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Facile synthesis of azocino[4,3-b]indoles by ring-closing metathesis

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Abstract—The azocino[4,3-b]indole system, tricyclic substructure of the indole alkaloids apparicine and ervaticine, is efficiently assembled by ring-closing metathesis of 2-allyl-3-(allylaminomethyl)indoles. The metathesis sites are introduced into the indole nucleus by reductive amination of a 3-formyl derivative with allylamine, followed by α-lithiation with subsequent electrophilic trapping with acrolein.

1. Introduction

Ruthenium-catalyzed ring-closing metathesis (RCM)1 has emerged as a powerful tool for the construction of a great variety of carbo- and heterocycles from acyclic precursors.2 In particular, the RCM methodology has turned out to be very useful for the synthesis of medium-sized rings,3 which is generally problematic due to disfavored entropic factors and transannular interactions. Our interest in the development of indole annulation methodologies led us to consider RCM reactions of indole-containing dienes4,5 for the efficient construction of medium-sized indolo 2,3-fused carbo- and azacycles, which are common structural arrangements in many natural and synthetic bioactive compounds.6 In this paper we report a direct synthetic approach to the azocino[4,3-b]indole system I by RCM of appropriate 2,3-dialkenylindoles incorporating a nitrogen atom in the tether linking the two double bonds (Scheme 1). It should be noted that I constitutes the tricyclic substructure of apparicine,7 an indole alkaloid known for 40 years but still awaiting its first total synthesis,8 and also the unprecedented 2-acylindole analogue ervaticine.9

Keywords: Ring-closing metathesis; Indole; Indole alkaloids.

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Scheme 1. Synthetic plan.

Scheme 2. Reagents and conditions: (a) Cl2CHOMe, TiCl4, CH2Cl2, −78 °C, 2 h, 90%; (b) allylamine, NaBH(OAc)3, AcOH, rt, overnight; (c) (t-BuOCO)2O, 4:1 MeOH–Et3N, reflux, 4 h, 65% (3a) or TsCl, Et3N, CH2Cl2, rt, overnight 65% (3b); (d) (PCy3)2(Cl)2Ru−CHPh, CH2Cl2, reflux, overnight, 60% (4a), 89% (4b).
protecting groups at the aliphatic nitrogen, were obtained in 65% overall yield from 2. Satisfactorily, ring closure of the N-Boc diene 3a took place in refluxing dichloromethane in the presence of the first generation Grubbs catalyst to give the azocino[4,3-b]indole 4a in 60% yield. The N-tosyl derivative 3b proved to be a better substrate as it led to 4b in a higher yield (89%).

With model azocino[4,3-b]indoles in hand, we sought to elaborate C-6 functionalized derivatives simply by extending the chemistry outlined above to an O-protected 2-(1-hydroxyallyl)indole. To this end, we selected silyl ether 6, which was easily prepared from aldehyde 5,12 by reaction with vinylmagnesium bromide followed by protection of the resulting alcohol with tert-butyldimethylsilyl chloride (63% overall yield, Scheme 3). Disappointingly, we were not able to introduce the formyl group needed for the reductive amination step since 6 gave only a complex mixture upon subjection to the above Friedel–Crafts protocol.

**Scheme 3.** Reagents and conditions: (a) BrMgCH=CH2, THF, −78 °C–rt, overnight; (b) TBDMSCl, DMF, imidazole, 55 °C, overnight, 63%.

This unsuccessful result prompted us to change the order of the synthetic steps. Functionalization at the 2-position of a properly 3-substituted indole by α-metalation followed by electrophilic trapping seemed to be the logical solution. With this aim, we focused our attention on 3-(aminomethyl)indoles 8 and 9, which were available from indole-3-carboxaldehyde 713 through reductive amination techniques, using tosylamine or acrolein, or tert-BuLi followed by acylation (Scheme 4). Unfortunately, treatment of these substrates with either LDA, sec-BuLi or tert-BuLi in THF under a variety of experimental conditions, followed by addition of DMF, HCOOMe, or acrolein led to the recovery of the starting product.

**Scheme 4.** Reagents and conditions: (a) TsNH2, toluene, reflux, 24 h, then NaBH₄, MeOH, rt, 24 h, 70%; (b) allylamine, NaBH(OAc)₃, AcOH, rt, overnight; (c) (t-BuOOC)₂O, 4:1 MeOH-Et₃N, reflux, 4 h, 72% (11a) or TsCl, Et₃N, CH₂Cl₂, rt, overnight (11b); (d) t-BuLi, THF, −78 °C, 2 h, then acrolein, −78 °C, 3.5 h, 79%; (d) MnO₂, CH₂Cl₂, rt, 60 h, 64%; (e) TBDMSCl, DMF, imidazole, 55 °C, overnight, 64%; (f) (PCy₃)₂(Cl)₂Ru=CHPh, CH₂Cl₂, reflux, overnight, 85% (15) or (Im)(PCy₃)(Cl)₂Ru=CHPh, CH₂Cl₂, rt, overnight, 86% (16); (g) H₂, Pd/C, MeOH, 12 h, 80% (17), 82% (18).

We were pleased to find that the desired α-lithiation did take place from 11a upon treatment with tert-BuLi in THF at −78 °C. After quenching with acrolein, the unstable alcohol 12 was isolated (79%) and immediately protected as the tert-butyldimethylsilyl ether 13 (64%) or, alternatively, oxidized with MnO₂ (64%) to the ketone 14. Satisfactorily, when 13 was subjected to the previously used RCM conditions (first generation Grubbs catalyst in refluxing dichloromethane) the expected tricyclic compound 15 was obtained in good yield (85%). However, no cyclization was observed from ketone 14 under the above protocol, probably due to the presence of an electron-poor double bond, and only dimeric products coming from intermolecular metathesis reactions were formed. This problem was circumvented simply by using the more efficient second generation Grubbs catalyst at room temperature, leading to tricyclic ketone 16 in 86% yield. Finally, the saturated forms of the eight-membered heterocycles 17 and 18 were obtained by catalytic hydrogenation over Pd/C.

**Scheme 5.** Reagents and conditions: (a) allylamine, NaBH(OAc)₃, AcOH, rt, overnight; (b) (t-BuOOC)₂O, 4:1 MeOH-Et₃N, reflux, 4 h, 72% (11a) or TsCl, Et₃N, CH₂Cl₂, rt, overnight (11b); (c) t-BuLi, THF, −78 °C, 2 h, then acrolein, −78 °C, 3.5 h, 79%; (d) MnO₂, CH₂Cl₂, rt, 60 h, 64%; (e) TBDMSCl, DMF, imidazole, 55 °C, overnight, 64%; (f) (PCy₃)₂(Cl)₂Ru=CHPh, CH₂Cl₂, reflux, overnight, 85% (15) or (Im)(PCy₃)(Cl)₂Ru=CHPh, CH₂Cl₂, rt, overnight, 86% (16); (g) H₂, Pd/C, MeOH, 12 h, 80% (17), 82% (18).

We have developed a new synthetic route to the azocino[4,3-b]indole system15,16 relying on RCM of 2-allyl-3-(allylaminomethyl)indoles. The efficiency of the cyclization

**3. Conclusion**

We have developed a new synthetic route to the azocino[4,3-b]indole system15,16 relying on RCM of 2-allyl-3-(allylaminomethyl)indoles. The efficiency of the cyclization
4.1. General methods

All nonaqueous reactions were performed under an argon atmosphere. All solvents were dried by standard methods. Reaction courses and product mixtures were routinely monitored by TLC on silica gel (precoated F254 Merck plates). Drying of organic extracts was carried out over anhydrous Na2SO4. The solvents were evaporated under reduced pressure with a rotary evaporator. Flash chromatography was carried out on SiO2 (silica gel 60, SDS, 0.04–0.06 mm). Melting points are uncorrected. Unless otherwise indicated, NMR spectra were recorded in CDCl3 at 300 MHz (1H) or 75.4 MHz (13C) using Me4Si as an internal reference. Melting points are uncorrected. Unless otherwise indicated, NMR spectra were recorded in CDCl3 at 300 MHz (1H) or 75.4 MHz (13C) using Me4Si as an internal reference.

4.1.4. 2-([(tert-Butoxycarbonyl)-7-(phenylsulfonyl)-1,2,3,6-tetrahydroazocino[4,3-b]]indole (4a). (PCy3)2Cl2Ru=CHPh (first generation Grubbs catalyst, 10 mol %) was added under Ar to a solution of amine 3a (90 mg, 0.19 mmol) in anhydrous CH2Cl2 (5 mL) and the resulting mixture was heated at reflux overnight. The reaction mixture was filtered and concentrated. Flash chromatography of the crude residue (1:1 hexanes–AcOEt) gave 4a: 50 mg (60%); 1H NMR (1:1 mixture of rotamers) δ 1.25 and 1.44 (2s, 9H), 3.88 and 4.02 (2br s, 2H), 4.55 and 4.68 (2s, 2H), 5.60 and 5.71 (2m, 1H), 5.85 (m, 1H), 7.22–7.53 (m, 7H), 7.73 (m, 1H), 8.20 (m, 1H); 13C NMR δ 23.4 (CH3), 28.3 (CH3), 42.6 (CH3), 45.9 and 46.5 (CH2), 79.9 (C), 114.8 (CH), 117.8 (CH), 118.6 (C), 123.3 (CH), 124.2 (CH), 126.2 (2CH), 127.1 (CH), 128.2 (CH), 129.0 (C), 129.1 (2CH), 133.5 (CH), 136.0 (2C), 139.0 (C), 155.0 (CO). Anal. Calcd for C22H21N3O3S: C, 64.36%; H, 5.41%; N, 5.38%. Found: C, 64.67%; H, 5.43%; N, 5.35%.

4.1.5. 7-(Phenylsulfonyl)-2-tosyl-1,2,3,6-tetrahydroazocino[4,3-b]indole (4b). Operating as above, from amine 3b (0.1 g, 0.19 mmol) 4b was obtained: 80 mg (89%); 1H NMR (DMSO-d6) δ 2.40 (s, 3H, Me), 3.76 (d, J = 6.6 Hz, 2H, 3-H), 3.98 (d, J = 6.9 Hz, 2H, 6-H), 4.51 (s, 2H, 1-H), 5.42 (m, 1H, 4-H), 5.92 (m, 1H, 5-H), 7.20–7.70 (m, 12H, Ar), 8.20 (d, J = 7.5 Hz, 1H, 8-H); 13C NMR (H2O) δ 21.5 (CH3), 25.0 (C-6), 42.1 (C-7), 45.0 (C-8), 114.8 (C-8), 115.3 (C-11b), 117.9 (C-11), 123.6 (C-10), 124.6 (C-9), 125.2 (C-4), 126.1 (CH2), 127.0 (CH2), 129.0 (C-11a), 129.2 (2CH), 129.6 (2CH), 129.8 (C-5), 133.7 (CH), 136.0 (2C), 136.4 (C), 138.8 (C), 143.3 (C); HRMS calcd for C22H21N3O3S: 492.6118, found 492.6110.
4.1.6. 2-[1-(tert-Butyldimethylsilyloxy)-2-propenyl]-1-(phenylsulfonyl)indole (6). BrMgCH₂ (1 M solution in THF, 2.96 mmol) was added to a solution of aldehyde 5₁² (0.65 g, 2.28 mmol) in THF (15 mL) at −78 °C and the resulting mixture was stirred at rt overnight. The reaction mixture was diluted with 10% aqueous NH₄Cl and extracted with Et₂O. The organic extracts were dried and concentrated and the residue was purified by flash chromatography (9:1 hexanes–AcOEt) to give 1-(phenylsulfonyl)-2-(1-hydroxy-2-propenyl)indole (0.57 g). This compound was dissolved in DMF (5 mL) and treated with TBDMSCl (0.40 g, 2-propenyl)indole (0.57 g). This compound was dissolved in MeOH (16 mL) and treated with (s-BuO)₂O (0.57 g, 2.65 mmol) and Et₃N (7.4 mL, 0.05 M) at rt overnight. After the mixture was heated at reflux for 4 h, the solvent was removed and the residue was dissolved in CH₂Cl₂ (12 mL) and treated with tosyl chloride (0.33 g, 1.75 mmol) and Et₃N (0.25 mL, 1.75 mmol) at rt overnight. The reaction mixture was diluted with CH₂Cl₂ and washed with 1 N HCl and brine prior to drying and solvent evaporation. The resulting residue was purified by flash chromatography (1:9 hexanes–CH₂Cl₂) to give 9b. 0.74 g (67%); mp 108 °C (Et₂O); ¹H NMR δ 2.44 (s, 3H), 3.70 (d, J = 6.0 Hz, 2H), 4.43 (s, 2H), 4.90 (m, 2H), 5.37 (m, 1H), 7.25–7.95 (m, 13H), 8.01 (d, J = 7.5 Hz, 1H); ¹³C NMR δ 21.4 (CH₃), 41.8 (CH₂), 49.5 (CH₃), 113.3 (CH), 117.2 (C), 118.9 (CH₂), 120.1 (CH), 123.4 (CH), 125.0 (CH), 126.3 (CH₂), 129.2 (CH₂), 129.6 (CH₂), 132.0 (CH), 132.7 (C), 137.8 (C), 138.9 (C), 143.3 (C), 144.4 (C); HRMS calcd for C₂₂H₂₂N₂O₄S: 426.1613, found 426.1610.

4.1.7. 1-(Phenylsulfonyl)-3-(tosylaminomethyl)indole (11a). Aldehyde 7 (0.65 g, 2.3 mmol) in CH₂Cl₂ (30 mL) was allowed to react as above with allylamine and the resulting secondary amine was dissolved in CH₂Cl₂ (12 mL) and treated with tosyl chloride (0.33 g, 1.75 mmol) and Et₃N (0.25 mL, 1.75 mmol) at rt overnight. The reaction mixture was diluted with CH₂Cl₂ and washed with 1 N HCl and brine prior to drying and solvent evaporation. The resulting residue was purified by flash chromatography (1:9 hexanes–CH₂Cl₂) to give 11a. 0.74 g (67%); mp 108 °C (Et₂O); ¹H NMR δ 2.44 (s, 3H), 3.70 (d, J = 6.0 Hz, 2H), 4.43 (s, 2H), 4.90 (m, 2H), 5.37 (m, 1H), 7.25–7.95 (m, 13H), 8.01 (d, J = 7.5 Hz, 1H); ¹³C NMR δ 21.4 (CH₃), 41.8 (CH₂), 49.5 (CH₃), 113.3 (CH), 117.2 (C), 118.9 (CH₂), 120.1 (CH), 123.4 (CH), 125.0 (CH), 126.3 (CH₂), 129.2 (CH₂), 129.6 (CH₂), 132.0 (CH), 132.7 (C), 137.8 (C), 138.9 (C), 143.3 (C), 144.4 (C); HRMS calcd for C₂₂H₂₂N₂O₄S: 426.1613, found 426.1610.

4.1.8. 3-[N-allyl-N-tosylaminomethyl]-1-(phenylsulfonyl)indole (9a). Allylamine (0.34 mL, 4.6 mmol), NaBH₄(OAc)₃ (1.46 g, 6.9 mmol), and AcOH (0.13 mL, 2.3 mmol) were successively added to aldehyde 7 (0.65 g, 2.3 mmol) in CH₂Cl₂ (15 mL) and the resulting mixture was stirred at rt overnight. The reaction mixture was diluted with H₂O, basified with 10% aqueous Na₂CO₃, and extracted with CH₂Cl₂. The organic extracts were dried and concentrated. Flash chromatography of the residue (98:2 CH₂Cl₂–MeOH) gave the secondary amine (0.5 g). This compound was dissolved in MeOH (16 mL) and treated with (s-BuO)₂O (0.57 g, 2.65 mmol) and Et₃N (7.4 mL, 5.3 mmol). After the mixture was heated at reflux for 4 h, the solvent was removed and the residue was diluted with CH₂Cl₂ and washed with 1 N HCl and brine. The organic extracts were dried and concentrated and the resulting residue was chromatographed (flash, 95:5 hexanes–AcOEt) to provide 9a: 0.66 g (68%); ¹H NMR δ 1.48 (s, 9H), 3.70 (br s, 2H), 4.52 (br s, 2H), 5.10 (m, 2H), 5.65 (m, 1H), 7.20–7.65 (m, 7H), 7.85 (m, 2H), 8.05 (d, J = 7.5 Hz, 1H); ¹³C NMR δ 28.3 (3CH₃), 40.8 (CH₃), 48.0 (CH₂), 79.9 (C), 113.5 (CH), 116.3 (CH₃), 119.6 (CH), 120.3 (CH), 123.2 (CH), 124.6 (CH), 124.8 (CH), 126.5 (CH₂), 128.8 (C), 129.1 (2CH), 133.4 (CH), 133.7 (CH), 135.3 (C), 137.9 (C), 155.3 (CO); HRMS calcd for C₁₉H₂₆N₂O₄S: 426.1613, found 426.1610.
5.72 (m, 2H, CHOH, CH=), 6.15 (m, 1H, CH=), 7.15 (m, 1H, ind 5-H), 7.24 (m, 1H, ind 6-H), 7.41 (d, J = 8.1 Hz, 1H, ind 7-H), 7.68 (d, J = 8.1 Hz, 1H, ind 4-H); 13C NMR δ 28.5 (3CH3), 39.3 (CH3), 47.9 (CH3), 55.8 (CH3), 66.6 (CH), 74.5 (CH3), 80.0 (C), 109.5 (CH), 111.6 (C), 115.1 (CH), 115.9 (CH2), 119.5 (CH), 120.5 (CH), 122.8 (CH), 128.0 (C), 134.0 (CH), 137.6 (C), 137.9 (C), 153.9 (CO), 155.7 (CO).

4.1.13. 3-[N-Allyl-N-tert-butoxycarbonyl]aminomethyl]-2-[1-(tert-butylidemethylsiloxyl)-2-propenoyl]-1-(methoxymethyl)indole (13). A solution of alcohol (0.21 g, 0.5 mmol), TBDMSI (0.25 g, 1.6 mmol), and imidazole (0.15 g, 2.1 mmol) in DMF (3 mL) was heated under Ar at 55% aqueous Na2CO3 and Et2O with 10% deuterium-deuterated hexanes–AcOEt to give ketone (0.15 g, 2.1 mmol) in DMF (3 mL) was heated under Ar at 55% aqueous Na2CO3 and Et2O with 10% deuterium-deuterated hexanes–AcOEt to give ketone (0.15 g, 2.1 mmol) in DMF (3 mL) was heated under Ar at 55% aqueous Na2CO3 and Et2O with 10% deuterium-deuterated hexanes–AcOEt to give ketone.

13C NMR δ 4.6 (2CH3), 18.4 (C), 26.0 (CH3), 28.7 and 28.8 (3CH3), 41.2 and 41.6 (C-1), 43.9 and 44.3 (C-3), 55.9 (OCH3), 66.4 and 66.5 (C-6), 75.2 and 75.4 (CH2O), 79.8 and 80.2 (C), 109.5 and 109.6 (C), 110.2 and 110.3 (C-8), 118.4 and 118.5 (C-11), 120.3 and 120.4 (C-10), 122.3 and 122.4 (C-9), 126.1 and 126.5 (C-5), 127.8 and 127.9 (C), 136.1 and 136.3 (C-4), 136.9 (C), 137.3 (C), 155.3 and 155.4 (CO); HRMS calcd for C26H39N2O4Si 543.2757, found 543.2750.

4.1.14. 2-(t-Butylthio)carboxyl-6-(t-tert-butylidemethylsilyloxy)-7-(methoxymethyl)-1,2,3,6-tetrahydroazocino[4,3-b]indole (17). Compound 15 (63 mg, 0.13 mmol) dissolved in MeOH (6 mL) was hydrogenated over Pd/C (5%, 0.35 mg) for 12 h. The catalyst was filtered, the filtrate was concentrated and the resulting residue was purified by flash chromatography (8:2 hexanes–AcOEt) to give azocinoindole 17: 25 mg (64%); 1H NMR δ 1.57 (s, 9H), 3.19 (s, 3H), 3.55 (br s, 2H); 13C NMR δ 28.7 (3CH3), 40.0 (CH), 47.5 (CH2), 56.3 (CH3), 75.4 (CH2), 80.0 (C), 111.1 (CH), 116.6 (CH2), 119.4 (C), 121.8 (CH), 122.2 (CH), 126.2 (CH2), 127.3 (C), 131.2 (CH3), 133.8 (CH), 135.2 (C), 137.3 (CH), 138.9 (C), 155.8 (CO), 187.7 (CO); HRMS calcd for C26H39N2O4Si 543.2757, found 543.2753.

4.1.15. 2-(t-Butylthio)carboxyl-6-oxo-1,2,3,4,5,6-hexahydroazocino[4,3-b]indole (16). (Im-PCy3)(Cl)2Ru=CPh (second-generation Grubbs catalyst, 10 mol %) was added under Ar to a solution of ketone (25 mg, 0.065 mmol) in CH2Cl2 (2 mL) and the resulting mixture was stirred at rt overnight. The reaction mixture was filtered, the filtrate was concentrated and the resulting residue was purified by flash chromatography (8:2 hexanes–AcOEt) to give 16: 20 mg (86%); 1H NMR (400 MHz) δ 1.48 (br s, 9H), 3.27 (s, 3H), 3.91 (br s, 2H), 4.83 (s, 2H), 5.99 (s, 2H), 6.44 (m, 1H), 6.63 (d, J = 11.7 Hz, 1H), 7.26 (m, 1H), 7.43 (m, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.90 (m, 1H); 13C NMR (100.6 MHz) δ 28.8 (3CH2), 37.2 (CH3), 39.6 (CH3), 56.3 (CH2), 75.4 (CH2), 81.1 (C), 111.6 (CH), 121.4 (CH, C), 122.0 (CH), 126.5 (C), 127.6 (CH), 133.7 (C), 135.7 (CH), 138.4 (C), 139.9 (CH), 154.6 (CO), 184.2 (CO). Anal. Calcd for C26H39N2O4Si: C, 65.74%; H, 6.90%; N, 7.67%. Found: C, 65.85%; H, 6.66%; N, 7.65%.

4.1.16. 2-(t-Butylthio)carboxyl-6-(t-tert-butylidemethylsilyloxy)-7-(methoxymethyl)-1,2,3,4,5,6-hexahydroazocino[4,3-b]indole (18). Operating as above, from 16 (0.28 g, 0.78 mmol) azocinoindole 18 was obtained after flash chromatography (6:4 hexanes–AcOEt): 0.23 g (82%); 1H NMR (1:1 mixture of rotamers) 1.19 and 1.45 (2s, 9H), 2.10 (br, 2H), 2.95 (br, 2H), 3.21 (3s, 3H), 3.55 and 3.65 (2m, 2H), 4.80 and 4.90 (2br s, 2H), 5.73 (br, 2H), 7.20 (t, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.50 (br d, J = 8.0 Hz, 1H), 7.70 (m, 1H); 13C NMR (1:1 mixture of rotamers) 25.3 and 25.6 (CH2),
28.2 and 28.3 (3CH₃), 41.7 and 41.9 (CH₂), 43.4 and 44.1 (CH₂), 46.1 and 47.9 (CH₂), 55.8 (CH₃), 74.7 (CH₂), 80.0 (C), 110.7 and 110.9 (CH), 120.2 and 120.5 (CH), 121.3 and 121.4 (CH), 122.3 (C), 125.8 and 126.0 (CH, C), 132.5 (C), 137.8 (C), 155.4 (CO), 197.6 and 198.2 (CO); and 121.4 (CH), 122.3 (C), 125.8 and 126.0 (CH, C), 110.7 and 110.9 (CH), 120.2 and 120.5 (CH), 121.3

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References and notes


