Solid-Supported Heterocumulenes: Preparation and Crystal Structure of Azaaplysinopsins

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Annulation of carbodiimides **6a**,**b**, on alumina solid support, selectively gives (*Z*)-hydantoins **8a**,**b** determined on the basis of X-ray analysis while thermal cyclization affords, after purification, **8a**,**b** with imidazolones **10a**,**b**. In the imidazopyrimidine series, thermal reaction of heterocumulenes **6d** yields, via a Dimroth rearrangement, the dipyridoimidazolic compound **11**. In all cases, mechanisms for the observed cyclizations have been proposed.

Introduction

Aplysinopsin (**1**) (Figure 1), isolated from the sponge *Aplysinopsis reticulata* (Dictyoceartida),[2] has been shown to be active as a specific cytotoxin of cancer cells[3] and to affect neurotransmission.[4] The classical approach to the synthesis of C-5 unsaturated hydantoins such as **2** is based on the coupling of an aromatic aldehyde and an appropriately substituted hydantoin. However, poor yields, purification difficulties, and the formation of mixtures of *E* and *Z* isomers are generally encountered.[5] Such inconveniences have been circumvented by the development of a tandem Staudinger/aza-Wittig reaction followed by electrocyclic ring closure.[6] Such methodology allows the formation of nitrogenated heterocycles from heterocumulenes which in turn are easily available from iminophosphoranes. Using this route, an elegant synthesis of several aplysinopsin-type alkaloids has been accomplished by Molina and co-workers.[7]

In the course of our studies on the reactivity of nitrogen bridgehead azaindolizines, and in view of the pharmacological[8] and theoretical[9] interest of azaindole structures, we embarked on the development of a model

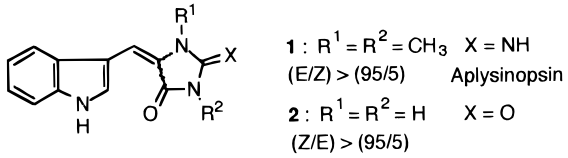

Figure 1.

system of imidazo[1,2-*a*](di)azines which may increase greatly the pharmacological profile.[10] We reported recently a highly effective method for the synthesis of azacarboline and -aplysinopsin mimic structures from heterocumulenes.[11] We describe now the synthesis of hydantoins **8**, potential selective competitive NMDA antagonists,[12] *via* stereospecific ring-opening/ring-closure of an azalactone obtained from an alumina-supported heterocumulene.

Results and Discussion

The 3-formyl derivative **3a**[9] was condensed with ethyl azidoacetate in the presence of sodium ethoxide at −30 °C to give azidovinyl **4a** (ν_{azido} 2050 cm^{-1}) in 78% yield. Measurement of the long-range $^{13}C-^{1}H$ coupling constant between the olefinic proton and the carbonyl carbon in the coupled ^{13}C NMR spectra proved to be diagnostic of a (*Z*) arrangement.[13] The preparation of iminophosphorane **5a** was accomplished by Staudinger's reaction of **4a** with triphenylphosphine in dichloromethane at room temperature in 81% yield (Scheme 1). Spectral and analytical data were consistent with the identity of compound **5a** and the (*Z*) configuration assignment ($^{3}J_{H-C\beta,CO}$ = 3.5 Hz).

An aza-Wittig type reaction of iminophosphorane **5a** with aliphatic or aromatic isocyanates in dry toluene at

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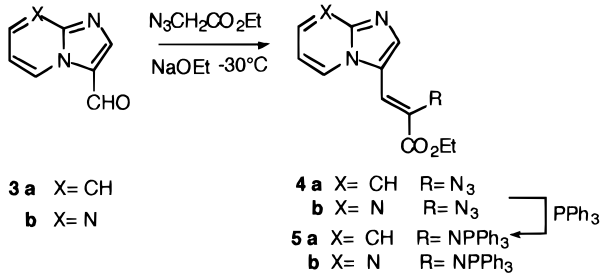
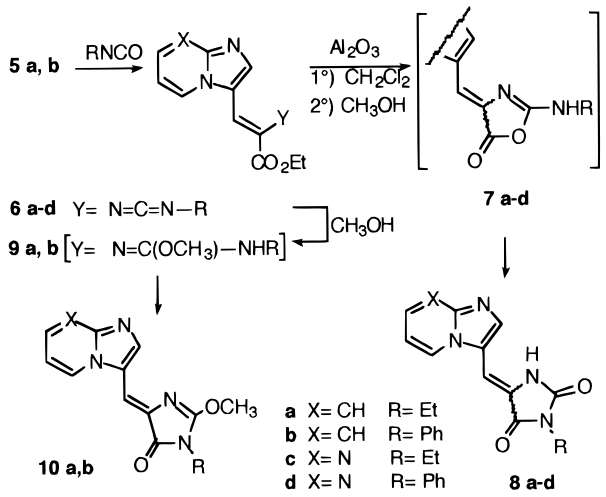
Scheme 1



Scheme 2



room temperature for 5−19 h gave the corresponding carbodiimides **6a**,**b**, isolated as yellow plates. Since, according to their usual behavior, indole carbodiimides are expected to give the corresponding fused pyridine or hydantoin annulation, our attention was turned to the reactivity of **6a**,**b**. Surprisingly, when carbodiimides **6a**,**b** were heated at 110 °C, and even when conditions were forced (160 °C, *o*-$Cl_2C_6H_4$), no evidence of the annulation was observed. However, when a toluene solution of **6a** or **6b** was heated at 110 °C for 3 h and the crude reaction product was chromatographed on alumina (CH_2Cl_2−MeOH, 98:2), azaaplysinopsins **8** were obtained together with compounds **10** (**8a**:**10a** = 98/2; **8b**:**10b** = 83/17). Heterocumulenes **6a**,**b** were then refluxed in methanol and yielded the corresponding imidazolones **10a**,**b**. The structural assignment of compounds **10a**,**b** was proved by the presence of a methoxy group signal in their ^{13}C NMR spectra. In contrast, when an alumina solid support was impregnated with methylene chloride solutions of heterocumulenes **6a**,**b**, followed by elution with methanol, a rapid, stereospecific, and quantitative formation of (*Z*)-hydantoins **8a**,**b** was obtained (Scheme 2). No reaction occurred when we performed the same experiment on silica gel, probably due to its acidic character. These experiments demonstrated that two different mechanisms lead to compounds **8** and **10**. In the first case, heterocumulenes **6a**,**b** undergo a ring closure across the ester functionality, followed by a spontaneous Dimroth lactone−lactam rearrangement to give hydantoins **8a**,**b**. In the second case, the former heterocumulenes would first be transformed into 2-methylisoureas **9a**,**b** which would lactamize to give imidazolones **10a**,**b**.

Interestingly, we noted a photoisomerization of **8a** in solution. Irradiation for 4 h at rt with 365 nm light of a solution of neat (*Z*)-**8a** in $(CD_3)_2SO$ was found to afford a mixture appreciably richer in the (*E*)-**8a** isomer (*E*/*Z* > 75/25). The structural constitutions of **8a**,**b** were inferred

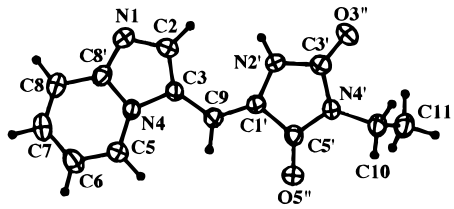


Figure 2. ORTEP drawing of **8a**; the sizes of H atoms have been reduced for clarity. Selected bond lengths (Å) and torsion angles (deg) are as follows: N4−C8a, 1.390(3); C9−C1, 1.335(3); C1′−N2′, 1.387(3); C1′−C5′, 1.478(4); N4′−C5′, 1.363(2); C3−N4−C8a−N1, 0.1(3); N4−C3−C9−C1′, −176.4(3); C3′−N4′−C5′−C1′, 1.1(3).

from the ^1H and ^{13}C NMR spectral data and confirmed by the MS analysis (Experimental Section). The structure and the (*Z*) configuration of **8a** were confirmed by its crystallographic data.[14] A projection of the molecule obtained with the ORTEP program[15] is given in Figure 2. The angle between the plane of the imidazopyridine ring and the hydantoin group was 2.2°, which proves the near planarity of the molecule. Bond distances and angles and torsion angles were mostly those expected from the hybridization of the atoms. The other angles and bond distances were similar to those of other methylene hydantoins recently reported.[16] The bond lengths measured in the imidazopyridine system were consistent with those of other compounds in the same series.[17]

Subsequent to the demonstration of the viability of the intramolecular annulation described above, and in order to further explore the synthetic potential of the alumina-supported reaction, we pursued its application to the imidazopyrimidine ring system. Thus, alumina-supported reaction of iminophosphorane **5b** with isocyanates yielded imidazolidindiones **8c**,**d** in 49 and 45% yields, respectively. The presence of an imidazolidindione functionality at the imidazopyrimidine C-3 position was based on the ^1H and ^{13}C NMR chemical shifts. This methodology avoids the Dimroth rearrangement and the consequent pyridinization which generally occurs in these heterocyclic structures.[11] The latter reaction is exemplified by the formation of **11** due to thermal reaction of **5b** with C_6H_5NCO (Scheme 3).

In conclusion,we have described an alternative methodology for obtaining the annulation of hydantoins, based on an alumina-supported reaction of heterocumulenes. A mechanistic explanation is given. The methodology proves to be general for the preparation of azaaplysinopsins and has been applied here to the synthesis of structures **8a**−**d**.

(14) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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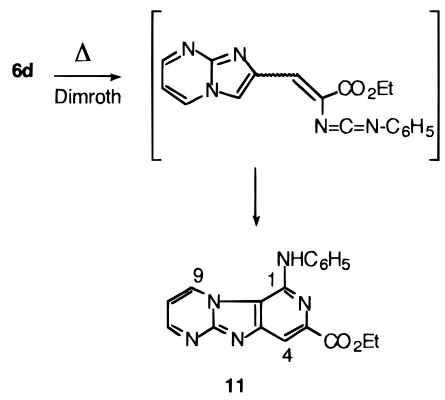
Scheme 3



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Experimental Section[18]

Preparation of Ethyl α-Azido-*β*-(imidazo[1,2-*a*]pyridin-3-yl)propenoate (4a). Ethyl azidoacetate (10.38 g, 80 mmol) was added dropwise at −30 °C to a stirred solution containing sodium (0.8 g, 35 mmol) in dry ethanol (25 mL). To this solution was added dropwise a mixture of aldehyde (8 mmol) in dry ethanol (10 mL). The reaction mixture was returned to rt and stirred for 3 h. The solution was poured into aqueous saturated NH_4Cl solution (100 mL) and then extracted with ether. The organic layers were dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The crude product was chromatographed on an alumina column eluting with CH_2Cl_2 to give **4a** (78%): mp 98−100 °C; IR (KBr) 2050, 1680, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3H, J = 7 Hz), 4.31 (q, 2H, J = 7 Hz), 6.87 (t, 1H, J = 7 Hz), 6.96 (s, 1H), 7.21 (ps t, 1H), 7.57 (d, 1H, J = 9 Hz), 8.11 (d, 1H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 62.1, 108.5, 113.4, 118.0, 119.7, 122.3, 123.1, 125.9, 138.7, 146.4, 162.8. Anal. Calcd for $C_{12}H_{11}N_5O_2$: C, 56.03; H, 4.28; N, 27.24. Found: C, 56.19; H, 4.29; N, 27.21.

Ethyl α-[(Triphenylphosphoranylidene)amino]-*β*-(imidazo[1,2-a]pyridin-3-yl)propenoate (5a). To a solution of vinylazide (6 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise, at 0 °C, a solution of triphenylphosphine (1.57 g, 6 mmol) in the same solvent (20 mL). The reaction mixture was stirred at rt for 12 h, and the solvent was removed *in vacuo*. The crude product was purified by chromatography on alumina column, eluting with CH_2Cl_2 to give the iminophosphorane **5a** (81%): mp 164−166 °C; IR (KBr) 1690, 1580, 1425, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (t, 3H, J = 7 Hz), 3.88 (q, 2H, J = 7 Hz), 6.83 (t, 1H, J = 7 Hz), 6.96 (d, 1H, $^4J_{H-P}$ = 7 Hz), 7.15 (ps t, 1H), 7.47 (m, 9H), 7.61 (d, 1H, J = 9 Hz), 7.74 (m, 6H), 8.20 (d, 1H, J = 7 Hz), 8.59 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 60.8, 101.9 (d, $^3J_{P-C}$ = 21 Hz), 111.9, 117.8, 123.5, 123.7, 124.1, 128.3 (d, $^3J_{P-C}$ = 12 Hz, 3C), 131.1, 132.3 (d, $^2J_{P-C}$ = 10 Hz, 6C), 132.6 (d, $^1J_{P-C}$ = 103 Hz, 3C), 135.34(d, $^2J_{P-C}$ = 6 Hz), 135.6, 144.9, 166.8 (d, $^3J_{P-C}$ = 7 Hz); *m/z* (%): 491 (M^+, 42), 156 (100). Anal. Calcd for $C_{30}H_{26}N_3O_2P$: C, 73.32; H, 5.30; N, 8.55. Found: C, 73.35; H, 5.28; N, 8.58.

Preparation of Carbodiimide 6b. To a solution of iminophosphorane (0.81 mmol) in dry toluene (50 mL) was added dropwise at 0 °C phenyl isocyanate (1.68 mmol). The solution was stirred at 0 °C for 30 min and then at rt for 5 h. The solvent was removed off under reduced pressure, and the crude product was washed with hexane to remove phosphine oxide and give **6b** (56%): mp: 164−166 °C; IR (KBr) 2130, 1690, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (t, 3H, J = 7 Hz), 4.41 (q, 2H, J = 7 Hz), 6.96 (t, 1H, J = 7 Hz), 7.16 (m, 1H), 7.30 (m, 6H), 7.67 (d, 1H, J = 9 Hz), 8.22 (d, 1H), 8.65 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.3, 62.3, 112.1, 113.5, 118.3, 120.5, 122.6, 123.3, 124.4 (2C), 125.4, 126.0, 129.4 (2C), 135.1, 138.0, 139.1, 146.7, 164.0; *m/z* (%): 332 (M^+, 34), 156 (100), 78 (50). Anal. Calcd for $C_{19}H_{16}N_4O_2$: C, 68.67; H, 4.82; N, 16.87. Found: C, 68.83; H, 4.81; N, 16.88.

General Procedure for the Preparation of Imidazolidine-2,4-dione 8a. The carbodiimide was poured onto an alumina column. Elution with CH_2Cl_2 then with CH_2Cl_2/methanol (80/20) afforded compound (*Z*)-5-[(imidazo[1,2-*a*]-pyridin-3-yl)methylidene]-3-ethyl-1*H*-imidazolidine-2,4-dione (**8a**) as yellow prisms (65%): mp > 260 °C; IR (KBr) 3120, 1730, 1670, 1640 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.15 (t, 3H, J = 7 Hz), 3.52 (q, 2H, J = 7 Hz), 6.99 (s, 1H), 7.08 (t, 1H, J = 7 Hz), 7.42 (ps t, 1H), 7.68 (d, 1H, J = 9 Hz), 8.37 (s, 1H), 8.87 (d, 1H, J = 7 Hz), 10.55 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 13.4, 32.9, 94.9, 113.3, 117.2, 119.2, 124.0, 125.2, 126.2, 135.9, 145.9, 154.5, 163.3; *m/z* (%): 256 (M^+, 100), 157 (87); UV (MeOH): 353, 272, 224, 203 nm. Anal. Calcd for $C_{13}H_{12}N_4O_2$: C, 60.94; H, 4.69; N, 21.87. Found: C, 61.05; H, 4.65; N, 21.92.

(*E*)-5-[(Imidazo[1,2-*a*]pyridin-3-yl)methylidene]-3-ethyl-1*H*-imidazolidine-2,4-dione (8a). Irradiations under UV (λ = 365 nm) of (*Z*)-**8a** (40 mg, 0.15 mmol) in $(CD_3)_2SO$ were carried out in a 5 mm NMR tube for 4 h, monitoring the transformations by ^1H and ^{13}C NMR. Clean (*Z*)-**8a** → (*E*)-**8a** isomerization was observed, without byproducts. The ratio of the mixture was (*E*)/(*Z*) > 75/25; (*E*)isomer ^1H NMR (DMSO-d_6) δ 1.15 (t, 3H, J = 7 Hz), 3.52 (q, 2H, J = 7 Hz), 6.71 (s, 1H), 7.05 (ps t, J = 6 Hz, 1H), 7.37 (ps t, 1H), 7.65 (d, 1H, J = 9 Hz), 8.50 (d, 1H, J = 7 Hz), 8.75 (s, 1H), 10.50 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 13.3, 32.7, 99.5, 113.29, 117.3, 119.2, 124.0, 125.2, 126.2, 137.4, 145.8, 152.8, 161.7; *m/z* (%): 256 (M^+, 100), 157 (87).

5-(Imidazo[1,2-*a*]pyridin-3-yl]methylidene)-3-ethyl-2-methoxyimidazolin-4-one (10a). A solution of **6a** (0.46 mmol) in methanol (40 mL) was heated at reflux for 4 h. After cooling, the solvent was removed off under reduced pressure, and the residue was chromatographed on an alumina column with CH_2Cl_2 as eluent to give the imidazoline **10a** as yellow prisms (27%); mp 180−182 °C; IR (KBr) 1700, 1640, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, 3H, J = 7 Hz), 3.61 (q, 2H, J = 7 Hz), 4.20 (s, 3H), 6.95 (t, 1H, J = 7 Hz), 7.11 (s, 1H), 7.28 (ps t, 1H), 7.69 (d, 1H, J = 9 Hz), 8.42 (d, 1H), 8.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 7.8, 30.2, 54.4, 108.5, 117.2, 122.3, 126.0, 128.7, 130.9, 141.3, 146.2, 153.7, 17O.8, 177.3; *m/z* (%): 270 (M^+, 57), 156 (100), 58 (83). Anal. Calcd for $C_{14}H_{14}N_4O_2$: C, 62.22; H, 5.19; N, 20.74. Found: C, 61.98; H, 5.20; N, 20.79.

A solution of carbodiimide **6a** or **6b** in toluene was heated at 110 °C for 3 h. After cooling, the residue was chromatographed on an alumina column, eluting with CH_2Cl_2−MeOH (98:2) to give the imidazolines **10a**,**b** and then the hydantoins **8a**,**b**. The ratios were **8a**/**10a**: 98/2 and **8b**/**10b**: 83/17.

Thermal Reaction of Iminophosphorane 5b with Phenyl Isocyanate. To a solution of iminophosphorane **5b** (2 mmol) in 25 mL of 1,2,4-trichlorobenzene was added phenyl isocyanate (2.2 mmol). The reaction mixture was stirred at room temperature for 3 h and then at 160 °C for 8 h. After cooling, the solution was washed with cold ethanol to remove phosphine oxide, and the resulting mixture was chromatographed on an alumina column eluting with CH_2Cl_2 to yield product **11** as yellow prisms (0.49 g, 72%): mp > 260 °C; IR (KBr) 3400, 1730, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (t, 3H, J = 7 Hz), 4.51 (q, 2H, J = 7 Hz), 7.11 (m, 2H), 7.42 (t, 2H), 8.07 (s, 1H), 8.12 (d, 2H), 8.21 (s, 1H), 8.78 (dd, 1H, J = 7 Hz, J = 2 Hz), 8.91 (dd, 1H, J = 4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.4, 61.7, 100.9, 108.8, 118.5, 122.4, 129.1, 130.1, 131.4, 133.8, 138.6, 140.0, 147.7, 150.6, 156.4, 165.9; *m/z* (%): 333 (M^+, 94), 260 (78), 79 (100). Anal. Calcd for $C_{18}H_{15}N_5O_2$: C, 64.86; H, 4.50; N, 21.02. Found: C, 65.05; H, 4.49; N, 21.04.

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Supporting Information Available: Experimental data for **4b**, **5b**, **6a**,**d**, **8b**−**d**, and **10b**, and crystal data for **8a** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(18) For general experimental details, consult ref 11.

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