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Microwave-assisted reductive cyclization: an easy entry to the indoloquinolines and spiro[2*H*-indole-2,3′-oxindole]†

Cite this: *RSC Adv.*, 2014, **4**, 22481

Received 31st March 2014
Accepted 12th May 2014

DOI: 10.1039/c4ra02814g

www.rsc.org/advances

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Synthesis of two linear indoloquinolines *i.e.* 6*H*-indolo[2,3-*b*]quinoline & 11-hydroxy-10*H*-indolo[3,2-*b*]quinoline, and spiro[2*H*-indole-2,3′-oxindole] from a common intermediate, (2-nitrophenyl)methylidene-dihydro-indolone derivative is described using microwave-mediated reductive cyclization as the key step.

Introduction

Cryptolepis sanguinolenta (a tropical shrub indigenous to West Africa) is a rich source of indoloquinoline alkaloids and so far 13 alkaloids containing the indoloquinoline framework have been isolated from this plant. Indoloquinoline alkaloids have received prominent attention in recent years due to their striking biological activities particularly DNA intercalating[1] and antimalarial[2,3] properties. In addition, these alkaloids have also been reported to show antimuscarinic, antibacterial, antiviral, antimicotic, antihyperglycemic and cytotoxic properties *in vitro* and antitumor activity *in vivo*.[4–9] Various alkaloids isolated from this plant includes cryptolepine[10] **1**, hydroxycryptolepine[11] **2**, cryptolepinone[11–13] **3**, 11-isocryptolepine[14] **4**, cryptospirolepine[12] **5**, cryptolepicarboline[15] **6**, cryptomisrine[16] **7**, bis-cryptolepine[17] **8**, cryptoquindoline[11] **9**, cryptoheptine[11] **10**, quindoline[18] **11**, quindolinone[13] **12**, neocryptolepine[17,19] **13** and isocryptolepine[19,20] **14** (Fig. 1).

Indoloquinoline alkaloids[21] particularly cryptolepine and neocryptolepine have been the targets of synthetic and medicinal chemists during the past decade due to their interesting structural features and diverse biological activities. Important reported methods for the synthesis of 10*H*-indolo[3,2-*b*]quinoline and 6*H*-indolo[2,3-*b*]quinoline (immediate chemical precursors of cryptolepine and neocryptolepine) are shown in Fig. 2 and 3 respectively.

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† Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR of all the synthesized compounds. See DOI: 10.1039/c4ra02814g

In our earlier communication,[44] we described the synthesis of neocryptolepine using isatin and (2-nitrobenzyl)triphenylphosphonium bromide as the starting material *via* intermediate **16**. In the present study, this intermediate **16** is further explored for the synthesis of two isomeric linear indoloquinolines and spiro-oxindole derivative using microwave mediated reductive cyclization approach.

Results and discussion

Our approach for the synthesis of two isomeric linear indoloquinolines is based on the retrosynthetic analysis (Scheme 1). It was anticipated that, linear indoloquinolines **11** and **15** can be synthesized from a common intermediate **16** *via* reductive cyclization reaction. The key intermediate **16** in turn can be obtained by Wittig reaction of (2-nitrobenzyl)triphenylphosphonium bromide with isatin. Hence compound **16** could be considered as an advance intermediate for preparation of alkaloids in present work.

Accordingly, intermediate **16**[44] was prepared by stirring the mixture of (2-nitrobenzyl)triphenylphosphonium bromide, isatin and Et_3N in $CHCl_3$ at room temperature (Scheme 2). The Wittig olefination product which precipitated out in $CHCl_3$ was isolated by simple filtration in 92% yield. The Wittig product was obtained as a mixture of geometrical isomers in 2 : 1 ratio as evident from ^{1}H NMR data. The stereochemistry of olefin was not of any consequence for further manipulation and hence, this mixture of Wittig product **16** was subjected to next step without any further purification. Initially, the Wittig product **16** was subjected to reductive cyclization using Fe powder in presence of catalytical amount of HCl in refluxing acetic acid to yield exclusively 6*H*-indolo[2,3-*b*]quinoline **15** in 77% yield.[44] During this step, four reactions took place in one-pot *i.e.* reduction of nitro group, isomerization of mixture of *E*/*Z* to *Z*-isomer, cyclization and finally dehydration. Regioselective methylation on quinoline nitrogen of 6*H*-indolo[2,3-*b*]quinoline using reported procedure[27] afforded the naturally occurring alkaloid – neocryptolepine (cryptotackieine) **13**.

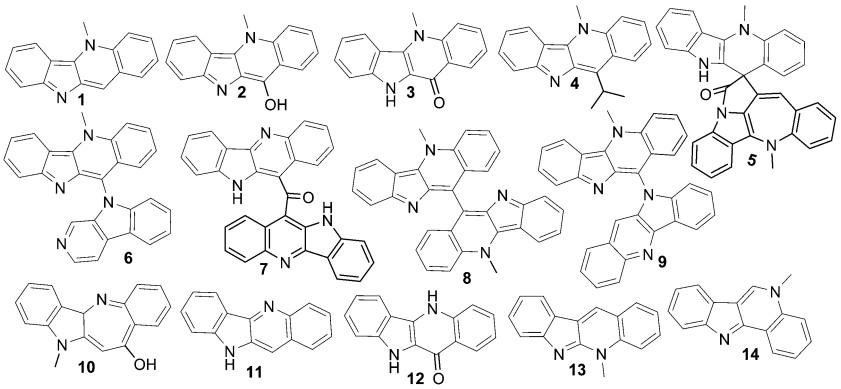


Fig. 1 Structures of indoloquinoline alkaloids isolated from *Cryptolepis sanguinolenta*.

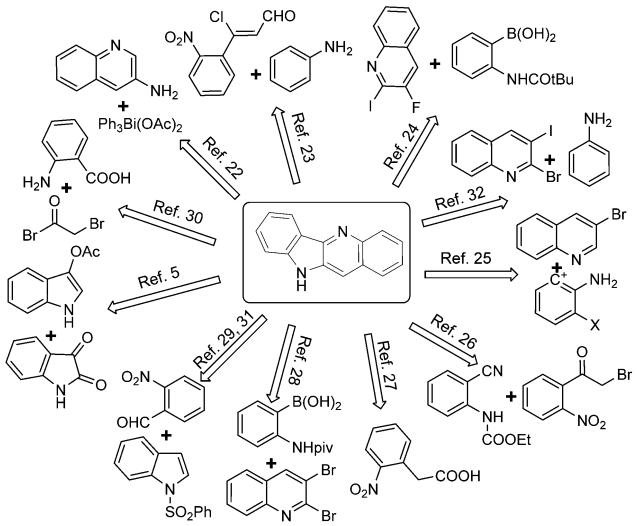


Fig. 2 Synthetic approaches to 10*H*-indolo[3,2-*b*]quinoline.

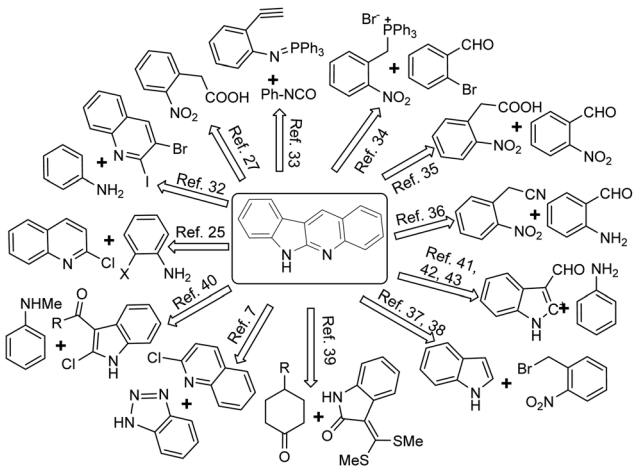
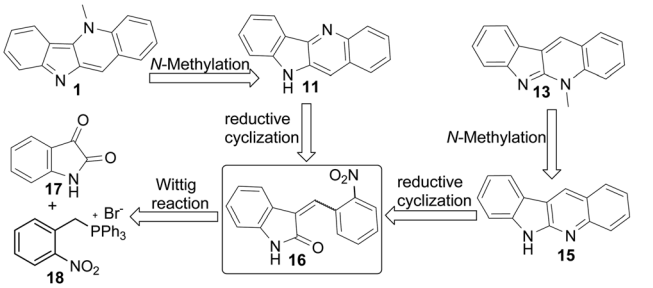
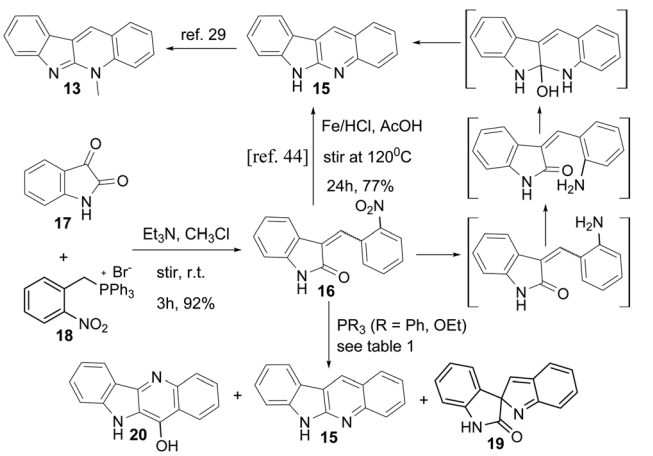


Fig. 3 Synthetic approaches to 6*H*-indolo[2,3-*b*]quinoline.



Scheme 1 Retrosynthetic analysis of cryptolepine and neocryptolepine.



Scheme 2 Synthesis of indoloquinolines and spiro[2*H*-indole-2,3′-oxindole].

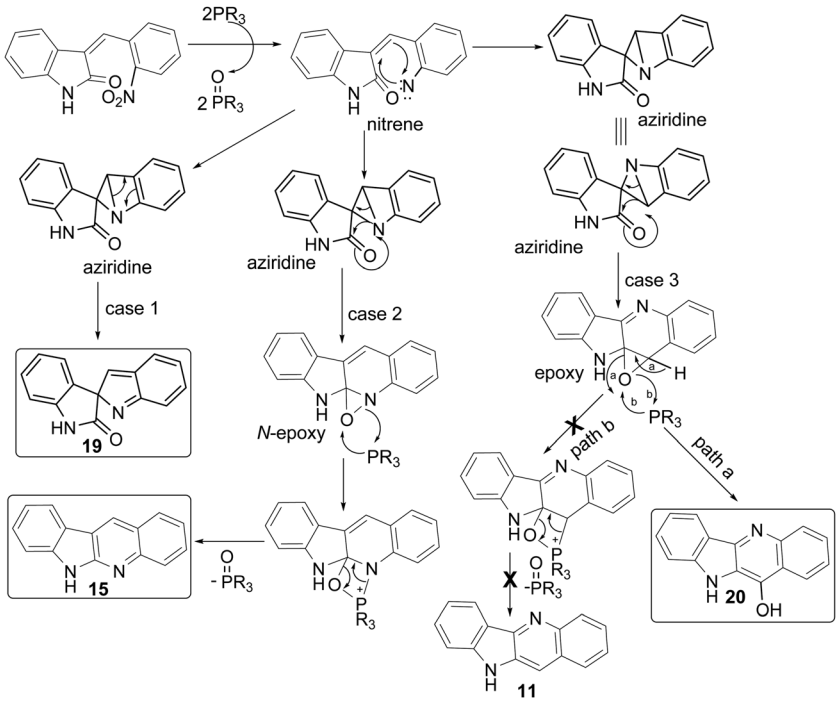
6*H*-Indolo[2,3-*b*]quinoline **15** itself is a natural product reported from the leaves of *Justica* betonica[45] and is known as quindoline[33] or norcryptotackieine.[27] For last several decades, Cadogan cyclization is used for the synthesis of various N-heterocycles which was first reported in 1963 by Cadogan and Bunyan[46] for the preparation of carbazoles. So we attempted the reductive cyclization (popularly known as Cadogan cyclization) using triphenyl phosphine (TPP) or triethyl phosphite (TEP) as a deoxygenating reagent (Table 1) with intension of getting both the linear indoloquinoline frameworks *i.e.* 6*H*-indolo[2,3-*b*]-quinoline **15** and 10*H*-indolo[3,2-*b*]quinoline **11** in one-pot. When the reductive cyclization was carried out using TPP in

Table 1 Optimization of reductive cyclization reaction conditions

Entry	Reagents and condition	Yield[a] [%] 19	15	20
1	PPh_3, Ph_2O, 260–270 °C, 5 h	25	13	—
2	PPh_3, Ph_2O, 180–200 °C, 15 h	Trace	—	—
3	$P(OEt)_3$, reflux, 3 h	19	10	—
4[b]	PPh_3, Ph_2O, MW, 150 °C, 15 min and then 180 °C, 10 min	10	3	—
5	$P(OEt)_3$, MW, 150 °C, 10 min	33	22	20

[a] Isolated yield. [b] 64% of starting material is recovered.

refluxing diphenyl ether (entry 1), two compounds were obtained. As expected, one compound was found to be 6*H*-indolo[2,3-*b*]quinoline **15** as evident from the NMR and mass data while the NMR and mass data of the other compound did not match with the other expected compound *i.e.* 10*H*-indolo[3,2-*b*]quinoline **11**. After careful observation of the NMR and mass data, we found that spiro[2*H*-indole-2,3′-oxindole] **19** was formed instead of 10*H*-indolo[3,2-*b*]quinoline **11**. Interestingly, the major compound **19** formed during this reaction contains the spiro-oxindole core which is present in various biologically important alkaloids[47] such as horsfiline, coerulescine, pteropodine and spirotryprostatin-B. Also some of the unnatural spiro-oxindoles such as spiroimides are known to be potent as aldose reductase inhibitors and antihyperglycemic agents.[48,49] The low yields of the products may be due to the decomposition of the intermediate as the reaction was carried out at high temperature *i.e.* 260–270 °C and also due to the low solubility of the products, some loss during purification by column chromatography. To overcome the decomposition of the intermediate, reaction was tried at lower temperature *i.e.* 180–200 °C (entry 2) but only trace amount of spiro[2*H*-indole-2,3′-oxindole] **19** was observed while most of the starting material remains unreacted (monitored by TLC) even after continuing the reaction for 15 hours. Carrying out the reductive cyclization reaction in refluxing TEP (entry 3), neither improve the yields of the two products nor it helps in forming the other expected rearranged product *i.e.* 10*H*-indolo[3,2-*b*]quinoline **11**. The low yields in this case may be due to the formation of *N*-alkylated side products[50] which are known to form when TEP is used as a deoxygenating reagent. Never the less, this report represents the new route to the spiro-derivative of oxindole **19**. In recent years, the use of microwave energy has become an increasingly popular technique in organic synthesis as it not only saves energy and time but sometimes also helps in getting the products which are not obtained by conventional oil-bath synthesis. So, we attempted the reductive cyclization using TPP in diphenyl ether under microwave irradiation (entry 4). The microwave reaction was carried out at 150 °C for 15 minutes and then at 180 °C for another 10 minutes. The products **19** and **15** were obtained in 10% and 3% yields while most of the starting material remains unreacted. Interestingly, microwave reaction using TEP at 150 °C (entry 5) resulted in the formation of three products. Two compounds were found to be spiro[2*H*-indole-2,3′-oxindole] **19** and 6*H*-indolo[2,3-*b*]quinoline **15** as expected while the NMR and mass data of the third compound did not match with the other expected possible compound *i.e.* 10*H*-indolo[3,2-*b*]quinoline **11**. After carefully analyzing the NMR and mass data, we found that 11-hydroxy-10*H*-indolo[3,2-*b*]-



Scheme 3 Proposed mechanism for the formation of indoloquinolines and spiro[2*H*-indole-2,3′-oxindole].

quinoline **20** is formed during the reaction. It is fascinating to note that, compound **20** is hydroxyl derivative of compound **11**. Repetition of this cyclization step under MW assisted condition delivered similar results indicating the reproducibility of this methodology. In case of entry 4 (Table 1), low yields of the two products (**19** and **15**) and no formation of compound **20** may be due to the temperature (150–180 °C) which is not sufficient for this substrate to undergo reductive cyclization when TPP is used as a deoxygenating agent even under microwave irradiation. This is evident from the recovery of most of the starting material and also from the entry 2 (Table 1) wherein only trace amount of compound **19** is observed. Finally, we had completed the synthesis of spiro[2*H*-indole-2,3′-oxindole] **19**, 6*H*-indolo[2,3-*b*]-quinoline **15** and 11-hydroxy-10*H*-indolo[3,2-*b*]quinoline **20** in 2-steps with an overall yield of 30%, 20%, and 18% respectively.

The probable mechanism for the formation of all the three products is shown in Scheme 3. Nitro compound reacts with phosphorus reagent to give nitrene intermediate which cyclizes to form aziridine intermediate. Opening of aziridine intermediate is possible in three different ways: (a) case 1 – to give directly stable spiro[2*H*-indole-2,3′-oxindole] **19**, (b) case 2 – to give labile *N*-epoxy intermediate which may be reacted with phosphorus reagent to give four-membered intermediate that loses triphenyl phosphine oxide to give 6*H*-indolo[2,3-*b*]quinoline **15** and (c) case 3 – to give epoxy intermediate. We are expecting epoxy intermediate to react with phosphorus reagent to give four-membered intermediate which then can undergo lose of triphenyl phosphine oxide to give 10*H*-indolo[3,2-*b*]-quinoline **11**. But, instead epoxy intermediate opens up to give directly 11-hydroxy-10*H*-indolo[3,2-*b*]quinoline **20**.

Conclusion

We have developed a method in which two linear indoloquinolines are formed in the same step along with spiro-oxindole derivative under microwave irradiation. Use of microwave irradiation for carrying out reductive cyclization, not only reduced energy and time but helps in forming 11-hydroxy-10*H*-indolo [3,2-*b*]quinoline which was not obtained with conventional oil-bath heating and also increases the yields of the other two products. Further work to extend this strategy for the synthesis of derivatives of these compounds for their biological studies are under progress.

Experimental section

General methods

The reagents were purchased commercially and used without further purification. The solvents were distilled prior to use. Column chromatography was performed on silica gel (60–120 mesh). Infrared spectra were recorded with an FTIR spectrophotometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in DMSO-d_6. TMS was used as an internal reference. HRMS data were recorded with an ES-QTOF. Melting points were recorded with a Thieles apparatus and are uncorrected.

3-[(2-Nitrophenyl)methylidene]-1,3-dihydro-2*H*-indol-2-one 16

Yield = 0.50 g, 92%. Experimental details, physical and spectroscopic data are same as that of published data.[44]

6*H*-Indolo[2,3-*b*]quinoline 15

Yield = 0.231 g, 77%. Experimental details, physical and spectroscopic data are same as that of published data.[44]

Typical procedure for reductive cyclization using PPh_3 or $P(OEt)_3$

(a)By conventional heating. (i) Using PPh_3: mixture of compound **16** (0.511 g, 1.92 mmol) and PPh_3 (1.209 g, 4.61 mmol) in Ph_2O (15 mL) was refluxed for 5 h. After cooling, the reaction mixture was chromatographed on silica gel and diphenyl ether was removed using hexanes as an eluent. Further elution with 10% ethyl acetate in hexanes afforded spiro[2*H*-indole-2,3′-oxindole] **19** (0.113 g, 25%) and with 20% ethyl acetate in hexanes afforded 6*H*-indolo[2,3-*b*]quinoline **15** (0.056 g, 13%).

(ii) Using $P(OEt)_3$: compound **16** (0.508 g, 1.91 mmol) in $P(OEt)_3$ (10 mL) was refluxed for 3 h. After cooling, excess $P(OEt)_3$ was distilled out under vacuum and the crude reaction mixture was chromatographed on silica gel. Elution with 10% ethyl acetate in hexanes afforded spiro[2*H*-indole-2,3′-oxindole] **19** (0.085 g, 19%) and with 20% ethyl acetate in hexanes afforded 6*H*-indolo[2,3-*b*]quinoline **15** (0.042 g, 10%).

(b)By microwave irradiation. Manufacturer – milestone and model – startsynth.

The reactions were carried out in sealed vessel.

The method of monitoring the reaction mixture temperature – internal probe.

The required temperature is reached in 10 min. and then maintained for the specified time in each experiment.

(i) Using PPh_3: mixture of compound **16** (0.206 g, 0.77 mmol) and PPh_3 (0.488 g, 1.86 mmol) in Ph_2O (10 mL) was irradiated in microwave reactor at 150 °C (200 W) for 15 min. and at 180 °C (200 W) for 10 min. After cooling, the reaction mixture was chromatographed on silica gel and diphenyl ether was removed using hexanes as an eluent. Further elution with 10% ethyl acetate in hexanes afforded spiro[2*H*-indole-2,3′-oxindole] **19** (0.018 g, 10%), with 20% ethyl acetate in hexanes afforded 6*H*-indolo[2,3-*b*]quinoline **15** (0.005 g, 3%) and with 30% ethyl acetate in hexanes recovered the starting material (0.132 g, 64%).

(ii) Using $P(OEt)_3$: compound **16** (0.203 g, 0.76 mmol) in $P(OEt)_3$ (10 mL) was irradiated in microwave reactor at 150 °C (200 W) for 10 min. After cooling, excess $P(OEt)_3$ was distilled out under vacuum and the crude reaction mixture was chromatographed on silica gel. Elution with 10% ethyl acetate in hexanes afforded spiro[2*H*-indole-2,3′-oxindole] **19** (0.059 g, 33%), with 20% ethyl acetate in hexanes afforded 6*H*-indolo[2,3-*b*]quinoline **15** (0.036 g, 22%) and with 40% ethyl acetate in hexanes afforded 11-hydroy-10*H*-indolo[3,2-*b*]quinoline **20** (0.036 g, 20%).

Spiro[2*H*-indole-2,3′-oxindole] 19

Physical and spectroscopic data are same as that of published data.[51]

6*H*-Indolo[2,3-*b*]quinoline 15

Physical and spectroscopic data are same as that of published data.[44]

11-Hydroy-10*H*-indolo[3,2-*b*]quinoline 20

Mp > 200 °C. IR (KBr): γ_{max} = 3215 (–NH), 3160 (–OH), 1637, 1612, 1554, 1456, 1396, 1215, 748 cm^{-1}. ^1H NMR (DMSO-d_6, 300 MHz) δ (ppm):7.23–7.31 (q, J = 7.8 Hz, 2H), 7.34–7.38 (t, J = 7.2 Hz, 1H), 7.48–7.50 (m, 2H), 7.60–7.62 (d, J = 8.1 Hz, 1H), 8.18 (br m, 2H), 11.41 (br s, –NH), 12.58 (br s, –OH). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 106.8, 112.1, 112.4, 116.5, 121.2, 121.5, 122.1, 122.5, 124.5, 124.8, 129.7, 138.2, 138.3, 141.2, 160.4. HRMS: m/z $[M + H]^+$ calcd for $C_{15}H_{11}N_2O$, 235.0919; found, 235.0937.

Acknowledgements

Authors thank the OCEAN FINDER and EU-FP7-KBBE-2009-3-245137 MAREX for financial assistance and are grateful to CSIR-NIO for the award of Scientist Fellow-QHS. Special thanks to Mr H. K. Kadam (Department of Chemistry, Goa University) for his help during this work.

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