Reactions of (Vinylimino)phosphoranes and Related Compounds: Access to the Azacarbolines and -aplysinopsines

Olivier Chavignon,[1a] Jean C. Teulade,*[1a] Danielle Roche,[1a] Michel Madesclaire,[1a] Yves Blache,[1b] Alain Gueiffier,[1b] Jean L. Chabard,[1a] and Gérard Dauphin[1c]

Département d'Analyse Structurale et de Pharmacologie, Faculté de Pharmacie, Université d'Auvergne, 63001-Clermont-Ferrand France, Université de Montpellier 1, URA CNRS 1111 34000 Montpellier, France, and Laboratoire de Chimie Organique Biologique, URA CNRS 485 Université B. Pascal 63170-Aubière, France

Received March 29, 1994®

Aza-Wittig-type reactions of iminophosphoranes **3a**, **14a,b** and **19**, derived from azidovinyl (or -phenyl) derivatives and triphenylphosphine, with methyl or phenyl isocyanates were used to construct the framework of the azacarboline structures **7a,b-10**, **20**, **21a–d** and aplysinopsine-type alkaloids **17a–d** by electrocyclic ring closure or heterocumulene-mediated annelation.

Imidazo[1,2-*a*](di)azine derivatives are an interesting class of heterocyclic compounds both pharmacologically and theoretically. The imidazo[1,2-*a*]pyrimidine (or pyridine) skeleton is a basic structure of natural alkaloids such as alchorneine.[2] Synthetic drugs such as Zolpiden[3] have human clinical applications and several of them have been marketed. Interestingly, the imidazodiazine structure was recently found in the Y base as a component of $tRNA^{Phe}$,[4] and new acyclovir analogs possessing this ring system exhibited an antiherpetic activity on HIV-1,2.[5] Also, these heterocyclic structures are building blocks for the preparation of polycyclic compounds.[6] Accordingly, nitro- (or azido-) phenylimidazo[1,2-*a*]pyridines have been investigated as archetypal compounds with an attractive site for attack by the nitrene species to yield the indole structure.[7] Following on from our previous studies on the reactivity of imidazoazines, our work has focused on synthetic approaches to azacarbolines and azaaplysinopsin-mimic structures since it has been demonstrated that the nitrogen atom can enhance or otherwise modify pharmacological activity.[8] Interestingly, recent synthetically attractive methods such as thermal treatment of azidoacrylates[9] or arylvinyl carbodiimides[10] have been successfully used in the synthesis of pharmacologically important indoles (e.g. antineoplasic agents)[11] and β-carbolines (as putative endogenous ligands via benzodiazepine receptors).[12] In the course of extensive studies on the reactivity of heterocycles with a bridgehead nitrogen atom, we prepared novel 2- and 3-(phosphoranylidenamino)imidazo[1,2-*a*]pyridines (or pyrimidines) and 2-[(2′-phosphoranylideneamino)phenyl]-imidazo[1,2-*a*]pyridine by the aza-Wittig type reaction with isocyanates. Imidazo[1,2-*a*]azine and diazines were expected to undergo regioselective electrophilic attack at the presumably more reactive unsubstituted imidazole 3-position,[13] and electrocyclic ring closure of the heterocumulene, insertion into the C-5, aryl C–H bond, or ester function, or electrophilic attacks at the N-1 nitrogen lone pair of the imidazolic moiety were also possible. We report the results of this work and discuss their mechanistic implications.

Results and Discussion

The required α-azidovinyl **2a** was prepared conventionally by condensation of **1a**[6] with ethyl azidoacetate in the presence of sodium ethoxide at −30 °C. The

* Present address: Département d'Analyse Structurale et de Pharmacologie, Université d'Auvergne, Faculté de Pharmacie, 28 Place H. Dunant, BP 38, 63001 Clermont-Ferrand Cedex, France.

® Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) (a) Clermont-Ferrand. (b) Montpellier. (c) Aubière.

(2) Büchi, G.; Rodriguez, A.; Yakushijin, K. *J Org. Chem.* **1989**, *54*, 4497.

(3) Arbilla, S.; Allen, J.; Wick, A.; Langer, S. *Eur. J. Pharmacol.* **1986**, *130*, 257.

(4) (a) Nakanishi, K.; Furutani, N.; Funamisu, M.; Grunberger, D.; Weinstein, J. B. *J. Am. Chem. Soc.* **1970**, *92*, 7617. (b) Takeda, K.; Shudo, K.; Okamoto, T.; Kosuge, T. *Chem. Pharm. Bull.* **1982**, *104*, 7637. (c) N'Goy, K.; De Meester, C.; Pairon, D.; Fabry, L.; Loukakou, B.; N'Zouzi, C.; Saint-Ruf, G.; Mercier, M.; Poncelet, F. *Mutat. Res.* **1984**, *23*, 136. (d) Lee, C. S.; Hashimoto, Y.; Shudo, K.; Nagao, M. *Heterocycles* **1984**, *22*, 2249.

(5) Boryski, J.; Golankiewics, B.; De Clercq, E. *J .Med. Chem.* **1988**, *31*, 1351.

(6) (a) Gueiffier, A.; Milhavet, J. C.; Blache, Y.; Chavignon, O.; Teulade, J. C.; Madesclaire, M.; Viols, H.; Dauphin, G.; Chapat, J. P. *Chem. Pharm. Bull.* **1990**, *38*, 2352. (b) Chavignon, O.; Teulade, J. C.; Chapat, J. P.; Dauphin G.; Gueiffier, A. *J. Heterocycl. Chem.* **1992**, *29*, 691.

(7) Teulade, J. C.; Gueiffier, A.; Viols, H.; Chapat, J. P.; Grassy, G.; Perly, B.; Dauphin, G. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1895.

(8) (a) Chermann, J. C.; Gruest, J.; Montagnier, L.; Wendling, F.; Tambourin, P.; Perrin, M.; Pochon, F.; Ducrocq, C.; Rivalle, C.; Bisagni, E. *C. R. Acad. Sci. Paris C.R.* **1977**, *285* Ser. D, 945. (b) Marsais, F.; Pineau, P.; Nivolliers, F.; Mallet, M.; Godard, A.; Quequiner, G. *J. Org. Chem.* **1992**, *57*, 565.

(9) (a) Moody, C. J.; Ward, J. G. *J. Chem. Soc., Perkin Trans 1* **1984**, 2903; (b) Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1333. (c) Hickey, D.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1119.

(10) (a) Molina, P.; Alajarin, M.; Ferao, A.; Perez de Vega, P. *J. Chem. Soc., Perkin Trans.1* **1987**, 2667. (b) Molina P.; Alajarin, M.; Ferao, A.; Lorenzo, A.; Vilaplana, M.; Aller, E.; Planes, J. *Heterocycles* **1988**, *27*, 161. (c) Molina, P.; Fresneda, P. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1819. (d) Molina, P.; Arques, A.; Fresneda, P.; Vinader, M.; Foces, M.; Cano, F. *Chem. Ber.* **1989**, *122*, 307. (e) Molina, P.; Alajarin, M.; Vidal, A. *Tetrahedron* **1990**, *46*, 1063. (f) Molina, P.; Tarraga, A.; Lidon, J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1727. (g) Molina, P.; Alajarin, M.; Vidal, A. *J. Org. Chem.* **1990**, *55*, 6140. (h) Molina, P.; Aller, E.; Lorenzo, A. *Tetrahedron* **1991**, *47*, 6737. (i) Rzepa, H.; Molina, P.; Alarajin, M.; Vidal, A. *Tetrahedron* **1992**, *48*, 7425. (j) Molina, P.; Alajarin, M.; Vidal, A. *J. Org. Chem.* **1992**, *57*, 6703. See also (k) Gololobov, Y.; Kazukin, L. *Tetrahedron* **1992**, *48*, 1353.

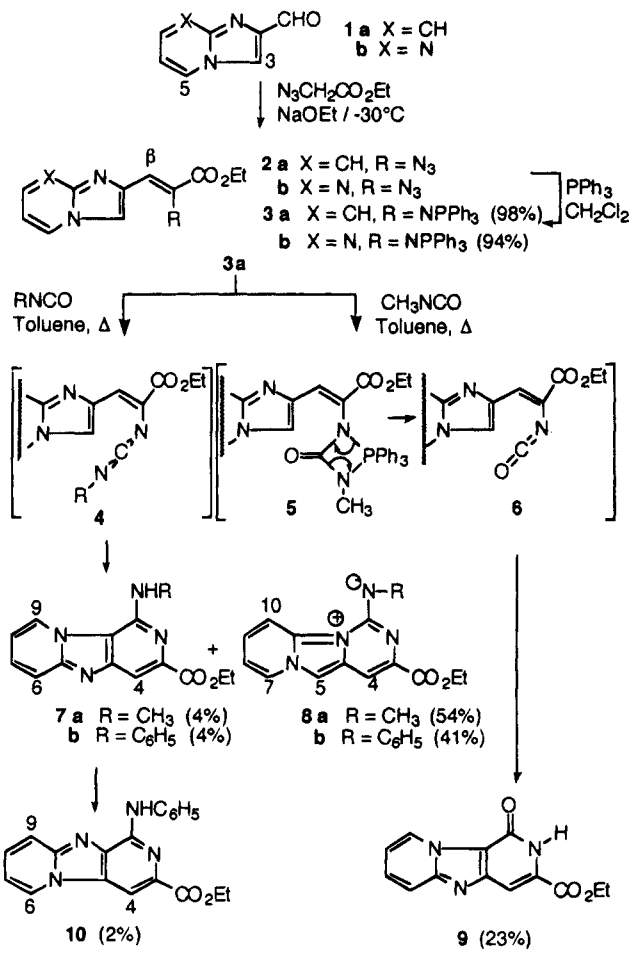
(11) Hollenbeak, K. H.; Schmitz, F. J. *Lloydia* **1977**, *40*, 479.

(12) (a) Baker, J.; Wells, R. *Natural Products as Medicinal Agents;* Beal, J., Reinhardt, K., Eds.; Hippokrates Verlag: Stuttgart, 1981, p 299. (b) Fattorusso, E.; Lanzotti, V.; Magno, S.; Novellino, E. *J. Nat. Prod.* **1985**, *48*, 924.

(13) (a) Paudler, W. W.; Blewitt, H. L. *J. Org. Chem.* **1965**, *30*, 4081. (b) Paolini, J. P.; Robins, R. K. *J. Org. Chem.* **1965**, *30*, 4085. (c) Hand, E. S.; Paudler, W. W. *J. Org. Chem.* **1975**, *40*, 2916. (d) Teulade, J. C.; Escale, R.; Rossi, J. C.; Chapat, J. P.; Grassy, G.; Payard, M. *Aust. J. Chem.* **1982**, *35*, 1761. (e) Grassy, G.; Rival, Y.; Bonnafous, M.; Adam, Y.; Teulade, J. C.; Chapat, J. P. *Eur. J. Med. Chem.* **1985**, *20*, 501.

0022-3263/94/1959-6413$04.50/0

Scheme 1



stereochemistry about the double bond is not known, but is assumed to be the more thermodynamically stable *Z*.[14] Iminophosphorane **3a** was prepared by Staudinger's reaction of **2a** with triphenylphosphine in dry dichloromethane at room temperature in 98% yield as in Scheme 1. The ^{13}C NMR spectra included a carbonyl carbon atom at δ 167.04 ($^3J_{PC}$ = 6 Hz), a quaternary carbon atom C-α at δ 137.24 ($^2J_{PC}$ = 7 Hz), and the C-β at δ 111.97 ($^3J_{PC}$ = 21 Hz). The pyridine annelation was achieved by the reaction of iminophosphorane **3a** with methyl and phenyl isocyanate in refluxing toluene. In this cyclization reaction, in the presence of excess isocyanate, the carbodiimide was formed only as a transient intermediate and could not be isolated as it spontaneously cyclized to give the desired pyridine derivatives **7a,b** and the pyrimidine **8a,b**. Two aza-Wittig reactions of the iminophosphorane **3a** with methyl isocyanate directly gave the corresponding azacarbolines **7a**, **9** and the zwitterionic pyrimidine structure **8a** in 4 , 23, and 54% yield, respectively. The structure of **7a** was assigned from spectroscopic data. Its infrared spectrum showed a carbonyl absorption at 1720 cm^{-1}, indicating an ester. The ^1H NMR spectrum indicated a NCH_3 group (δ 3.28), four pyridine protons, and a characteristic singlet proton H-4. These data, together with the mass spectrum, which showed a molecular ion at *m*/*z* 270 (80%), and ^{13}C NMR spectral analysis with five methine signals established the structure for **7a**. Compound **9** was identified by mass spectrometry (*m*/*z* 257, 100%) and ^1H and ^{13}C NMR. The ^1H NMR spectra included a pyridine proton shifted far downfield to δ 9.37, strongly suggesting a location in the deshielding region of the carbonyl group (peri effect).[6] ^{13}C NMR spectral data are also consistent with structure **9**. Weak peaks at δ 161.67 (CO), 154.85 (C-1), and 118.34 (C-10a) supported this triazabenzofluorene structure. We suggest a mechanism to explain the formation of lactam **9** involving a sequence of formation of the intermediates **5** and **6**, which through ring closure leads to cycloadducts. These transient species are usually unstable[15] and undergo elimination of RN = PPh_3, giving the corresponding heterocyclic isocyanates, which through ring closure of **6** yield crystalline **9** as in Scheme 1. Spectral (MS, ^1H and ^{13}C NMR) properties of **8a** were consistent with the proposed structure. In particular, **8a** (*m*/*z* 270, 65%) exhibited diagnostic singlets at δ 6.76 and 7.68 for H-4 and H-5 and a characteristic downfield shift δ 9.65 of H-10. The ^{13}C NMR assignments obtained from JMPC, quantitative experiments, and 2D LR confirmed the zwitterionic structure. The reactivity of the iminophosphorane **3a** with phenyl isocyanate parallels that of methyl isocyanate. The crude reaction mixture of **3a** with phenyl isocyanate in refluxing toluene gave, after chromatographic purification over neutral alumina, **7b**, **8b**, and **10** in 4, 41, and 2% yields, respectively. The structures of **7b**, **10** were deduced from mass spectra (*m*/*z* 332) and ^1H, and ^{13}C NMR spectra. Thus **7b**, **10** exhibited 10 resonances corresponding to the expected hydrogen nuclei of the pyridine and phenyl and consistent with reported data. Formation of **10** is explained by Dimroth rearrangement of **7b**, already observed in the imidazo[1,2-*a*]pyridine series.[16] This is supported by the fact that the tricyclic structure **7b** was partially converted into structure **10** by thermal treatment at 180 °C for 2 h. Zwitterion **8b** was identified by ^1H and ^{13}C NMR spectra. Salient spectral features included a characteristic downfield shift δ 9.78 of H-10 and upfield shifts of C-4, C-5 at δ 89.79 and 102.93, respectively.

On the other hand, reaction of the vinyl azide **2b**[6b] with triphenylphosphine under the above standard conditions afforded the corresponding iminophosphorane **3b** in 94% yield. Unlike the pyridine series, treatment with methyl or phenyl isocyanate in hot toluene produced only intractable byproducts; other attempts (modification of the temperature between 50 and 160 °C, solvents: benzene, 1,3-dichlorobenzene, and reaction time) to produce the aza-Wittig compounds were unsuccessful.

In our ongoing work on the chemistry of 3-vinyl iminophosphoranes, we wished to study the reactivity of precursor azides **12a–c**. The coupling of ethyl azidoacetate with aldehydes **11a,b**[17] was difficult, but under homogeneous conditions using 10 equiv of ethyl azidoacetate with aldehydes in ethanol at −30 °C, coupling proceeded smoothly and was complete after 3 h to give **12a,b**. Precautions were taken to ensure that solutions containing the thermally unstable azido esters were kept below 5 °C. In addition, esters **13a,b** were obtained via

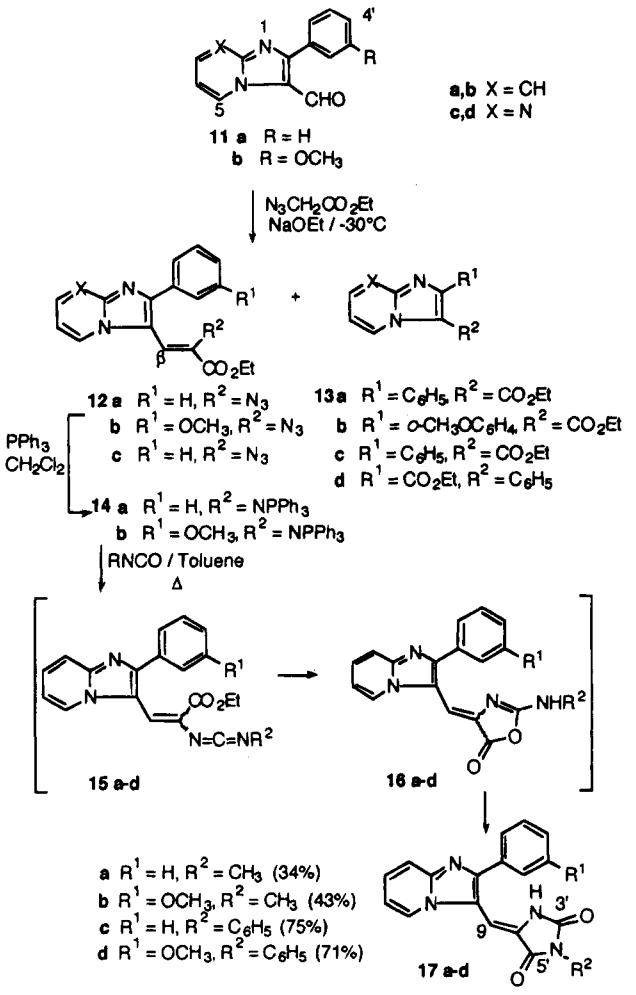
(14) Henn, L.; Hickey, D.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2189.

(15) (a) Richter, R.; Ulrich, H. *Chem. Ber.* **1970**, *103*, 3525. (b) Ulrich, H.; Tucker, B.; Saylgh, A. A. *Angew. Chem., Int. Ed. Engl.* **1968**, *8*, 938. (c) Abdel-Rahman, M. A. *Bull. Chem. Soc. Jpn* . **1993**, *66*, 510.

(16) Jacquier, R.; Lopez, H.; Maury, G. *J. Heterocycl. Chem.* **1973**, *10*, 755.

(17) (a) Sim, A.; Anasimova, V. A.; Avdyunina, N. I. *Otkrytiya, Izobret., Tavarnya Znaki* **1977**, *54*, 76. (b) Fujisawa Pharmaceutical Co., Japan Kokai Tokkyo Koho JP 86 56, 180 (Cl. CO70471/04). (c) Öhler, E.; Zbiral, E.; El-Badawi, M. *Tetrahedron Lett.* **1983**, *24*, 5599.

Scheme 2



a Tischenko reaction.[18] The azido esters were produced in good yields as yellow plates. The structures of **12a,b** deduced from their ^{1}H NMR spectra showed the following features: (a) a singlet at δ 7.13–7.26 corresponding to the vinyl proton H-β ; (b) in the ^{13}C NMR the C-β carbon appears at δ 117.28–119.59. Their IR spectra showed a ν_{azide} 2080–2110 cm^{-1}. Since azides **12a,b** were unstable, they were used in the next step without further purification. In the imidazopyrimidine series, a large quantity of **11c**[17] was prepared and subsequently reacted with ethyl azidoacetate. From **11c**, this reaction invariably produced the two isomers **13c,d** and the azide **12c** in a 2:1:5 ratio. In our hands compound **12c** proved extremely air- and light-sensitive, and decomposed at room temperature. The formation of isomers in this step and the instability of the azide made this pathway impractical. Accordingly, the pyrimidine system was abandoned.

We thus turned our attention to the azide **12a,b**. Iminophosphoranes **14a,b** were prepared by the same method as **3a,b**. Treatment of iminophosphoranes **14a,b** with methyl or phenyl isocyanate resulted in the loss of the ethoxy group to give compounds isolated in 34–75% yields. It seemed possible that **14a,b** might take two different reaction paths (Scheme 3): (A) formation of the skeleton of azalactones **16a–d** from intramolecular cyclization across the ester function of **15a–d**, or (B) iminophosphorane to **16a–d**, followed by a typical Dimroth rearrangement with ring-opening and ring-closure

(18) Tischenko, W. *J. Russ. Phys. Chem. Soc.* **1906**, *38*, 547.

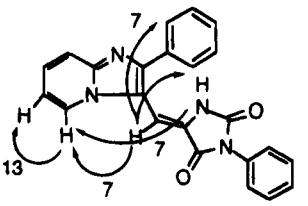


Figure 1.

to produce aplysinopsine-type structure[19] **17a–d**. Differentiation and subsequent transformation of the lactone or lactam group was thus our next task.

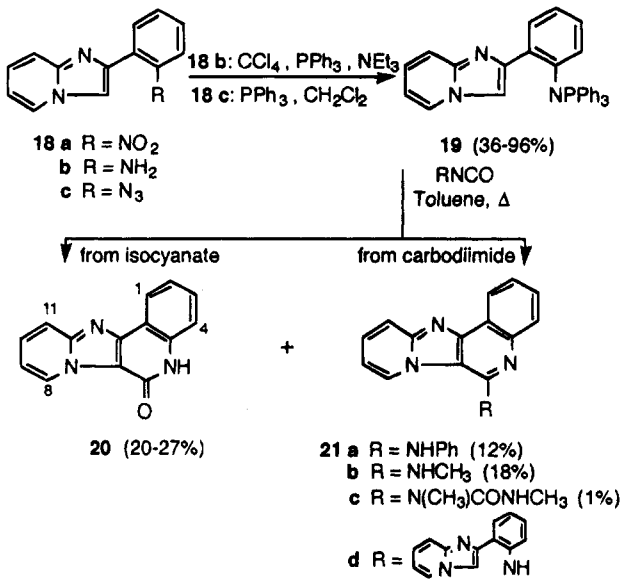
The IR spectra for these compounds afforded a characteristic C=O absorption at 1782–1745 cm^{-1}. ^{1}H NMR spectra are highly complicated in the aromatic region. However, they are moderately informative, showing characteristic δ values 6.72–6.90 and 8.03–8.28 for H-9 and H-5, respectively. The stereochemistry was secured by interpretation of NOE experiments (Figure 1). Particularly diagnostic were the observed NOE's between the vinylic proton H-9 and both *o*-phenyl protons (7%) and H-5 (7%), as well as the NOE's between the lactam NH group and H-5 (7%). These NOE differences supported the (*Z*) structure. The steric repulsions between phenyl group and HN(2′) force the five-menbered ring out the plane of the imidazopyridine nucleus. The ^{13}C NMR spectra afford the characteristic signals δ 95.67–96.34, 153.19–154.52, and 162.25–163.58, corresponding to the C-9, C=O(3′), and C=O(5′), respectively. Configuration (*Z*)-9 is conclusively assigned on the basis of small values of the H-C(9), C(5′) ^{1}H–^{13}C coupling constant (5.2 Hz).[19] Mass spectra agreed with the reported structures with *m/z* 318, 380, 348, and 420, respectively. The MS data, showing fragmentation at both N(2′)–C(3′) and C(1′)–C(5′) are consistent with these conclusions (see Experimental Section). Presumably, the conversion of **14a,b** into **17a–d** involves initial aza-Wittig reaction between **14a,b** and isocyanates to give the carbodiimides **15a–d**, which undergo electrocylic ring-closure to give the intermediate lactone functionality.

Readily available nitro compound **18a** was the starting point for **19**. Standard operations provided the known amine **18b** and azide **18c**.[6] Treatment of **18c** with triphenylphosphine or **18b** with a mixture of carbon tetrachloride, triphenylphosphine, and triethylamine at room temperature by the Staudinger reaction yielded **19** in 96 and 36% yield, respectively (Scheme 1). Proton and carbon spectral data of **18c**, previously unattributed (2D COSY, JMPC, and irradiation), were the basis for the assignment for compound **19**.

At this stage of our work, it was interesting to investigate the reactivity of iminophosphorane **19** with phenyl isocyanate. Treatment of iminophosphorane **19** with phenyl isocyanate led to a complex mixture of products from which the lactam **20** could be obtained in 27% yield. The residual reaction mixture was partially resolved by flash chromatography to give the desired quinoline **21a** admixed with **21d**, 12% yield, overall). **21a** could not be purified.

(19) (a) Guella, G.; Mancini, I.; Zibrowins, H.; Pietra, F. *Helv. Chim. Acta* **1988**, *71*, 773. (b) *Ibid.* **1989**, *72*, 1444. (c) Unfortunately, we were unable to obtain a single crystal of **17a–d**, but a similar reactivity had been observed in the formation of hydantoins (conclusively determined by X-ray crystallography) from imidazo[1,2-*a*]azines and diazines without 2-substitution. Synthetic and reactivity studies on the azaplysinopsinic system are in progress in our laboratory and the results are to be published in due course.

Scheme 3



The structure of quinolone **20** (m/z 235) was assigned from spectroscopic data. The ^{1}H NMR spectrum showed H-8 as a doublet (J = 7 Hz) at δ 9.29. This distinctly low field chemical shift resulted from the "peri" deshielding effect by the C6 carbonyl group. Further support for this assignment was the quaternary downfield carbon at δ 155.52 corresponding to CO. The infrared spectrum showed amine and carbonyl absorptions at 2920 and 1664 cm^{-1}, indicating the lactam function. The ^{1}H NMR spectra of **21a** show in particular typical hydrogen absorptions of pyridine and quinoline nuclei. The mass spectra afford the corresponding molecular ion (M$^+$, 310). The structure of compound **21d** was tentatively established from MS spectral data, which showed a parent ion at m/z 426 (75%) and fragments at 425 (100%), 213 (32%). Chemical means were used to eliminate other structures. The conversion of **19** into **21d** involves initial formation of the lactam **20** as an intermediate, which reacts with the starting iminophosphorane **19** to give **21d**. When product **20** was boiled for 6 h with iminophosphorane **19**, the reaction afforded a complex final reaction mixture of products in which the "coupling" amine **21d** was identified by mass spectrometry.

With these results in hand, we investigated the reaction of iminophosphorane **19** with methyl isocyanate under similar conditions. Addition of compound **19** to an excess (2 equiv) of methyl isocyanate with prolonged reflux (12 h) in toluene afforded three products (see Experimental Section). A large amount of the product with the high R_f was isolated after preparative chromatography in 18% yield and identified as the quinoline **21b**. The assignment of pyridine and benzene protons was possible by analysis of the NMR splitting patterns and was a good indication of the C-3 annelation. The COSY spectrum gave H-1 (7.91), H-2 (7.62), H-3 (7.43), H-4 (8.51), H-8 (8.57), H-9 (6.92), H-10 (7.43) and H-11 (7.83) connectivities and lacked an imidazolic signal consistent with results obtained in a ^{13}C–^{1}H correlation experiment. The presence of six quaternary carbons rule out the alternate zwitterion structure. This structure was confirmed on the basis of mass spectral evidence which showed ions at m/z 248 (M$^+$, 95%) and 219 (M$^+$ – NCH$_3$, 100%). The middle R_f compound was isolated pure in 20% yield) and analysis of the ^{1}H NMR spectrum showed it to be the lactam **20**. The low R_f compound was also purified in 9% yield and identified as **21c**, the mass spectrum of which showed m/z 305 (M$^+$, 48%) and m/z 247 (M$^+$ – NHCOCH$_3$, 100%). The two characteristic ABXY systems, the presence of the NCH$_3$ and NHCH$_3$ groups, and the absence of the imidazole signal in the ^{1}H NMR spectrum provide further confirmation.

In conclusion, the intramolecular aza-Wittig-type reaction starting from vinyl (or aryl) iminophosphoranes in the imidazopyridine series, which are of considerable pharmacological interest, provides information on mechanism as well as a useful method for the synthesis of azacarboline derivatives. The azaplysinopsin-mimic stuctures are challenging: they are the focus of a new synthetic approach to substituted 1-aminocyclopropane-1-carboxylic acids (ACC's)[20] and are attracting increasing pharmacological interest for their specific cytotoxicicity against cancer cells and their activity in neurotransmission.[21]

Experimental Section

Melting points were determined on a Büchi capillary melting point apparatus and are not corrected. NMR (proton or ^{13}C) spectra were recorded on a Bruker MSL 300 (300 or 75 MHz) or AC 400 spectrophotometer using $CDCl_3$, CD_2Cl_2, or DMSO-d_6 as solvent with internal TMS standard. Infrared spectra were recorded on a Beckman Acculab 2 spectrophotometer. Mass spectral analyses were performed on a Hewlett-Packard 5985B or 5989A instrument. Elemental analyses were performed by the Microanalytical Center, Montpellier. The purity of compounds not submitted for combustion analysis was assessed from their proton or carbon NMR spectra. All reactions employing dry solvents were run under argon. CH_2Cl_2 was distilled from CaH_2, and toluene from Na. Dry solvents were stored over molecular sieves under argon.

Aldehydes **1a,b**[6b] and **11a–c**[17] are known compounds. Azidovinyls **2a,b** were prepared according to literature procedure.[6] Phenyl 1,4-diazaindenes **18a–c** were prepared as described.[7] Complete characterization of compounds **2a,b, 3b, 12b, 14a,b, 17c–d, and 18c** is supplied in the supplementary material.

General Procedure for the Preparation of Azidovinyl Compounds (12a,c). A mixture of ethyl azidoacetate (20 mmol) and the appropriate aldehyde (2 mmol) was added dropwise under nitrogen at −30 °C to a well-stirred solution containing sodium (9 mg-atom) in 30 mL of dry ethanol. The reaction mixture was stirred 2 h at −30 °C and was allowed to warm to room temperature for 3 h. After this, it was poured into aqueous 30% ammonium chloride (8 mL) and then extracted with dimethyl ether. The organic layers were washed with water (30 mL) and dried over sodium sulfate, and the solvent was removed under reduced pressure at 30 °C. The residual material was purified by column chromatography to afford esters **13a–d** and azides **12a–c**.

Ethyl 2-Azido-3-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)-propenoate (12a). Chromatography on silica gel eluted with ether gave the ester **13a** (4%) as a paste: IR (KBr) 1706, 1218 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25 (t, 3H, CH_3), 4.35 (q, 2H, CH_2), 7.07 (t, 1H, J = 7 Hz, H-6), 7.45 (m, 4H, ArH), 7.78 (m, 3H, ArH), 9.45 (d, 1H, H-5); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.05 (CH_3), 60.60 (CH_2), 114.33 (C-6), 117.48 (C-8), 127.67 (C-7),128.24 (2C, Ph), 128.46 (Ph), 128.87 (2C, Ph), 130.30 (C-5); MS m/z (rel intensity) 266 (M$^+$, 38), 239 (37), 237 (12), 194 (100), 78 (17). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.18; H, 5.26; N, 10.53. Found: C, 72.08; H, 5.25; N, 10.50. Further elution gave the azide **12a** (60%) as yellow needles: mp 70–72 °C; IR (KBr) 2110, 1680, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (t, 3H, CH_3), 4.30 (q, 2H, CH_2), 6.84 (t, 1H, J = 7 Hz, H-6), 7.13 (s, 1H, H-β), 7.22 (pst, 1H, H-7), 7.35 (m, 3H, Ph), 7.59 (d, 1H, J = 9 Hz, H-8), 7.69 (d, 2H, Ph), 8.07 (d, 1H, H-5);

(20) King, J.; Riordan, J.; Holt, E. *J. Org. Chem.* **1982**, *47*, 3270.
(21) Kostinen, A.; Munoz, L. *J. Org. Chem.* **1993**, *58*, 879.

^{13}C NMR ($CDCl_3$, 75 MHz) δ_{CH} 13.85 (CH_3), 62.32 (CH_2), 112.45 (C-6), 112.55 (C-8), 114.73 (C-3), 117.28 (C-β), 125.79 (C-7), 125.81 (C-α), 126.37 (C-5), 128.17 (Ph), 128.24 (2C, Ph), 128.34 (2C, Ph), 134.03 (C-2), 146.31 (C-8a), 147.19 (Ph), 162.42 (CO). Anal. Calcd for $C_{18}H_{15}N_5O_2$: C, 64.86; H, 4.50; N, 21.02. Found: C, 64.97; H, 4.49; N, 21.08.

Ethyl 2-Azido-3-(2-phenylimidazo[1,2-*a*]pyrimidin-3-yl)propenoate (12c). Chromatographic workup (neutral alumina, dichloromethane as eluent) afforded the first-eluting isomer **13c** (21%): mp 111–113 °C; IR (KBr) 1684, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.27 (t, 3H, CH_3), 4.35 (q, 2H, CH_2), 7.13 (dd, 1H, J = 7, 5 Hz, H-6), 7.45 (m, 3H, Ph), 7.86 (m, 2H, Ph), 8.75 (dd, 1H, J = 2 Hz, H-7), 9.71 (dd, 1H, J = 2 Hz, H-5); MS m/z (rel intensity) 267 (M^+, 79), 238 (35), 222 (26), 195 (100), 77 (15). Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.42; H, 4.87; N, 15.73. Found: C, 67.53; H, 4.88; N, 15.70. The second-eluting isomer was identified as ester **13d** (12%): mp 179–181 °C; IR (KBr) 1700, 1226 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25 (t, 3H, CH_3), 3.80 (q, 2H, CH_2), 6.99 (m, 1H, H-6), 7.41 (m, 1H, Ph), 7.46 (m, 2H, Ph), 8.14 (d, 2H, Ph), 8.33 (dd, 1H, J = 2 Hz, H-5), 8.67 (m, 1H, H-7) MS m/z (rel intensity) 267 (M^+, 73), 238 (34), 222 (15), 195(100), 77(13). Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.42; H, 4.87; N, 15.73. Found: C, 67.39; H, 4.86; N, 15.76. Further elution yielded the vinyl azide **12c** (60%): mp 116–118 °C; IR (KBr) 2095, 1685, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (t, 3H, CH_3), 4.47 (q, 2H, CH_2), 7.01 (dd, 1H, J = 7, 5 Hz, H-6), 7.21 (s, 1H, H-β), 7.52 (m, 3H, Ph), 7.92 (m, 2H, Ph), 8.54 (dd, 1H, J = 2 Hz, H-5), 8.64 (dd, 1H, H-7). Anal. Calcd for $C_{17}H_{14}N_6O_2$: C, 61.08; H, 4.19; N, 25.15. Found: C, 61.24; H, 4.18; N, 25.09.

General Procedure for the Preparation of Iminophosphoranes. To a stirred solution of triphenylphosphine (3 mmol) in dry dichloromethane (15 mL) was added dropwise at 0 °C under argon a solution of the appropriate azide (3 mmol) in the same solvent (10 mL). The mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo and the crude product was chromatographed on neutral alumina eluting with dichloromethane to yield the desired products **3a,b, 14a,b,** and **19.**

Ethyl 3-(Imidazo[1,2-*a*]pyridin-2-yl)-2-[(triphenylphosphoranyliden)amino]propenoate (3a): 98% yield; mp 104–106 °C; IR (KBr) 1690, 1598, 1420, 1220 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (t, 3H, CH_3), 3.87 (q, 2H, CH_2), 6.59 (t, 1H, J = 7 Hz, H-6), 7.0 (pst, 1H, H-7), 7.14 (d, 1H, $^4J_{PH}$ = 7.5 Hz, H-β), 7.43 (m, 10H, Ar), 7.72 (m, 7H, Ar), 8.43 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.93 (CH_3), 60.68 (CH_2), 111.39 (C-3), 111.97 ($^3J_{PC}$ = 21 Hz, C-β), 113.39 (C-6), 116.62 (C-8), 123.51 (C-7), 125.07 (C-5), 128.13 (6C, $^3J_{PC}$ = 12 Hz, Ph), 131,02 (3C, Ph), 132.22 (6C, $^2J_{PC}$ = 10 Hz, Ph), 132.69 (3C, $^1J_{PC}$ = 103 Hz, Ph), 137.24 ($^2J_{PC}$ = 7 Hz, C-α), 144.08 (2C, C-8a, C-2), 167.04 ($^3J_{PC}$ = 6 Hz, CO); MS m/z (rel intensity) 491(M^+, 37) 462 (40), 262 (86), 201 (97), 183 (100), 108 (69). Anal. Calcd for $C_{30}H_{26}N_3O_2P$: C, 73.32; H, 5.30; N, 8.55. Found: C, 73.53; H, 5.29; N, 8.53.

2-[2-[(Triphenylphosphoranylidene)amino]phenyl]-imidazo[1,2-*a*]pyridine (19). General method: 96% yield; mp 149–151 °C; IR (KBr) 1580, 1465, 1420, 1325, 1100, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.58 (m, 1H, H-3′), 6.63 (t, 1H, J = 7 Hz, H-6), 6.84 (m, 2H, H-4,′5′), 7.06 (pst, 1H, H-7), 7.49 (m, 9H, Ph), 7.59 (d, 1H, J = 9 Hz, H-8), 7.79 (m, 6H, Ph), 7.87 (d, 1H, H-5), 8.37 (m, 1H, H-6′), 8.77 (s, 1H, H-3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 111.38 (C-6), 113.09 (C-3), 116.78 (C-8 or C-5′), 117.79 (C-5′ or C-8), 122.21 ($^3J_{PC}$ = 12 Hz, C-3′), 123.61 (C-7), 125.25 (C-5), 126.91 ($^2J_{PC}$ = 22 Hz, C-2′), 127.31 (C-4′), 128.65 (7C, $^3J_{PC}$ = 11 Hz, Ph, C-6′), 130.53 (3C, $^1J_{PC}$ = 100 Hz, 3C, Ph), 131.88 (3C, Ph), 132.56 (6C, $^2J_{PC}$ = 10 Hz, Ph), 143.79 (C-2), 144.34 (C-8a), 148.17 (C-1′); MS m/z (rel intensity) 469 (M^+, 85), 392 (60), 262 (78), 208 (33), 183 (100), 108 (25), 78 (28). Anal. Calcd for $C_{31}H_{24}N_3P$: C, 79.32; H, 5.12; N, 8.96. Found: C, 79.53; H, 5.11; N, 8.94.

Other Method. To a solution of the amine **18b** (10 mmol) in 25 mL of dry acetonitrile were added triphenylphosphine (20 mmol), 15 mL of triethylamine, and 10 mL of CCl_4. The resultant mixture was then stirred at room temperature overnight. Triethylammonium chloride was separated by filtration and the filtrate concentrated to dryness. The crude product was chromatographed on neutral alumina eluting with dichloromethane to yield the desired product **19** (36%).

Reaction of Iminophosphoranes 3a,b, 14a,b, and 19 with Methyl (or phenyl) Isocyanates. To a solution of the iminophosphorane (2.4 mmol) in 30 mL of dry toluene was added the appropriate isocyanate (2.4 mmol). The reaction mixture was stirred at room temperature for 4 h and then at reflux temperature for 14 h. After cooling, the solution was concentrated in vacuo to dryness, the residual material was washed with cold ethanol to remove phosphine oxide, and the resulting mixture was chromatographed on neutral alumina eluting with dichloromethane.

A. From iminophosphorane **3a** and methyl isocyanate, first elution yielded azacarbolinone **9**: 23% yield; mp 204–206 °C; IR (KBr) 2960, 1730, 1658, 1300, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (t, 3H, CH_3), 4.47 (q, 2H, CH_2), 7.10 (t, 1H, J = 7 Hz, H-8), 7.59 (pst, 1H, H-7), 7.62 (s, 1H, H-4), 7.79 (d, 1H, J = 9 Hz, H-6), 9.37 (d, 1H, H-9); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.25 (CH_3), 62.86 (CH_2), 106.12 (C-8), 113.54 (C-6), 117.28 (C-7), 118.34 (C-10a), 128.37 (C-9), 130.46 (2C, C-4, C-4a), 149.82 (C-5a), 150.12 (C-3), 154.85 (C-1), 161.67 (CO); MS m/z (rel intensity) 257 (M^+, 100), 229 (15), 183 (55), 78 (23). Anal. Calcd for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.28; N, 16.34. Found: C, 60.82; H, 4.29; N, 16.38. Further elution yielded azacarboline **7a:** 4% yield; mp 119–121 °C; IR (KBr) 1724, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.46 (t, 3H, CH_3), 3.28 (s, 3H, NCH_3) 4.47 (q, 2 H, CH_2), 7.01 (t, 1H, J = 7 Hz, H-8), 7.47 (pst, 1H, H-7), 7.78 (d, 1H, J = 9 Hz, H-6), 8.07 (s,1H, H-4), 8.89 (d, 1H, H-9); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_{CH} 14.42 (CH_3), 29.13 (NCH_3), 61.76 (CH_2), 109.54 (C-8), 112.62 (C-6), 118.01 (C-7), 127.64 (C-9), 130.05 (C-4); MS m/z (rel intensity) 270 (M^+, 80), 241 (18), 224 (17), 196 (100), 195 (90), 182 (50), 168 (20), 78 (20). Anal. Calcd for $C_{14}H_{14}N_4O_2$: C, 62.22; H, 5.19; N, 20.74. Found: C, 62.06; H, 5.20; N, 20.80. Further elution yielded zwitterion **8a:** 54% yield; mp 200–202 °C; IR (KBr) 1700, 1642, 1238, 760 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.46 (t, 3H, CH_3), 3.41 (s, 3H, NCH_3), 4.42 (q, 2H, CH_2), 6.76 (s, 1H, H-4), 7.38 (t, 1H, J = 6.5 Hz, H-8), 7.64 (pst, 1H, H-9), 7.68 (s, 1H, H-5), 8.44 (d, 1H, H-7), 9.65 (d, 1H, J = 9 Hz, H-10); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 14.29 (CH_3), 34.32 (NCH_3), 61.65 (CH_2), 87.23 (^1J = 176 Hz, C-4), 101.85 (^1J = 202 Hz, C-5), 117.02 (^1J = 180, ^2J = 6.5 Hz, C-10), 118.55 (^1J = 172, ^2J = 6.5 Hz, C-8), 124.85 (^1J = 186 Hz, C-7), 127.81 (^1J = 171, ^2J = 6.5 Hz, C-9), 133.71 (C-10a), 137.48 (^2J = 11, ^2J = 6.5 Hz, C-4a), 146.22 (C-3), 149.38 (^3J = 5.5 Hz, C-1), 166.41 (^3J = 3 Hz, CO); MS m/z (rel intensity) 270 (M^+, 65), 241 (65), 213 (18), 196 (83), 157 (77), 156 (100), 78 (30). Anal. Calcd for $C_{14}H_{14}N_4O_2$: C, 62.22; H, 5.19; N, 20.74. Found: C, 62.32; H, 5.17; N, 20.70.

B. From iminophosphorane **3a** and phenyl isocyanate, first elution yielded the zwitterion **8b**: 41% yield; mp 194–196 °C; IR (KBr) 1700, 1572, 1528, 1430, 730 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.43 (t, 3H, CH_3), 4.37 (q, 2H, CH_2), 6.89 (s, 1H, H-4), 6.95 (t, 1H, Ph), 7.20 (t, 2H, Ph), 7.38 (t, 1H, J = 6.5 Hz, H-8), 7.62 (d, 2 H, Ph), 7.68 (pst, 1 H, H-9), 7.71 (s, 1 H, H-5), 8.38 (d, 1 H, H7), 9.78 (d, 1 H, J = 9 Hz, H-10); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 14.43 (CH_3), 61.72 (CH_2), 89.79 (^1J =176 Hz, C-4), 102.93 (^1J = 207 Hz, C-5), 117.76 (^1J = 174, ^2J = 6.5 Hz, C-10), 119.07 (^1J = 168, ^2J = 6.5 Hz, C-8), 121.55 (^1J = 157, ^3J = 8.5, ^2J = 6.5 Hz, Ph), 124.28 (2C, ^1J = 157, ^2J = 6.5, Hz, Ph), 125.69 (^1J = 189, ^2J = 4 Hz, C-7), 128.51 (^1J = 170, ^2J = 4.5 Hz, C-9), 128.66 (2C, ^1J = 155, ^2J = 8.5 Hz, Ph), 134.24 (C-10a), 137.14 (^2J = 8.5 Hz, C-4a), 145.76 (Ph), 146.67 (C-3), 149.87 (^3J = 6 Hz, C-1), 166.22 (CO); MS m/z (rel intensity) 332 (M^+, 50), 259 (20), 258 (100), 257 (21), 78 (5). Anal. Calcd for $C_{19}H_{16}N_4O_2$: C, 68.67; H, 4.82; N, 16.87. Found: C, 68.57; H, 4.83; N, 16.92. Further elution yielded azacarboline **7b:** 4% yield; mp 169–171 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.46 (t, 3H, CH_3), 4.46 (q, 2H, CH_2), 7.01 (pst, 1H, H-8), 7.28 (m, 3H, Ph), 7.57 (m, 2H, Ph), 7.64 (pst, 1H, H-7), 7.84 (d, 1H, J = 9 Hz, H-6), 8.06 (s, 1H, NH), 8.63 (s, 1H, H-4), 8.75 (d, 1H, J = 7 Hz, H-9); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_{CH} 14.41 (CH_3), 61.99 (CH_2), 113.01 (C-8), 116.78 (C-6), 118.13 (C-7), 127.16 (2C, Ph), 127.54 (C-9), 128.54 (Ph), 129.01 (2C, Ph), 132.45 (C-4); MS m/z (rel intensity) 332 (M^+, 43), 259 (28), 258 (100), 257 (21), 78 (16). Anal. Calcd for $C_{19}H_{16}N_4O_2$: C, 68.67; H,

4.82; N, 16.87. Found: C, 68.72; H, 4.83; N, 16.83. Further elution yielded the azacarboline **10**: 2% yield; mp 214–216 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.47 (t, 3H, CH_3), 4.53 (q, 2H, CH_2), 6.78 (m, 3H, Ph), 7.01 (t, 1H, J = 7 Hz, H-7), 7.22 (pst, 2H, Ph), 7.28 (s, 1H, NH), 7.50 (pst, 1H, H-8), 7.81 (d, 1H, J = 9 Hz, H-9), 8.07 (d, 1H, H-6), 8.45 (s, 1H, H-4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_{CH} 14.45 (CH_3), 61.94 (CH_2), 111.88 (C-8), 113.86 (C-6), 117.45 (C-7), 122.84 (C-9), 129.48 (C-4), 129.98 (4C, Ph), 131.22(Ph); MS m/z (rel intensity) 332 (M^+, 53), 259 (25), 258 (100), 257 (20), 78 (12). Anal. Calcd for $C_{19}H_{16}N_4O_2$: C, 68.67; H 4.82; N, 16.87. Found: C, 68.75; H, 4.81; N, 16.89.

When compound **7b** was heated for 6 h in 1,3-dichlorobenzene, the azacarboline **10** were obtained in 72% yield.

C. From iminophosphorane **14a** and methyl isocyanate, elution yielded **17a**: 34% yield; mp 280–282 °C; IR (KBr) 1755, 1700, 1650, 1438, 1150, 750 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.94 (s, 3H, CH_3), 6.72 (s, 1H, H-9), 6.98 (t, 1H, J = 7 Hz, H-6), 7.33 (m, 2H, Ph), 7.43 (m, 2H, Ph, H-7), 7.64 (d, 1H, J = 9 Hz, H-8), 7.85 (d, 2H, Ph,), 8.12 (d, 1H, H-5), 10.25 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 24.25 (CH_3), 95.67 (C-9), 112.64 (C-6), 113.86 (C-3), 116.63 (C-8), 125.74 (C-7), 126.28 (C-5), 127.61 (2C, Ph), 127.95 (Ph), 128.59 (2C, Ph), 130.56 (C-1'), 134.13 (Ph), 143.88 (C-2), 145.21 (C-8a), 154.52 (CO-3'), 163.29 (CO-5'); MS m/z (rel intensity) 318 (M^+, 100), 260 (15), 245 (35), 233 (42), 232 (47), 205 (25), 78 (15); diazomethane derivative m/z (rel intensity) 332 (100), 274 (23), 245 (51), 232 (45), 78 (28). Anal. Calcd for $C_{18}H_{14}N_4O_2$: C, 67.92; H, 4.40; N, 17.61. Found: C, 68.08; H, 4.39; N, 17.59.

D. From iminophosphorane **19** and methyl isocyanate, first elution yielded (18%) of quinoline **21b**: mp 234–236 °C; IR (KBr) 3400, 1621, 1580, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.28 (s, 3H, NCH_3), 4.83 (s, 1H, NH), 6.92 (t, 1H, J = 7 Hz, H-9), 7.43 (m, 2H, H-10, H-3), 7.62 (t, 1H, J = 7.5 Hz, H-2), 7.83 (d, 1H, J = 9 Hz, H-11), 7.91 (d, 1H, H-1), 8.51 (d,1H, J = 8 Hz, H-4), 8.57 (d, 1H, H-8); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.02 (NCH_3), 112.57 (C-9), 113.15 (C-6a), 118.04 (C-11), 119.17 (C-12b), 122.53 (C-4), 123.02 (C-3 or C-10), 126.33 (C-8), 126.79 (C-1), 128.08 (C-10 or C-3), 128.78 (C-2) and 145.15, 147.48, 147.6, 148.49 (C-4a, C-6, C-11a, C-12a); MS m/z (rel intensity) 248 (M^+, 95), 219 (100), 124 (25), 78 (75). Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.58; H, 4.84; N, 22.58. Found: C, 72.69; H, 4.83; N, 22.54. Further elution yielded **20:** 20% yield; mp >300 °C; IR (KBr) 2920, 1664, 1430, 1340, 727 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.20 (t, 1H, J = 7 Hz, H-9), 7.27 (pst, 1H, H-3), 7.47 (m, 2H, H-1, H-2), 7.64 (pst, 1H, H-10), 7.84 (d, 1H, J = 9 Hz, H-11), 8.18 (d, 1H, J = 8 Hz, H-4), 9.29 (d, 1H, H-8), 11.81 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 113.56, 113.74 (CH), 115.58, 116.28 (CH), 116.79 (CH), 122.17 (CH), 122.72 (CH), 127.57 (CH), 129.47 (CH), 129.87 (CH), 137.51, 147.17, 148.45, 155.52; MS m/z (rel intensity) 235 (M^+,100), 217 (15), 78 (10). Anal. Calcd for $C_{14}H_9N_3O$: C, 71.49; H, 3.83; N, 17.87. Found: C, 71.65; H, 3.84; N, 17.82. Last elution yielded **21c**: 1% yield; mp 248–250 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.78 (d, 3H, J = 4 Hz, $NHCH_3$), 3.56 (s, 3H, NCH_3), 5.08 (d, 1H, NH), 7.13 (t,1H, J = 7 Hz, H-9), 7.66 (pst, 1H, J = 7 Hz, H-10), 7.75 (pst, 1H, H-3), 7.81 (t, 1H, J = 9 Hz, H-2), 7.94 (d, 1H, J = 9 Hz, H-11), 8.18 (d, 1H, H-1), 8.63 (d, 1H, H-8), 8.73 (d, 1H, J = 8 Hz, H-4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_{CH} 27.71 (NCH_3), 35.42 ($NHCH_3$), 113.35, 118.04, 122.86, 127.09, 127.85, 129.03, 129.38, 130.53; MS m/z (rel intensity) 305 (M^+, 48), 247 (100), 219 (98), 192 (15), 124 (20), 78 (45). Anal. Calcd for $C_{17}H_{15}N_5O$: C, 66.88; H, 4.92; N, 22.95. Found: C, 66.69; H, 4.94; N, 23.02.

E. From iminophosphorane **19** and phenyl isocyanate, first elution yielded quinolinone **20:** 27%. Further elution yielded (12%) of quinoline **21a** admixed with **21d** in the ratio of 5/1. Due to the complexity of the product mixture, only ^{1}H NMR of **21a** and MS signals are listed: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (t, 1H, J = 7 Hz, H-9), 7.18 (t, 1H, J = 7 Hz, H-10), 7.32 (pst, 3H, Ph), 7.48 (t, 1H, J = 8 Hz, H-2), 7.6 (m, 2H, Ph), 7.68 (t, 1H, J = 9 Hz, H-3), 7.77 (d, 1H, J = 8 Hz, H-11), 7.92 (d, 1H, J = 9 Hz, H-1), 8.46 (d, 1H, H-4), 9.12 (s, 1H, NH), 9.16 (d, 1H, H-8); MS m/z (rel intensity) 310 (65), 309 (100), 155 (25), 78 (15). Further elution yielded compound tentatively attributed **21d**: MS m/z (rel intensity) 426 (M^+, 75), 425 (100), 321 (15), 213 (32), 78 (20).

A solution of **20** (mmol) and **19** (mmol) in toluene (1 mL) was heated to reflux (6 h). The solvent was removed in vacuo, and the residue was directly examined by mass spectroscopy. Inspection of MS spectra indicated the formation of **21d**.

Acknowledgment. We express our grateful acknowledgment to Mr. Jacques Queille, Henri Viols, and Nour E. Benchat for skillful experimental work. We thank the University of Clermont 1 for financial support (B.Q.R.).

Supplementary Material Available: Compound characterization data for **2a,b**, **3b**, **12b**, **14a,b**, **17b-d**, and **18c** (4 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.