] was formed exclusively in excellent yield. Similarly, when the substrate **5a** was condensed with molecular iodine under the reaction condition stated above, the pyridoquinolone **9a** was

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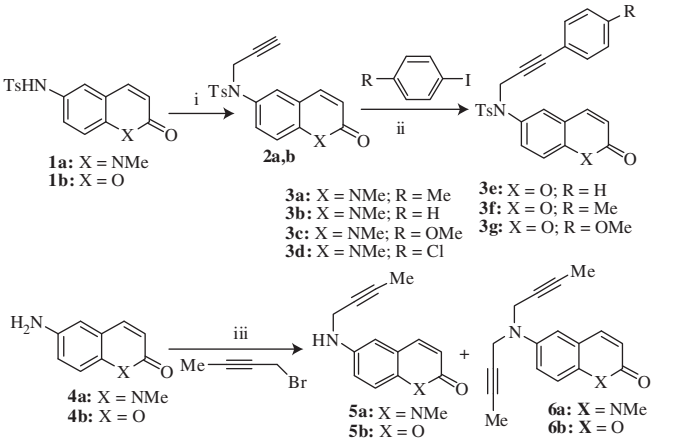
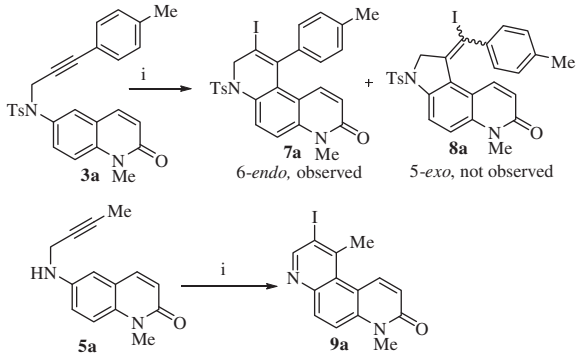
0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.11.066



Scheme 1. Reagents and conditions: (i) propargyl bromide, anhydrous K_2CO_3, NaI, dry acetone, reflux, 6 h; (ii) 3 mol % $Pd(PPh_3)_2Cl_2$, 3 mol % CuI, Et_3N, DMF, rt, 2 h; (iii) anhydrous K_2CO_3, dry acetone, reflux 3 h.



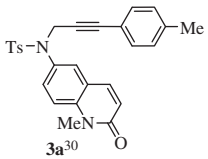
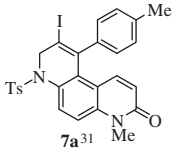
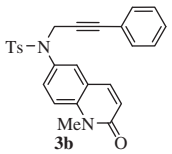
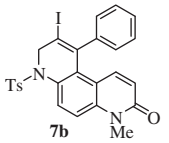
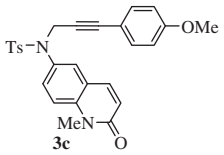
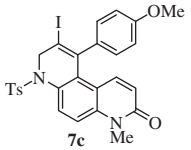
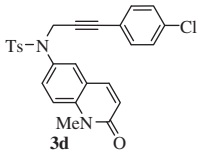
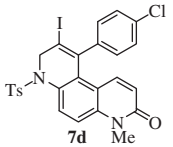
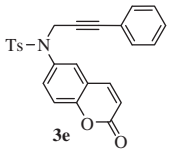
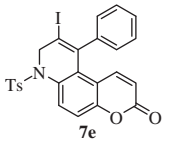
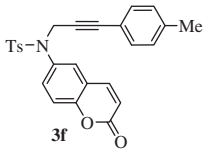
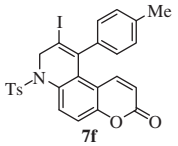
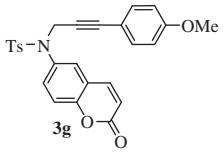
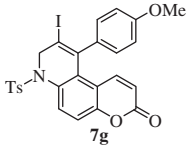
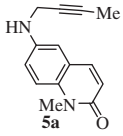
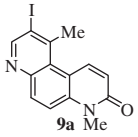
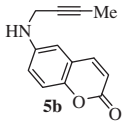
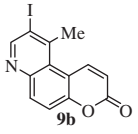
Scheme 2. Reagents and conditions: (i) I_2, $NaHCO_3$, CH_3CN, rt.

Table 1
Optimization of Iodine-mediated reactions

Entry	Solvent	Base (equiv)	I_2 (equiv)	Time (h)	Yield[a] (%)
1	CH_3CN	$NaHCO_3$ (3)	1	13	42
2	CH_3CN	$NaHCO_3$ (3)	1.5	13	60
3	CH_3CN	$NaHCO_3$ (3)	3	24	90
4[b]	CH_3CN	$NaHCO_3$ (3)	3	13	92
5	CH_3CN	$NaHCO_3$ (3)	5	13	88
6	CH_3CN	$NaHCO_3$ (1)	3	13	45
7	CH_3CN	—	3	13	NR[c]
8	CH_3CN	K_2CO_3 (3)	3	13	59
9	CH_2Cl_2	$NaHCO_3$ (3)	3	13	38
10	CH_3OH	$NaHCO_3$ (3)	3	13	42

[a] Isolated yield.
[b] Optimized reaction condition.
[c] NR indicates no reaction.

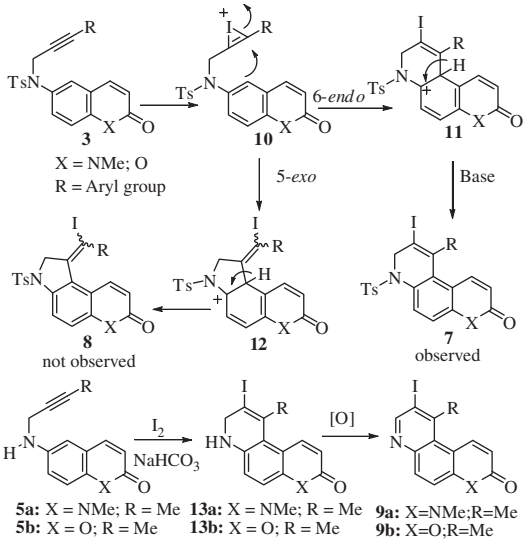
Table 2
Synthesis of pyridoquinolone and pyridocoumarin derivatives

Entry	Substrate(s)	Product(s)	Time (h)	Yield (%)
1	 **3a**[30]	 **7a**[31]	13	92
2	 **3b**	 **7b**	15	88
3	 **3c**	 **7c**	12	95
4	 **3d**	 **7d**	17	60
5	 **3e**	 **7e**	18	62
6	 **3f**	 **7f**	16	66
7	 **3g**	 **7g**	10	70
8	 **5a**	 **9a**	10	70
9	 **5b**	 **9b**	12	75

obtained. The formation of the product **9a**, supports the 6-*endo* mode of cyclization (Scheme 2).

To standardize the reaction condition a series of experiments were performed with or without the base ($NaHCO_3$/K_2CO_3) and varying amounts of molecular iodine in different solvents, such as CH_3CN, CH_3OH, and CH_2Cl_2. The substrate **3a** was used as a representative for this standardization and the results are summarized in Table 1.

When the substrate **3a** was reacted with 3 equiv of I_2 and 3 equiv of $NaHCO_3$ in CH_3CN (5 mL) at room temperature for 13 h, a 92% isolated yield of the product **7a** was obtained. Solvents, like CH_2Cl_2 and CH_3OH resulted in lower yields of the products. Reducing the amount of I_2 from 3 equiv to 1.5 equiv and 1 equiv afforded the compound **7a** in 60% and 42% yields, respectively. Increase in the amount of iodine from 3 equiv to 5 equiv did not improve the yield. Increasing the reaction time from 13 h to 24 h and longer also did not improve the yield of the cyclized product. The presence of a base proved to be important for the reaction. The reaction does not occur without a base. The effect of K_2CO_3 as a base was also investigated. However, it provided a drastically lower yield of the cyclized product **7a** than that when $NaHCO_3$ was used. Based on the above optimization efforts, the combination of



Scheme 3. Plausible mechanism for the formation of 6-*endo* cyclized products.

3 equiv of I_2, 3 equiv of $NaHCO_3$, and the use of CH_3CN as the solvent at room temperature afford the best result.

To test the generality of the reaction, compounds **3a**–**g** and **5a**,**b** were subjected to the molecular iodine-mediated cyclization at optimized reaction condition to afford the cyclized products **7a**–**g** and **9a**,**b** in 60–95% yields. An introduction of a substituent at the terminal position of the alkyne part has a considerable effect on the yield of the reaction. Substituents were first introduced onto the aromatic ring attached to the alkyne. Electron-donating groups, like Me and OMe in the para position, gave good yields while an electron-withdrawing group, a Cl group, gave relatively poor yield of 60%. The results are summarized in Table 2.

The reaction is believed to proceed[28c] via initial formation of an iodonium intermediate by attack of the electrophile on the triple bond, followed by nucleophilic attack of the aromatic π-electrons on the activated triple bond. Loss of a proton from the intermediate **11** in the presence of $NaHCO_3$ may give the 7,8-dihydropyridoquinolone and pyridocoumarin derivatives **7** (Scheme 3). In case of the substrates **5a**,**b**, initially formed 7,8-dihydro derivatives **13a**,**b** might have got oxidized in the presence of I_2 to afford the pyridoquinolone **9a** and pyridocoumarin **9b** derivatives, respectively.

Linear-pyridoquinoline derivatives have been synthesized by several methods[14–20] which are expensive as well as multistep reactions but angular-pyridoquinoline derivatives are not reported. On the other hand, different methods including transition metal-catalyzed reactions are available[13] for the formation of the pyridocoumarin derivatives. However, organotin-mediated protocols suffer from toxicity[11] as well as separation problems[12] and palladium-mediated reactions need high temperature.[13a,b] In this regard the iodine-mediated protocol seems to be superior to the above methods as this involves very simple reaction conditions and occurs at room temperature.

In conclusion we have developed an easy and efficient method for the synthesis of angularly fused pyridoquinolone and pyridocoumarin derivatives with potential bioactivity. The reaction condition is mild, and the products are easily isolable in good to excellent yields. Moreover an iodine atom is introduced in the final product which offers scope for further functionalization.

Acknowledgments

We thank the CSIR (New Delhi) and DST (New Delhi) for financial assistance. Two of us are grateful to the UGC (New Delhi) (I.A.) and to the CSIR (New Delhi) (S.S.) for their research fellowships. We also thank the DST (New Delhi) for providing NMR, CHN-analyzer, and IR spectrometers under the DST-FIST program.

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30. *Synthesis of 4-methyl-N-(1-methyl-2-oxo-1,2-dihydro-quinolin-6-yl)-N-(3-p-tolylprop-2-ynyl)benzenesulfo-namide* (**3a**): To a magnetically stirred solution of **2a** (500 mg, 1.36 mmol), 4-methyliodobenzene (445 mg, 2.04 mmol) and dry Et_3N (2 mL) in dry DMF (8 mL) was degassed under nitrogen atmosphere. Then the catalyst $Pd(PPh_3)_2Cl_2$ (29 mg, 0.04 mmol) and co-catalyst CuI (8 mg, 0.04 mmol) were added to this magnetically well stirred solution. After stirring the reaction mixture for 2 h, the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was washed with water (5 × 20 mL), brine (20 mL), and dried over anhydrous Na_2SO_4 and then the solvent was removed to give a crude mass which was chromatographed over silica gel using ethyl acetate–petroleum ether (2:3) as eluant to furnish the desired product **3a** as a solid with yield 85%; mp 158–159 °C; IR (KBr): 1655, 2242, 2927 cm^{-1}.
^1H NMR ($CDCl_3$, 400 MHz): δ_H = 2.34 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C*H*$_3$), 3.71 (s, 3H, NC*H*$_3$), 4.68 (s, 2H, NC*H*$_2$), 6.72 (d, 1H, *J* = 9.6 Hz, C$_3$-*H* of quinolone), 7.05–7.12 (m, 4H, Ar*H*), 7.21 (d, 2H, *J* = 7.6 Hz, Ar*H*), 7.30 (d, 1H, *J* = 9.2 Hz, Ar*H*), 7.51 (d, 1H, *J* = 9.2 Hz, Ar*H*), 7.55–7.60 (m, 4H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 21.5, 21.6, 29.6, 42.2, 82.6, 86.1, 114.8, 119.0, 120.8, 122.4, 128.1, 128.6, 129.0, 129.4, 130.8, 131.3, 133.8, 135.6, 138.6, 138.8, 139.5, 143.8, 162.1. MS: *m*/*z* = 479 $[M+Na]^+$. Anal. Calcd for $C_{27}H_{24}N_2O_3S$: C, 71.03; H, 5.30; N, 6.14. Found: C, 71.24; H, 5.42; N, 6.07.
31. *Synthesis of 9-iodo-10-(4-methoxyphenyl)-4-methyl-7-tosyl-7,8-dihydro-4,7-phenanthrolin-3(4H)-one* (**7a**): A mixture of compound **3a** (150 mg, 0.33 mmol), $NaHCO_3$ (83 mg, 0.99 mmol), molecular iodine (251 mg, 0.99 mmol) in 5 mL CH_3CN was stirred at room temperature for 13 h. Then the reaction mixture was quenched with 10% sodium thiosulphate solution and then it was extracted with CH_2Cl_2 (3 × 15 mL), washed with water (2 × 10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed to give a crude mass which was chromatographed over silica gel (230–400 mesh) using ethyl acetate–pet ether (40%) as eluant to furnish the desired product **7a** as a white solid with yield 92%; mp 177–178 °C; IR (KBr): 1657, 2920 cm^{-1}.
^1H NMR ($CDCl_3$, 400 MHz): δ_H = 2.33 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C*H*$_3$), 3.72 (s, 3H, NC*H*$_3$), 4.91 (s, 2H, NC*H*$_2$), 6.14 (d, 1H, *J* = 10.4 Hz, C$_3$-*H* of quinolone), 6.33 (br s, 2H, Ar*H*), 6.91 (d, 1H, *J* = 10 Hz, C$_4$-*H* of quinolone), 6.98 (d, 2H, *J* = 7.6 Hz, Ar*H*), 7.09 (d, 2H, *J* = 8 Hz, Ar*H*), 7.43 (d, 1H, *J* = 9.2 Hz, ArH), 7.52 (d, 2H, *J* = 8 Hz, Ar*H*), 8.15 (d, 1H, *J* = 9.2 Hz, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 100 Hz): δ_c = 21.4, 21.5, 30.0, 58.4, 94.4, 115.2, 116.7, 120.3, 127.6, 128.5, 128.9, 129.0, 129.1, 129.5, 131.5, 135.5, 136.5, 138.2, 139.0, 139.9, 140.5, 144.1, 161.1. HRMS: Calcd for $C_{27}H_{23}IN_2O_3S$: 605.0372 $[M+Na]^+$. Found: 605.0379 $[M+Na]^+$.