Stachybotrin B (2): ^1H and ^{13}C NMR data, see Table II; HPLC t_R 4.05 min; mp 178–180 °C dec; $[\alpha]_D$ = +39.1° (c 0.11 g/dL; MeOH); IR (neat) 3293, 2919, 1653, 1608, 1457, 1350, 1080 cm^{-1}; EIMS (70 eV) m/z 385 (M^+; rel int 36), 311 (22), 232 (13), 216 (16), 190 (23), 178 (38), 177 (30), 147 (9), 123 (13), 109 (15), 95 (16), 81 (25), 69 (100); HREIMS obsd for $C_{23}H_{31}NO_4$ 385.2270, calcd 385.2254.

Acetylation of Stachybotrin A. A sample of stachybotrin A (4 mg) was dissolved in 0.2 mL of 1:1 pyridine-Ac_2O. The mixture was stirred and heated at 70 °C for 3 h and then allowed to stand at room temperature for 48 h. H_2O (1 mL) was added, and the solution was then extracted with $CHCl_3$ (2 × 2 mL). The $CHCl_3$ solution was dried and evaporated to afford 5 mg of yellow oil. Further purification was accomplished by preparative TLC on silica gel plates (12 × 4 × 0.1 cm) with $CHCl_3$–acetone (95:5) as the eluent. The MeOH extract of the band at R_f 0.7 was evaporated to afford the triacetate (2.5 mg; 48% yield) as a colorless oil with: ^1H NMR signals at 7.09 (s, 1 H), 5.39 (t, J = 7.4 Hz; 1 H), 5.16 (t, J = 5.0 Hz, 1 H), 5.05 (br m, 1 H), 4.52 (br s, 2 H), 4.37 (s, 2 H), 3.02 (dd, J = 18.0, 5.0 Hz, 1 H) 2.70 (dd, J = 18.0, 5.0 Hz, 1 H), 2.31 (s, 3 H), 2.26 (m, 2 H), 2.04 (s, 3 H), 2.03 (m, 4 H), 1.94 (s, 3 H), 1.67 (m, 2 H), 1.65 (s, 3 H), 1.55 (s, 3 H), 1.35 ppm (s, 3 H); IR (neat) 2918, 1734, 1646, 1602, 1570, 1450, 1380, 1228, 809 cm^{-1}; EIMS (70 eV) 526 $[(M - H)^+$, rel int (0.2), 468 (0.4), 418 (0.8), 414 (0.3), 360 (1.4), 332 (1.2), 316 (2.1), 300 (7.9), 274 (3.8), 258 (18), 230 (4.2), 216 (11), 177 (4.9), 129 (4.1), 95 (6.2), 69 (12), 55 (16), 43 (100).

Acetylation of Stachybotrin B. The procedure described above was repeated using 4 mg of stachybotrin B to afford the diacetate (2.2 mg; 45% yield): EIMS (70 eV) m/z 469 (M^+, rel int 0.3), 424 (0.4), 369 (6.8), 353 (1.7), 318 (1.3), 300 (5.1), 285 (2.1), 258 (7.9), 236 (11), 213 (3.6), 185 (4.6), 152 (8.1), 97 (66), 83 (39), 69 (57), 55 (66), 43 (100).

Methylation of Stachybotrin B. An ethereal solution of CH_2N_2 (3.5 mL) was added to a solution of 2 (10 mg) in 0.5 mL of MeOH. After standing at rt for 24 h, the solvents were evaporated and the residue was subjected to preparative TLC on silica gel (100- × 50- × 0.25-mm plates) eluting twice with 95:5 $CHCl_3$–MeOH. The major band at R_f 0.6 was collected and extracted with MeOH. Filtration and concentration of the resulting solution afforded 6.1 mg of the methyl ether derivative 3 (59% yield) as a colorless oil with: NMR assignments (based in part on HMQC and HMBC data); ^1H NMR 6.73 (s, 1 H; H-4), 5.13 (br t, 1 H, 6.0; H-16), 5.05 (br t, 1 H, 6.0; H-20), 4.28 (d, 1 H, 15.4; H-13), 4.24 (d, 1 H, 15.4; H-13), 3.88 (s, 3 H; C5-OMe), 3.87 (m, 1 H; H-8), 2.95 (dd, 1 H, 18.0, 5.1; H-7), 2.65 (dd, 1 H, 18.0, 6.9; H-7), 2.17 (m, 2 H; H-15), 2.03 (m, 2 H; H_2-19), 1.95 (br t, 2 H; H_2-18), 1.65 (m, 2 H; H_2-14), 1.62 (br s, 3 H; H_3-22), 1.56 (s, 3 H; H_3-24), 1.54 (s, 3 H; H_3-23), 1.28 ppm (s, 3 H; H_3-25); ^{13}C NMR, 174.1 (C-2), 160.3 (C-5), 150.0 (C-11), 136.2 (C-17), 132.6 (C-3), 132.2 (C-21), 126.0 (C-12), 125.4 (C-16), 125.3 (C-20), 114.4 (C-6), 96.7 (C-4), 80.3 (C-9), 68.2 (C-8), 56.3 (C-5-OMe), 44.2 (C-13), 40.8 (C-18), 38.4 (C-14), 27.7 (C-19, C-7), 25.8 (C-22), 22.6 (C-15), 18.8 (C-25), 17.7 (C-23), 15.9 (C-24).

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Supplementary Material Available: ^1H NMR spectra of stachybotrins A and B and the ^{13}C NMR spectrum of stachybotrin A (2 pages). This material is contained in many 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.

Reactivity and Synthetic Applications of Bis(iminophosphoranes). One-Pot Preparation of Pyrido[2,3,4-*de*]quinazolines and Benzo[*de*][1,6]naphthyridines

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Aza-Wittig reaction of bis(iminophosphorane) 4 with 2 equiv of isocyanate leads directly to pyrido[2,3,4-*de*]quinazolines 5. Iminophosphoranes 8, available from 4 and 1 equiv of the appropriate isocyanate, react either with 1 equiv of isocyanate or ketene to give pyrido[2,3,4-*de*]quinazolines 9 or benzo[*de*][1,6]naphthyridines 10, respectively. Bis(iminophosphorane) 4 by sequential treatment with aldehydes and isocyanates yielded 2,3-dihydropyrido[2,3,4-*de*]quinazolines 17.

The intramolecular version of the aza-Wittig-type reaction has attracted considerable attention recently because of its high potential for the synthesis of a wide variety of nitrogen heterocycles, which can be attributed in good measure to the rapid progress in the preparation of functionalized iminophosphoranes, and several interesting heterocyclization reactions involving iminophosphoranes have been reviewed.[1] These compounds can be easily converted through aza-Wittig reactions with isocyanates, carbon dioxide, or carbon disulfide into functionalized heterocumulenes which exhibit a rich chemistry of unusual synthetic promise. However, the chemistry of bis(iminophosphoranes) remains almost unexplored.[2] Bis(iminophosphoranes) are expected to have synthetic potential because they provide a reaction system in which the two iminophosphorane groups can react either with a reagent having two functionalities or with two separate reagents bearing the same functionality (mode A). It is expected that the utility of the bis(iminophosphoranes) could be improved if the two iminophosphorane moieties show different reactivity toward the same functionality. In this

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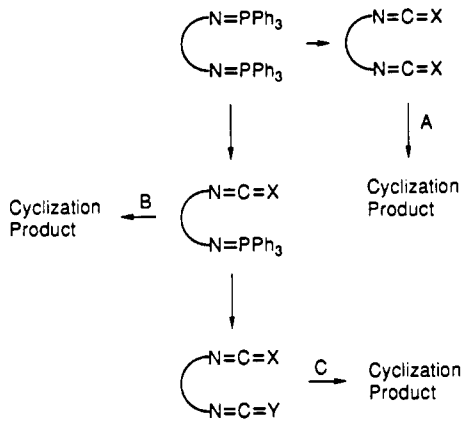
0022-3263/92/1957-6703$03.00/0

Chart I



case, after the first aza-Wittig reaction one iminophosphorane group survives which could undergo either cyclization across the heterocumulene portion (mode B) or subsequent aza-Wittig reaction with another reagent having different functionality leading to a difunctionalized compound which could undergo a plethora of heterocyclization reactions (mode C) (Chart I).

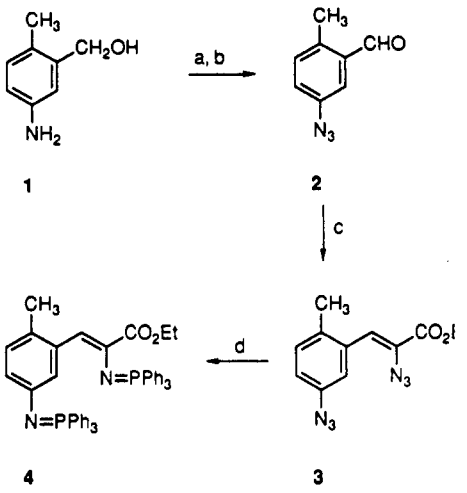
We have shown that *C,N*-bis(iminophosphoranes),[3] in which the *N*-iminophosphorane group is more reactive that the *C*-iminophosphorane group, are useful building blocks for the one-pot preparation of fused benzotriazepines.[4] In addition, aza-Wittig reactions of *C,C*-bis(iminophosphoranes), in which one iminophosphorane group is directly linked to an aromatic ring and the other is on an vinyl side chain at the ortho position, lead to iminophosphoranes derived from the indole ring.[5]

It was convenient to study the behavior of this type of *C,C*-bis(iminophosphoranes) in aza-Wittig reactions, when the two iminophosphorane groups (aryl and vinyl) are placed at the meta position. At first this type of bis(iminophosphoranes) by aza-Wittig reactions with isocyanates and related compounds would give rise to bis(heterocumulenes) able to undergo a one-pot double annelation either by an electrocyclic ring-closure/intramolecular amination process[6] or by intramolecular hetero-Diels–Alder cycloaddition[7] (Chart II). This new annelation approach has surprisingly been found to be useful in the simultaneous formation of pyridine and pyrimidine or two fused pyridine rings.

Results and Discussion

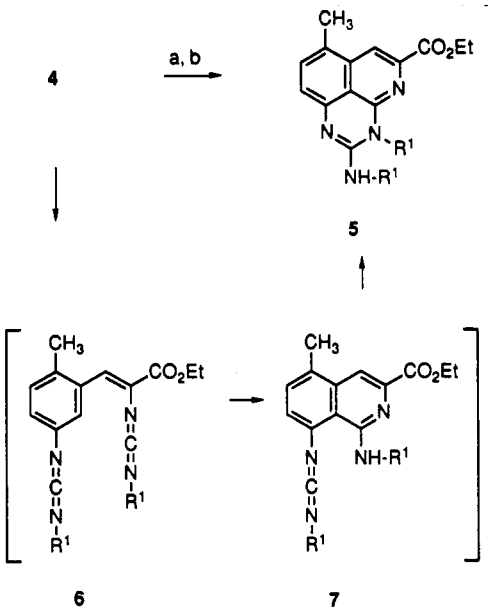
The key iminophosphorane **4** was easily prepared in 50% overall yield from 5-amino-2-methylbenzyl alcohol[8] **1** by standard chemistry: (a) diazotation followed by addition of sodium azide; (b) oxidation with pyridinium chlorochromate; (c) condensation with ethyl azidoacetate; and (e) Staudinger reaction with triphenylphosphine (Scheme I). The ^{31}P NMR spectrum of compound **4** shows two signals at δ 0.06 and 4.51 ppm due to the aromatic and β-styryl iminophosphorane moieties, respec-

Scheme I[a]



[a] Reagents: (a) $NaNO_2$, HCl/H_2O, 0 °C, then NaN_3; (b) pyridinium chlorochromate, CH_2Cl_2, rt (83%); (c) $EtO_2CCH_2N_3$, NaOEt, EtOH, −15 °C (67%); (d) PPh_3, ether, rt (91%).

Scheme II[a]



[a] Reagents: (a) $2R^1NCO$, toluene, rt; (b) sealed tube, toluene, 160 °C.

Table I. Pyrido[2,3,4-*de*]quinazoline Derivatives 5, 9, 14, 17, and 18

entry	R^1	R^2	yield, %	mp, °C
5a	$C_6H_5CH_2$		54	198
5b	C_6H_5		53	222–223
5c	3-ClC_6H_4		50	226–227
5d	4-ClC_6H_4		46	168–169
5e	4-$CH_3C_6H_4$		40	207–208
5f	4-$CH_3OC_6H_4$		47	168–169
9a	4-$CH_3OC_6H_4$	4-ClC_6H_4	50	188
9b	4-ClC_6H_4	4-$CH_3OC_6H_4$	43	113–115
14a	4-$CH_3C_6H_4$		70	226–227
14b	4-$CH_3OC_6H_4$		69	235
17a	4-NCC_6H_4	4-$CH_3OC_6H_4$	36	105–107
17b	4-$O_2NC_6H_4$	C_6H_5	30	241–242
17c	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	47	198
17d	4-$O_2NC_6H_4$	4-$CH_3OC_6H_4$	35	244–245
18a	4-NCC_6H_4	4-$CH_3OC_6H_4$	20	115–116
18b	4-$O_2NC_6H_4$	C_6H_5	23	181–182
18c	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	11	245–246
18d	4-$O_2NC_6H_4$	4-$CH_3OC_6H_4$	19	111–112

(3) We denote as *C,N*-bis(iminophosphoranes) to those compounds where one iminophosphorane group is directly linked to aromatic, heteroaromatic or an unsaturated carbon–carbon side chain while the other is on a nitrogen atom belonging to a heteroaromatic ring. In *C,C*-bis(iminophosphoranes) both iminophosphorane groups are placed either on an aromatic, heteroaromatic, or unsaturated carbon–carbon side chain.

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(8) Sucholeiki, I.; Lynch, V.; Phan, L.; Wilcox, C. S. *J. Org. Chem.* **1988**, *53*, 98.

Chart II

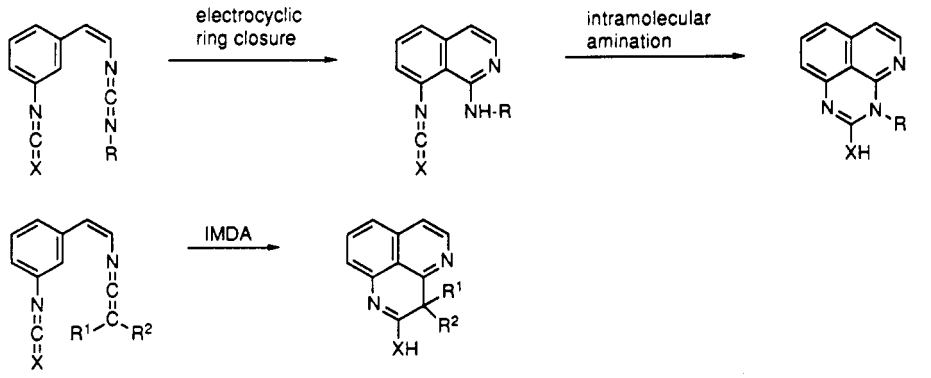


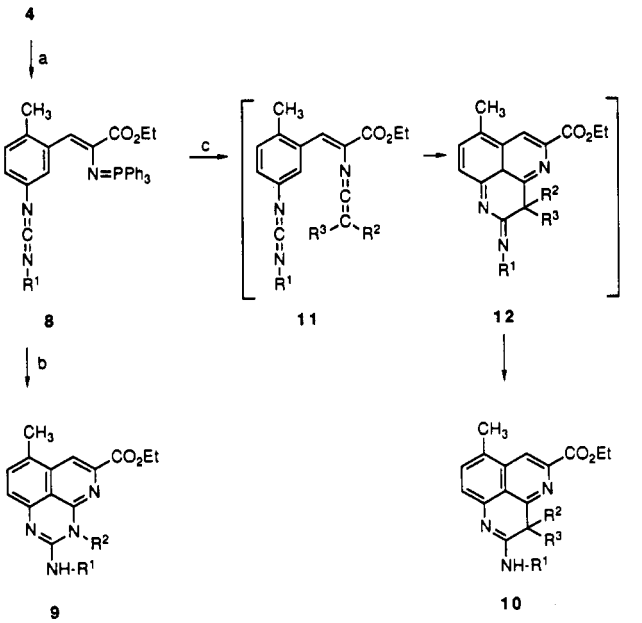
Table II. Benzo[*de*][1,6]naphthyridine Derivatives 10

entry	R^1	R^2	R^3	yield, %	mp, °C
10a	4-ClC_6H_4	C_6H_5	C_2H_5	45	193
10b	4-$CH_3OC_6H_4$	C_6H_5	C_2H_5	51	216–217
10c	4-ClC_6H_4	C_6H_5	C_6H_5	58	236–237
10d	4-$CH_3OC_6H_4$	C_6H_5	C_6H_5	65	230–231

tively. Aza-Wittig reaction of bis(iminophosphorane) **4** with 2 equiv of isocyanate in toluene at room temperature and then at 160 °C leads directly to the previously unreported pyrido[2,3,4-*de*]quinazolines **5** in moderate yields (Table I). The conversion **4** → **5** probably involves two initial aza-Wittig reactions to yield a bis(carbodiimide) **6** as intermediate (as evidenced by a strong absorption band around 2120 cm^{-1} in the IR). Pyrido annelation occurs by electrocyclic ring closure of the styryl carbodiimide portion to give **7**, and finally pyrimido annelation takes place through an intramolecular amination process (Scheme II). However, aza-Wittig reaction between bis(iminophosphorane) **4** and 1 equiv of isocyanate in methylene chloride at room temperature led to iminophosphoranes **8** bearing a carbodiimide moiety directly linked to an aromatic ring, which could be isolated as viscous oils. The ^{31}P NMR spectrum of compound **8a** (R^1 = 4-$CH_3OC_6H_4$) only shows a signal at δ 6.98 ppm, while the ^{13}C NMR spectrum shows that the carbonyl and C_α and C_β atoms of the styryl portion are coupled with the phosphorus atom. Moreover, the IR spectrum shows a strong band at 2129 cm^{-1} due to the carbodiimide function. These data support the proposed structure **8**.

The conversion **4** → **8** clearly shows for the first time the preferential reactivity of aryl iminophosphoranes with respect to β-styryl iminophosphoranes in aza-Wittig reactions. After addition of a second equivalent of isocyanate to a toluene solution of the iminophosphorane **8**, the resulting bis(carbodiimide) was heated in a sealed tube at 160 °C to give the tricyclic compounds **9** in moderate yields (Table I) in which the groups R^1 and R^2 can be different. Likewise, iminophosphoranes **8** reacted with ketenes under same conditions to give benzo[*de*][1,6]naphthyridines **10** in fair yields (Table II). The conversion **8** → **10** can be understood by an initial aza-Wittig reaction to give the difunctionalized compound **11**, which undergoes an intramolecular hetero-Diels–Alder cycloaddition whereby the aryl carbodiimide moiety has functioned as a 2-aza diene using one cumulative double bond and one carbon–carbon double bond of the aromatic ring,[9] and the carbon–carbon bond of the styryl ketene imine group has taken the role of the dienophile. A final aromatization of the cycloadduct **12** by [1,5] proton shift furnishes the tricyclic compound **10** (Scheme III).

Scheme III[a]



[a] Reagents: (a) R^1NCO, toluene, rt; (b) R^2NCO, sealed tube, toluene, 160 °C; (c) $R^2R^3C{=}C{=}O$, toluene, rt, then sealed tube, toluene, 160 °C.

In a similar way but changing the sequential addition of the reagents, bis(iminophosphorane) **4** reacted with 1 equiv of diphenyl ketene in methylene chloride at room temperature to give the iminophosphorane **13** in 81% yield as viscous oil. The IR spectrum of **13** shows a strong band at 1999 cm^{-1} due to the heterocumulene bond. The ^{31}P NMR spectrum only shows a signal at δ 7.08 ppm, which is in good agreement with previously reported values for β-styryl iminophosphoranes,[5] while the ^{13}C NMR spectrum shows that the carbonyl and C_α and C_β atoms of the styryl portion are coupled to the phosphorus atom. Moreover, the β-carbon of the ketene imine moiety appears at δ 76.95 ppm.[10] Iminophosphorane **13** by reaction with 1 equiv of isocyanate at room temperature and then heating at 160 °C led to pyrido[2,3,4-*de*]quinazolines **14** in good yields (Table I). Aza-Wittig reaction of bis(iminophosphorane) **4** with 2 equiv of diphenyl ketene under the above mentioned reaction conditions led to the benzo[*de*][1,6]-naphthyridine **15** in 93% yield (Scheme IV).

On the other hand, bis(iminophosphorane) **4** reacted with aromatic aldehydes in toluene at 80 °C to give aldimines **16** which were used without purification for the next step. When compounds **16** were treated with isocyanate

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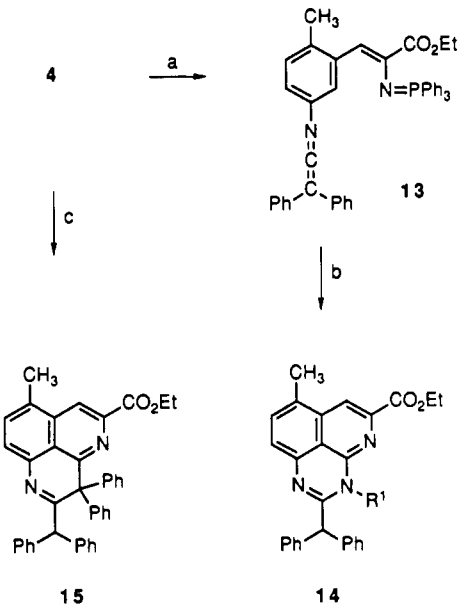
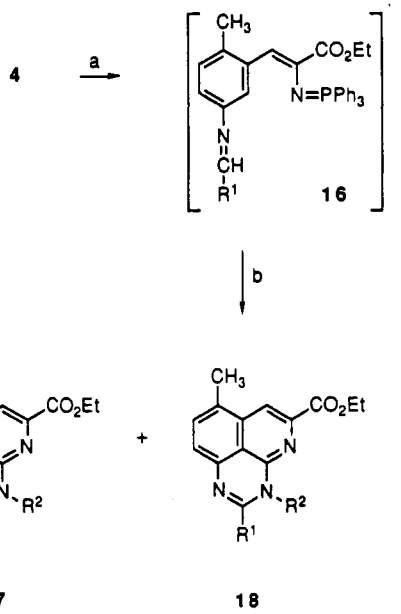
Scheme IV[a]



[a] Reagents: (a) $Ph_2C{=}O{=}O$, toluene, rt; (b) R^1NCO, toluene, rt, then sealed tube, toluene, 160 °C; (c) $2Ph_2C{=}C{=}O$, toluene, rt, then sealed tube, toluene, 160 °C.

Scheme V[a]

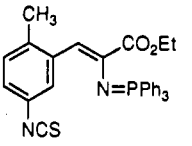


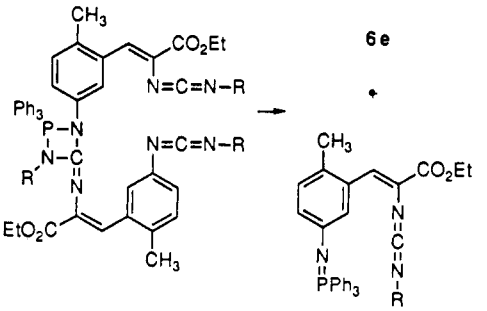
[a] Reagents: (a) R^1CHO, toluene, 80 °C; (b) R^2NCO, sealed tube, toluene, 160 °C.

in toluene at room temperature and then heated in a sealed tube at 160 °C, after the usual workup, the 2,3-dihydropyrido[2,3,4-*de*]quinazolines **17** (30–47%) together with the pyrido[2,3,4-*de*]quinazolines **18** (11–23%) were obtained, which were separated by column chromatography. The conversion **16** → **17** can be rationalized in terms of an initial aza-Wittig reaction to give a β-styryl carbodiimide which undergoes cyclization either by electrocyclic ring closure followed by [1,3] proton shift and finally intramolecular amination on the aldimine carbon–nitrogen double bond[11] or by intramolecular hetero-Diels–Alder cycloaddition whereby the aryl aldimine has functioned as 2-aza diene[12] and one cumulative double bond of the carbodiimide moiety has taken the role of the dienophile. Compound **18** arises from **17** by dehydrogenation under the reaction conditions (Scheme V).

Finally, the reaction of bis(iminophosphorane) **4** with carbon disulfide has been studied. Compound **4** reacted with carbon disulfide in benzene at reflux temperature to give the bis(isothiocyanate) **19** in 23% yield together with the carbodiimide **20** in 41% yield, which were separated by column chromatography. Compound **19** by treating with [N-(4-methylphenyl)imino]triphenylphosphorane in benzene at 40 °C led to **21** (R = 4-$CH_3C_6H_4$) in 65% as a viscous oil, which was also prepared directly in 71% yield from **4** by sequential treatment with the appropriate isocyanate and further with carbon disulfide. However, reaction of carbodiimide **20** with 3 equiv of [*N*-(4-methylphenyl)imino]triphenylphosphorane led to **5e** in 48% yield together with the iminophosphorane **22** in 51% yield, which by treatment with carbon disulfide at 140 °C led to the pyrido[2,3,4-*de*]quinazoline **23** in 68% yield (Scheme VI). We assume for the conversion **4** → **19** + **20** the initial formation of an iminophosphorane type **24** which by aza-Wittig reaction with a second equivalent of carbon disulfide leads to **19**. Reaction between the iminophosphorane **24** with **19** across the isothiocyanate group

Chart III





directly linked to the aromatic ring yields **20**. Probably the conversion **20** → **5** + **22** involves the initial formation of the intermediate **25** which undergoes fragmentation[13] to give **6e** and **26**. Finally, electrocyclic ring closure of these carbodiimides affords **5e** and **22**, respectively (Chart III).

Concluding Remarks

We have developed a simple but effective general one-pot strategy for the synthesis of a variety of highly functionalized pyrido[2,3,4-*de*]quinazolines and benzo[*de*]-[1,6]naphthyridines. Several trends have surfaced from

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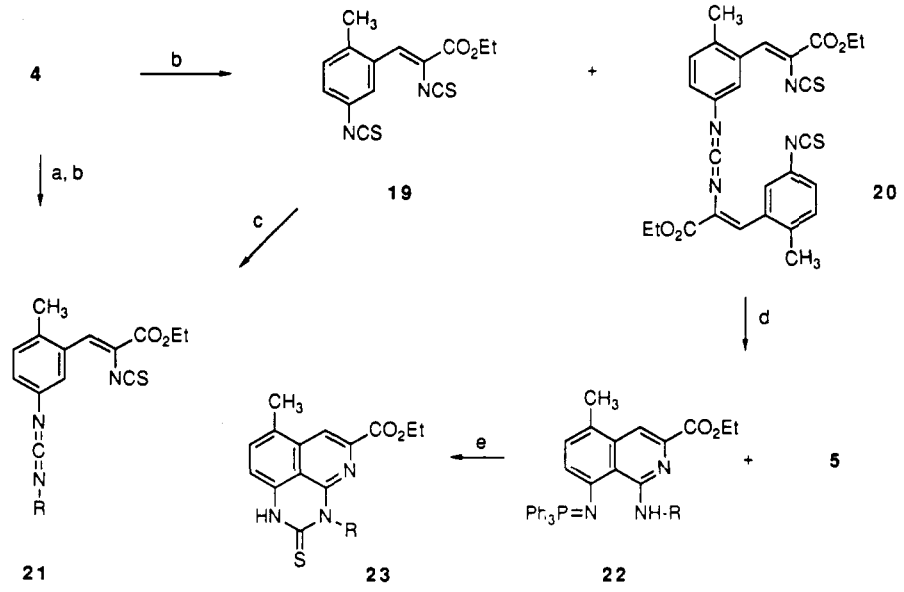
(12) Normura, Y.; Kimura, M.; Takeuchi, Y.; Tomodo, S. *Chem. Lett.* **1978**, 267; Shono, T.; Matsumura, Y.; Inoue, K.; Ohmizu, H.; Kashimura, S. *J. Am. Chem. Soc.* **1982**, *104*, 5753.

(13) It has been described that the reaction between iminophosphoranes and carbodiimides yields 1,2,4-phosphadiazetidines as intermediates, which undergo reactions to give different products depending on the nature of the starting materials: Huisgen, R.; Wulff, J. *Chem. Ber.* **1969**, *102*, 1948. Bödeker, J.; Köckritz, P.; Courault, K. *Z. Chem.* **1979**, *19*, 59. Molina, P.; Alajarin, M.; López-Leondardo, C.; Claramunt, R. M.; Foces-Foces, M. C.; Cano, F. H.; Catalán, J.; de la Paz, J. L. G.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 355.

Scheme VI[a]



[a] Reagents: (a) RNCO, CH_2Cl_2, rt; (b) CS_2, benzene, reflux; (c) RN=PPh_3, benzene, 50 °C; (d) 3RN=PPh_3, toluene, reflux, then sealed tube, toluene, 150 °C; (e) CS_2, sealed tube, toluene, 140 °C.

our studies. First, the consecutive pyrido/pyrimido annelation takes place through an electrocyclic ring closure/intramolecular amination process, whereas the double pyrido annelation occurs via an intramolecular hetero-Diels–Alder [4 + 2] cycloaddition. Second, it is possible to reverse the position of the substituents in the pyridine or pyrimidine ring by modulating the order of the two initial aza-Wittig processes with the order of reactivity of the iminophosphorane functionalities. Third and foremost, in accordance with previous results[5] the order of reactivity of iminophosphoranes toward isocyanates, ketenes, and aldehydes is the following: *N*-iminophosphorane > aryl iminophosphorane > β-styryl iminophosphorane. Further studies aimed at the application of this methodology to the preparation of structurally complex nitrogen heterocycles related the aaptamine alkaloids are underway in our laboratory.

Experimental Section

General Methods. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions on a Nicolet FT-5DX spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 and on a Varian Unity-300 instrument, and chemical shifts are expressed in parts per million (δ) relative to tetramethylsilane. ^{31}P NMR spectra were observed at 121.42 MHz, and phosphorus chemical shifts are referenced to 85% H_3PO_4. Electron-impact mass spectra were carried out on a Hewlett-Packard 5993C spectrometer at an ionization potential of 70 eV. Microanalyses were performed on a Perkin-Elmer 240C instrument.

Preparation of 5-Azido-2-methylbenzaldehyde (2). To a solution of 5-amino-2-methylbenzyl alcohol 1 (5.48 g, 40 mmol) in a mixture of water (60 mL) and concentrated sulfuric acid (10 mL) cooled to −5 °C was added dropwise a solution of sodium nitrite (3.45 g, 50 mmol) in 20 mL of water, while the temperature of the reaction mixture was kept between −5 and 0 °C. After 30 min of stirring, a solution of sodium azide (3.25 g, 50 mmol) in 20 mL of water was added dropwise, and stirring was continued for 3 h. The mixture was extracted with methylene chloride (3 × 40 mL). The combined organic layers were washed with water (3 × 30 mL) and dried over $MgSO_4$.

The $MgSO_4$ was removed by filtration, and to the filtrate, 5-azido-2-methylbenzyl alcohol, was added pyridinium chlorochromate (10.78 g, 50 mmol), and then the mixture was stirred at room temperature for 4 h. The solution was filtered over $MgSO_4$, and the residue was extracted with boiling ether (3 × 40 mL). The new filtrate and the ether were mixed, the solvent was removed, and the resulting material was passed through a column of silica gel, with ether/*n*-hexane (1:1) as the eluant to give **2**: yield 83%; mp 56–57 °C; colorless prisms (ether/*n*-hexane); IR (Nujol) 2118, 1671 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.63 (s, 3 H), 7.10 (dd, 1 H, J = 2.5, 8.2 Hz), 7.24 (d, 1 H, J = 8.2 Hz), 7.44 (d, 1 H, J = 2.5 Hz), 10.24 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.57 (CH_3), 120.79 (C6), 124.05 (C4), 133.21 (C3), 134.98 (s), 137.05 (s), 138.64 (s), 191.30 (CHO); mass spectrum, m/z (relative intensity) 161 (M^+, 46), 104 (100), 78 (66). Anal. Calcd for $C_8H_7N_3O$: C, 59.62; H, 4.37; N, 26.07. Found: C, 59.47; H, 4.29; N, 26.13.

Preparation of Ethyl α,5-Diazido-2-methylcinnamate (3). A mixture of ethyl azidoacetate (15.49 g, 120 mmol) and 5-azido-2-methylbenzaldehyde **2** (4.83 g, 30 mmol) was added dropwise to a well-stirred solution containing sodium (2.75 g, 120 mmol) in 100 mL of dry ethanol under nitrogen at −20 °C. The reaction mixture was stirred for 5 h, poured into aqueous 35% ammonium chloride (150 mL) and then extracted with ether (3 × 100 mL). The organic layers were washed with water (2 × 100 mL) and dried over $MgSO_4$. The $MgSO_4$ was filtered and the solvent concentrated to dryness. The resulting material was recrystallized to give **3**: yield 67%; mp 75–76 °C; colorless needles (ethanol); IR (Nujol) 2134, 2114, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3 H, J = 7.1 Hz), 2.31 (s, 3 H), 4.37 (q, 2 H, J = 7.1 Hz), 6.86 (dd, 1 H, J = 2.4, 8.2 Hz), 7.02 (s, 1 H), 7.15 (d, 1 H, J = 8.2 Hz), 7.65 (d, 1 H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.15 (CH_3CH_2O), 19.46 (CH_3), 62.43 (CH_3CH_2O), 119.41 (C4), 119.96 (C6), 121.56 (C_β), 127.12 (C_α), 131.43 (C3), 133.27 (s), 134.23 (s), 137.59 (s), 163.18 (CO); mass spectrum, m/z (relative intensity) 272 (M^+, 12), 143 (59), 117 (100). Anal. Calcd for $C_{12}H_{12}N_6O_2$: C, 52.94; H, 4.44; N, 30.86. Found: C, 52.81; H, 4.25; N, 30.73.

Preparation of Ethyl 2-Methyl-α,5-bis[(triphenylphosphoranylidene)amino]cinnamate (4). To a solution of triphenylphosphine (5.24 g, 20 mmol) in 40 mL of dry ether was added, in small portions, ethyl α,5-diazido-2-methylcinnamate **3** (2.72 g, 10 mmol). The reaction mixture was stirred at room temperature for 12 h, and the separated solid was filtered and recrystallized to give **4**: yield 91%; mp 219–220 °C; colorless prisms (benzene); IR (Nujol) 1689, 1412, 1327, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, 3 H, J = 7.0 Hz), 2.22 (s, 3 H), 3.83 (q, 2 H, J = 7.0 Hz), 6.27 (d, 1 H, J = 8.0 Hz), 6.67 (d, 1 H, J = 8.0 Hz), 6.81 (d, 1 H, $^4J_{P-H}$ = 6.6 Hz), 7.19–7.46 (m, 18 H), 7.68–7.84 (m, 12 H), 8.64 (d, 1 H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.05 (CH_3CH_2O), 19.42 (CH_3), 60.44 (CH_3CH_2O), 115.17 (d, $^3J_{P-C}$ = 19.6 Hz, C_β), 119.49 (d, $^3J_{P-C}$ = 11.2 Hz, C4), 125.53 (C2), 126.74

(d, $^3J_{P-C}$ = 23.9 Hz, C6), 128.01 (d, $^3J_{P-C}$ = 12.1 Hz, C_m), 128.39 (d, $^3J_{P-C}$ = 11.8 Hz, C_m), 130.07 (d, $^1J_{P-C}$ = 86.8 Hz, C_i), 130.53 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 131.29 (d, $^4J_{P-C}$ = 2.5 Hz, C_p), 132.64 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 132.68 (d, $^2J_{P-C}$ = 9.5 Hz, C_o), 133.76 (d, $^1J_{P-C}$ = 89.1 Hz, C_i), 135.22 (d, $^2J_{P-C}$ = 6.7 Hz, C_a), 136.99 (d, $^4J_{P-C}$ = 3.0 Hz, C1), 148.02 (d, $^2J_{P-C}$ = 2.3 Hz, C5), 168.55 (d, $^3J_{P-C}$ = 6.8 Hz, CO), C3 was not observed; ^{31}P NMR ($CDCl_3$) δ 0.06 (Ph_3P=N-C5), 4.51 (Ph_3P=N-C_α); mass spectrum, m/z (relative intensity) 741 (M^+, 16), 405 (100), 183 (83). Anal. Calcd for $C_{48}H_{42}N_2O_2P_2$: C, 77.82; H, 5.71; N, 3.78. Found: C, 77.67; H, 5.59; N, 3.85.

Preparation of Carbodiimide 8 (R^1 = 4-$CH_3OC_6H_4$). To a solution of the bis(iminophosphorane) **4** (0.74 g, 1 mmol) in 25 mL of dry methylene chloride was added at room temperature 4-methoxyphenyl isocyanate (0.15 g, 1 mmol) in the same solvent (25 mL) during 4–5 h. Afterwards, the solvent was removed under reduced pressure and the residual material was chromatographed (silica gel; *n*-hexane/ethyl acetate, 8:3) to give **8** (R^1 = 4-$CH_3OC_6H_4$): yield 83%; viscous oil; IR (neat) 2129, 1699, 1249, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7.1 Hz), 2.34 (s, 3 H), 3.72 (s, 3 H), 3.85 (q, 2 H, J = 7.1 Hz), 6.67–7.10 (m, 7 H), 7.34–7.41 (m, 9 H), 7.67–7.78 (m, 6 H), 8.80 (d, 1 H, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.07, 19.85, 55.49, 60.80, 112.04 (d, $^3J_{P-C}$ = 19.8 Hz), 114.61, 121.11, 124.90, 125.01, 128.25 (d, $^3J_{P-C}$ = 12.2 Hz), 130.43, 131.01 (d, $^4J_{P-C}$ = 2.8 Hz), 131.74 (s), 131.84 (s), 132.49 (d, $^2J_{P-C}$ = 9.6 Hz), 133.44 (s), 134.75 (d, $^1J_{P-C}$ = 85.5 Hz), 136.01 (s), 137.28 (d, $^2J_{P-C}$ = 6.5 Hz), 137.94 (s), 157.07 (s), 168.01 (d, $^3J_{P-C}$ = 6.8 Hz); ^{31}P NMR ($CDCl_3$) δ 6.98; mass spectrum, m/z (relative intensity) 612 (M^+, 21), 183 (100). Anal. Calcd for $C_{38}H_{34}N_3O_3P$: C, 74.62; H, 5.60; N, 6.87. Found: C, 74.47; H, 5.49; N, 6.78.

Preparation of Ketene Imine 13. To a solution of the bis(iminophosphorane) **4** (0.74 g, 1 mmol) in 25 mL of dry methylene chloride was added at room temperature diphenylketene (0.19 g, 1 mmol) in the same solvent (25 mL) during 4–5 h. Afterwards, the solvent was removed under reduced pressure, and the residual material was chromatographed (silica gel; *n*-hexane/ethyl acetate, 8:3) to give **13**: yield 81%; viscous oil; IR (neat) 1999, 1699, 1234, 1110 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H, J = 7.0 Hz), 2.37 (s, 3 H), 3.83 (q, 2 H, J = 7.0 Hz), 6.77 (d, 1 H, J = 6.7 Hz), 7.10–7.37 (m, 21 H), 7.66–7.78 (m, 6 H), 9.00 (d, 1 H, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.00, 19.97, 60.73, 76.95 (s), 111.79 (d, $^3J_{P-C}$ = 19.7 Hz), 119.93, 125.97, 126.04, 127.67, 128.15 (d, $^3J_{P-C}$ = 12.1 Hz), 128.69, 129.96 (s), 130.54, 130.94 (d, $^4J_{P-C}$ = 2.8 Hz), 131.70 (s), 132.40 (d, $^2J_{P-C}$ = 9.7 Hz), 133.75 (s), 134.56 (s), 136.64 (d, $^1J_{P-C}$ = 99.8 Hz), 137.51 (d, $^2J_{P-C}$ = 6.1 Hz), 138.13 (s), 167.86 (d, $^3J_{P-C}$ = 7.5 Hz); ^{31}P NMR ($CDCl_3$) δ 7.08. Anal. Calcd for $C_{44}H_{37}N_2O_2P$: C, 80.47; H, 5.68; N, 4.26. Found: C, 80.38; H, 5.55; N, 4.20.

General Procedure for the Preparation of 3-Alkyl(aryl)-2-(alkyl(aryl)amino)-5-(ethoxycarbonyl)-7-methylpyrido[2,3,4-*de*]quinazolines (5). To a solution of the bis(iminophosphorane) **4** (1.29 g, 1.75 mmol) in 30 mL of dry toluene was added the appropriate isocyanate (3.5 mmol). The reaction mixture was stirred at room temperature for 1 h and then heated in a sealed tube at 160 °C for 24 h. After cooling, the solvent was removed under reduced pressure, and the residual material was purified by chromatography on a silica gel column eluting with *n*-hexane/ethyl acetate (7:3) and recrystallization.

5a: yield 54%; mp 198 °C; yellow needles (ethyl acetate/*n*-hexane); IR (Nujol) 3381, 1717, 1265 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (t, 3 H, J = 7.1 Hz), 2.61 (s, 3 H), 4.37 (q, 2 H, J = 7.1 Hz), 4.53 (d, 2 H, J = 4.9 Hz), 4.71 (t, 1 H, J = 4.9 Hz), 5.56 (s, 2 H), 6.97–7.04 (m, 3 H), 7.17–7.31 (m, 8 H), 7.39 (d, 1 H, J = 7.9 Hz), 7.89 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.38 (CH_3CH_2O), 18.17 (CH_3), 45.17 (CH_2N), 46.00 (CH_2NH), 61.23 (CH_3CH_2O), 114.83 (C6), 115.14 (C9b), 117.17 (C9), 123.87 (C6a or C7), 126.83, 127.35, 127.51, 127.95, 128.57, 129.22, 134.17 (C8), 135.61 (C6a or C7), 135.98 (s), 138.21 (s), 140.79 (C5), 144.28 (C9a), 150.10 (C2), 152.65 (C3a), 167.27 (CO); mass spectrum, m/z (relative intensity) 450 (M^+, 45), 359 (54), 285 (45), 155 (5), 91 (100), 65 (13). Anal. Calcd for $C_{28}H_{26}N_4O_2$: C, 74.64; H, 5.81; N, 12.43. Found: C, 74.57; H, 5.67; N, 12.32.

5b: yield 53%; mp 222–223 °C; yellow needles (ethyl acetate/*n*-hexane); IR (Nujol) 3415, 1736, 1269 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 7.0 Hz), 2.43 (s, 3 H), 4.19 (q, 2 H, J = 7.0 Hz), 5.91 (s, 1 H), 7.02 (t, 1 H, J = 7.4 Hz), 7.10 (d, 1 H, J = 7.8 Hz), 7.26 (t, 2 H, J = 7.6 Hz), 7.37–7.68 (m, 8 H), 7.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.06 (CH_3CH_2O), 18.12 (CH_3), 61.00 (CH_3CH_2O), 114.85 (C6), 115.31 (C9b), 117.91 (C9), 120.64 (C2′ and C6′), 123.57 (C4′), 124.95 (C6a or C7), 128.75 (C3′ and C5′), 129.71 (C4″), 129.89 (C2″ and C6″), 130.79 (C3″ and C5″), 133.96 (C8), 135.33 (C1′), 135.41 (C6a or C7), 138.14 (C1″), 140.86 (C5), 143.06 (C9a), 146.49 (C2), 153.32 (C3a), 165.87 (CO); mass spectrum, m/z (relative intensity) 422 (M^+, 100), 421 (35), 350 (27). Anal. Calcd for $C_{26}H_{22}N_4O_2$: C, 77.91; H, 5.25; N, 13.26. Found: C, 77.80; H, 5.09; N, 13.12.

5c: yield 50%; mp 226–227 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 136.56 1716, 1292 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.22 (t, 3 H, J = 7.0 Hz), 2.36 (s, 3 H), 4.14 (q, 2 H, J = 7.0 Hz), 6.75 (d, 1 H, J = 7.7 Hz), 6.92 (d, 1 H, J = 7.7 Hz), 7.07 (t, 1 H, J = 8.0 Hz), 7.23–7.67 (m, 9 H); ^{13}C NMR (DMSO-d_6) δ 13.86 (CH_3CH_2O), 17.50 (CH_3), 60.44 (CH_3CH_2O), 113.82 (C6), 114.68 (C9b), 117.12 (C9), 120.94 (C6′), 122.07 (C2′), 122.64 (C4′), 123.91 (C6a or C7), 128.76 (C6″), 129.08 (C5′), 129.35 (C2″), 130.61 (C4″), 131.17 (C5″), 132.35 (C1″), 133.69 (C3″), 133.86 (C8), 134.58 (C3′), 136.56 (C6a or C7), 140.45 (C1′), 140.56 (C5), 142.80 (C9a), 147.05 (C2), 152.91 (C3a), 164.69 (CO); mass spectrum, m/z (relative intensity) 494 (M^+ + 4, 13), 492 (M^+ + 2, 67), 490 (M^+, 100), 418 (23). Anal. Calcd for $C_{26}H_{20}Cl_2N_4O_2$: C, 63.55; H, 4.10; N, 11.40. Found: C, 63.41; H, 4.01; N, 11.26.

5d: yield 46%; mp 168–169 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3426, 1721, 1270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 7.1 Hz), 2.39 (s, 3 H), 4.12 (q, 2 H, J = 7.1 Hz), 5.83 (s, 1 H), 7.05 (d, 1 H, J = 8.0 Hz), 7.22 (d, 2 H, J = 8.6 Hz), 7.36 (d, 1 H, J = 8.0 Hz), 7.43 (m, 4 H), 7.56 (d, 2 H, J = 8.6 Hz), 7.75 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.11 (CH_3CH_2O), 18.13 (CH_3), 61.10 (CH_3CH_2O), 115.11 (C9b), 115.16 (C6), 118.03 (C9), 121.95 (C2′ and C6′), 125.40 (C6a or C7), 128.61 (C4′), 128.71 (C3′ and C5′), 131.06 (C3″ and C5″), 131.50 (C2″ and C6″), 133.66 (C1″), 133.99 (C8), 135.19 (C4″), 135.71 (C6a or C7), 136.63 (C1′), 140.55 (C5), 141.46 (C9a), 145.84 (C2), 152.89 (C3a), 165.65 (CO); mass spectrum, m/z (relative intensity) 494 (M^+ + 4, 13), 492 (M^+ + 2, 74), 490 (M^+, 100), 418 (29). Anal. Calcd for $C_{26}H_{20}Cl_2N_4O_2$: C, 63.55; H, 4.10; N, 11.40. Found: C, 63.37; H, 3.99; H, 11.27.

5e: yield 40%; mp 207–208 °C; yellow needles (ethyl acetate/*n*-hexane); IR (Nujol) 3421, 1704, 1224 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3 H, J = 7.1 Hz), 2.27 (s, 3 H), 2.44 (s, 3 H), 2.46 (s, 3 H), 4.21 (q, 2 H, J = 7.1 Hz), 5.92 (s, 1 H), 7.03–7.10 (m, 3 H), 7.32–7.43 (m, 7 H), 7.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.06 (CH_3CH_2O), 18.06 (CH_3-C7), 20.75 (CH_3), 21.32 (CH_3), 60.93 (CH_3CH_2O), 114.67 (C6), 115.27 (C9b), 117.75 (C9), 120.96, 124.56 (C6a or C7), 129.19, 129.47, 131.36, 132.62 (s), 133.13 (s), 133.89 (C8), 135.28 (s), 135.54 (C6a or C7), 139.62 (s), 140.86 (C5), 143.31 (C9a), 146.94 (C2), 153.43 (C3a), 165.85 (CO); mass spectrum, m/z (relative intensity) 450 (M^+, 100), 378 (23), 91 (7). Anal. Calcd for $C_{28}H_{26}N_4O_2$: C, 74.64; H, 5.81; N, 12.43. Found: C, 74.58; H, 5.75; N, 12.51.

5f: yield 47%; mp 168–169 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3409, 1718, 1246 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 3 H, J = 7.1 Hz), 2.47 (s, 3 H), 3.78 (s, 3 H), 3.90 (s, 3 H), 4.26 (q, 2 H, J = 7.1 Hz), 5.92 (s, 1 H), 6.84 (d, 2 H, J = 8.9 Hz), 7.09 (d, 1 H, J = 8.0 Hz), 7.14 (d, 2 H, J = 8.9 Hz), 7.35–7.44 (m, 5 H), 7.88 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.18 (CH_3CH_2O), 18.18 (CH_3), 55.57 (CH_3O), 55.63 (CH_3O), 61.09 (CH_3CH_2O), 114.08 (C3′ and C5′), 114.83 (C6), 115.38 (C9b), 116.05 (C3″ and C5″), 117.81 (C9), 123.19 (C2′ and C6′), 124.69 (C6a or C7), 127.69 (C1″), 130.96 (C2″ and C6″), 131.18 (C1′), 134.04 (C8), 135.47 (C6a or C7), 141.03 (C5), 143.39 (C9a), 147.67 (C2), 153.67 (C3a), 156.31 (C4′), 160.29 (C4″), 166.02 (CO); mass spectrum, m/z (relative intensity) 482 (M^+, 100), 481 (31). Anal. Calcd for $C_{28}H_{26}N_4O_4$: C, 69.69; H, 5.43; N, 11.61. Found: C, 69.55; H, 5.34; N, 11.49.

General Procedure for the Preparation 3-Aryl-2-(arylamino)-5-(ethoxycarbonyl)-7-methylpyrido[2,3,4-*de*]quinazolines (9). To a solution of the bis(iminophosphorane) **4** (1.29 g, 1.75 mmol) in 25 mL of dry methylene chloride was added at room temperature the corresponding isocyanate (1.75 mmol) in the same solvent (25 mL) during 4–5 h. Afterwards, the solvent was removed under reduced pressure, and the resulting material was dissolved in 30 mL of dry toluene, and the appropriate isocyanate (1.75 mmol) was added at room temperature. The new reaction mixture is treated in the same way as in preparation of compounds **5**.

9a: yield 50%; mp 188 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3426, 1722, 1244 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, 3 H, J = 7.1 Hz), 2.41 (s, 3 H), 3.76 (s, 3 H), 4.19 (q, 2 H, J = 7.1 Hz), 5.70 (s, 1 H), 6.82 (d, 2 H, J = 8.8 Hz), 7.03 (d, 1 H, J = 7.8 Hz), 7.32–7.36 (m, 3 H), 7.43 (d, 2 H, J = 8.5 Hz), 7.57 (d, 2 H, J = 8.5 Hz), 7.79 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.13 (CH_3CH_2O), 18.08 (CH_3), 55.49 (CH_3O), 61.06 (CH_3CH_2O), 114.00 (C3′ and C5′), 115.01 (C6), 117.90 (C9), 123.23 (C2′ and C6′), 124.84 (C6a or C7), 130.96 (C3″ and C5″), 131.51 (C2″ and C6″), 134.00 (C8), 135.25 (C4″), 135.59 (C6a or C7), 140.66 (C5), 143.08 (C9a), 146.77 (C2), 153.08 (C3a), 156.36 (C4′), 165.79 (CO), C1′, C1″ and C9b were not observed; mass spectrum, m/z (relative intensity) 488 (M^+ + 2, 35), 486 (M^+, 100), 414 (35). Anal. Calcd for $C_{27}H_{23}ClN_4O_3$: C, 66.59; H, 4.76; N, 11.50. Found: C, 66.46; H, 4.67; N, 11.29.

9b: yield 43%; mp 113–115 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3409, 1722, 1251 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, 3 H, J = 7.1 Hz), 2.43 (s, 3 H), 3.87 (s, 3 H), 4.20 (q, 2 H, J = 7.1 Hz), 6.01 (s, 1 H), 7.06 (d, 1 H, J = 8.0 Hz), 7.09 (d, 2 H, J = 8.8 Hz), 7.21 (d, 2 H, J = 8.8 Hz), 7.32–7.46 (m, 5 H), 7.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.12 (CH_3CH_2O), 18.12 (CH_3), 55.53 (CH_3O), 61.06 (CH_3CH_2O), 114.89 (C6), 115.37 (C9b), 116.02 (C3″ and C5″), 117.87 (C9), 121.82 (C2′ and C6′), 125.10 (C6a or C7), 127.30 (C1″), 128.37 (C4′), 128.66 (C3′ and C5′), 130.93 (C2″ and C6″), 133.95 (C8), 135.31 (C6a or C7), 136.85 (C1′), 140.83 (C5), 142.83 (C9a), 146.68 (C2), 153.44 (C3a), 160.29 (C4″), 165.84 (CO); mass spectrum, m/z (relative intensity) 488 (M^+ + 2, 35), 486 (M^+, 100). Anal. Calcd for $C_{27}H_{23}ClN_4O_3$: C, 66.59; H, 4.76; H, 11.50. Found: C, 66.45; H, 4.59; N, 11.37.

General Procedure for the Preparation of 3-Alkyl-(aryl)-2-(arylamino)-5-(ethoxycarbonyl)-7-methyl-3-phenylbenzo[*de*][1,6]naphthyridines (10). To a solution of the bis(iminophosphorane) 4 (1.29 g, 1.75 mmol) in 25 mL of dry methylene chloride was added at room temperature a solution of the corresponding isocyanate (1.75 mmol) in the same solvent during 4–5 h. Afterwards, the solvent was removed under reduced pressure, the resulting material was dissolved in 30 mL of dry toluene, and the appropriate ketene (1.75 mmol) was added. The new reaction mixture was stirred at room temperature for 30 min and then heated in a sealed tube at 160 °C for 24 h. After cooling, the solvent was removed under reduced pressure, and the residual material was purified by chromatography on a silica gel column eluting with *n*-hexane/ethyl acetate (7:3) and recrystallization.

10a: yield 45%; mp 193 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3409, 1715, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (t, 3 H, J = 7.1 Hz), 1.37 (t, 3 H, J = 7.1 Hz), 2.49 (dq, 1 H, J = 7.1, 13.5 Hz), 2.61 (s, 3 H), 3.29 (dq, 1 H, J = 7.1, 13.5 Hz), 4.35 (q, 2 H, J = 7.1 Hz), 6.34 (s, 1 H), 7.11–7.27 (m, 5 H), 7.41–7.58 (m, 4 H), 7.66 (d, 2 H, J = 8.7 Hz), 8.34 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.33 (CH_3CH_2), 14.34 (CH_3CH_2O), 18.39 (CH_3), 34.41 (CH_3CH_2), 53.13 (C3), 61.53 (CH_3CH_2O), 118.09 (C9b), 118.41 (C6), 121.63 (C2′ and C6′), 123.13 (C9), 127.40 (C4″), 127.51 (C3′ and C5′), 128.01 (C4′), 128.73 (C3″ and C5″), 128.87 (C2″ and C6″), 130.04 (C6a or C7), 133.01 (C8), 134.56 (C6a or C7), 138.18 (C1′), 140.88 (C5), 142.86 (C9a), 143.99 (C1″), 160.52 (C2 or C3a), 161.00 (C2 or C3a), 165.94 (CO); mass spectrum, m/z (relative intensity) 486 (M^+, + 2, 9), 487 (M^+, 27), 173 (100). Anal. Calcd for $C_{29}H_{26}ClN_3O_2$: C, 71.97; H, 5.41; N, 8.68. Found: C, 71.80; H, 5.36; N, 8.55.

10b: yield 51%; mp 216–217 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3421, 1732, 1259 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (t, 3 H, J = 7.1 Hz), 1.38 (t, 3 H, J = 7.0 Hz), 2.46 (dq, 1 H, J = 7.1, 13.5 Hz), 2.60 (s, 3 H), 3.28 (dq, 1 H, J = 7.1, 13.5 Hz), 3.77 (s, 3 H), 4.37 (q, 2 H, J = 7.0 Hz), 6.23 (s, 1 H), 6.86 (d, 2 H, J = 8.8 Hz), 7.13–7.30 (m, 4 H), 7.38 (d, 1 H, J = 7.5 Hz), 7.49 (d, 2 H, J = 7.3 Hz), 7.57 (d, 2 H, J = 8.8 Hz), 8.33 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.36 (CH_3CH_2), 14.34 (CH_3CH_2O), 18.34 (CH_3), 34.57 (CH_3CH_2), 54.99 (C3), 55.55 (CH_3O), 61.27 (CH_3CH_2O), 114.05 (C3′ and C5′), 118.18 (C9b), 118.36 (C6), 122.38 (C2′ and C6′), 122.75 (C9), 127.25 (C4″), 127.56 (C3″ and C5″), 128.78 (C2″ and C6″), 129.27 (C6a or C7), 132.65 (C1′), 133.04 (C8), 134.54 (C6a or C7), 141.53 (C5), 142.76 (C9a), 144.38 (C1″), 155.87 (C4′), 160.75 (C2 or C3a), 161.39 (C2 or C3a), 166.03 (CO); mass spectrum, m/z (relative intensity) 479 (M^+, 100), 451 (42), 450 (42). Anal. Calcd for $C_{30}H_{29}N_3O_3$: C, 75.13; H, 6.09; N, 8.76. Found: C, 75.01; H, 5.95; N, 8.67.

10c: yield 58%; mp 236–237 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3392, 1706, 1268 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3 H, J = 7.1 Hz), 2.59 (s, 3 H), 4.36 (q, 2 H, J = 7.1 Hz), 6.43 (s, 1 H), 7.19–7.34 (m, 8 H), 7.42–7.50 (m, 6 H), 7.62 (d, 2 H, J = 8.8 Hz), 8.39 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.32 (CH_3CH_2O), 18.40 (CH_3), 61.28 (CH_3CH_2O), 61.39 (C3), 117.65 (C9b), 118.80 (C6), 121.20 (C2′ and C6′), 123.22 (C9), 127.64 (C4″), 128.16 (C4′), 128.66 (C3″ and C5″), 128.77 (C3′ and C5′), 129.84 (C2″ and C6″), 130.31 (C6a or C7), 132.89 (C8), 134.59 (C6a or C7), 137.91 (C1′), 140.32 (C5), 142.85 (C9a), 143.12 (C1″), 158.86 (C2 or C3a), 161.10 (C2 or C3a), 165.97 (CO); mass spectrum, m/z (relative intensity) 533 (M^+, + 2, 39), 531 (M^+, 100). Anal. Calcd for $C_{33}H_{26}ClN_3O_2$: C, 74.50; H, 4.92; N, 7.89. Found: C, 75.32; H, 4.99; N, 7.73.

10d: yield 65%; mp 230–231 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3386, 1707, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H, J = 7.1 Hz), 2.57 (s, 3 H), 3.74 (s, 3 H), 4.36 (q, 2 H, J = 7.1 Hz), 6.33 (s, 1 H), 6.84 (d, 2 H, J = 8.9 Hz), 7.22–7.58 (m, 14 H), 8.38 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.30 (CH_3CH_2O), 18.31 (CH_3), 55.52 (CH_3O), 61.22 (CH_3CH_2O), 61.34 (C3), 114.03 (C3′ and C5′), 117.77 (C9b), 118.78 (C6), 121.85 (C2′ and C6′), 122.80 (C9), 127.48 (C4″), 128.54 (C3″ and C5″), 129.46 (C6a or C7), 129.91 (C2″ and C6″), 132.52 (C1′), 132.93 (C8), 134.53 (C6a or C7), 140.97 (C5), 142.67 (C9a), 143.34 (C1″), 155.90 (C4′), 159.21 (C2 or C3a), 161.33 (C2 or C3a), 166.04 (CO); mass spectrum, m/z (relative intensity) 528 (M^+, 100), 77 (40). Anal. Calcd for $C_{34}H_{29}N_3O_3$: C, 77.40; H, 5.54; N, 7.96. Found: C, 77.20; H, 5.39; N, 7.78.

General Procedure for the Preparation of 3-Aryl-2-(diphenylmethyl)-5-(ethoxycarbonyl)-7-methylpyrido[2,3,4-*de*]quinazolines (14). To a solution of the bis(iminophosphorane) 4 (1.29 g, 1.75 mmol) in 25 mL of dry methylene chloride was added at room temperature a solution of diphenylketene (0.34 g, 1.75 mmol) in the same solvent during 4–5 h. Afterwards, the solvent was removed under reduced pressure, the resulting material was dissolved in 30 mL of dry toluene, and the appropriate isocyanate (1.75 mmol) was added. The new reaction mixture was stirred at room temperature for 30 min and then heated in a sealed tube at 160 °C for 24 h. After cooling, the solvent was removed under reduced pressure, and the residual material was purified by chromatography on a silica gel column eluting with *n*-hexane/ethyl acetate (7:3) and recrystallization.

14a: yield 70%; mp 226–227 °C; colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 1706, 1276, 1223 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 7.0 Hz), 2.42 (s, 3 H), 2.46 (s, 3 H), 4.21 (q, 2 H, J = 7.0 Hz), 5.14 (s, 1 H), 6.97 (d, 2 H, J = 8.0 Hz), 7.20–7.28 (m, 13 H), 7.44 (d, 1 H, J = 7.8 Hz), 7.84 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.04 (CH_3CH_2O), 18.34 (CH_3-C_7), 21.33 (CH_3), 54.68 (CH), 61.03 (CH_3CH_2O), 114.65 (C6), 117.62 (C9b), 126.94 (C4′), 127.48 (C6a or C7), 128.24 (C3′ and C5′), 129.12 (C2″ and C6″), 129.31 (C2′ and C6′), 130.43 (C3″ and C5″), 133.65 (C8), 135.27 (C4″), 135.48 (C6a or C7), 138.70 (C1″), 140.30 (C1′), 141.58 (C5), 142.46 (C9a), 154.24 (C3a), 157.66 (C2), 165.79 (CO); mass spectrum, m/z (relative intensity) 511 (M^+, 35), 165 (100), 91 (77). Anal. Calcd for $C_{34}H_{29}N_3O_2$: C, 79.82; H, 5.71; N, 8.21. Found: C, 79.68; H, 5.59; N, 8.26.

14b: yield 69%; mp 235 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 1704, 1277, 1244 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (t, 3 H, J = 7.0 Hz), 2.45 (s, 3 H), 3.83 (s, 3 H), 4.22 (q, 2 H, J = 7.0 Hz), 5.16 (s, 1 H), 6.97 (s, 4 H), 7.14–7.34 (m, 11 H), 7.43 (d, 1 H, J = 7.8 Hz), 7.85 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.05 (CH_3CH_2O), 18.29 (CH_3), 54.78 (CH), 55.45 (CH_3O), 61.02 (CH_3CH_2O), 114.65 (C6), 114.95 (C3″ and C5″), 117.59 (C9b), 119.91 (C9), 126.92 (C4′), 127.48 (C6a or C7), 128.22 (C3′ and C5′), 129.30 (C2′ and C6′), 130.46 (C2″ and C6″), 133.62 (C8), 135.46 (C6a or C7), 140.25 (C1′), 141.59 (C5), 142.39 (C9a), 154.33 (C3a), 157.86 (C2), 159.62 (C4″), 165.79 (CO), C1″ was not observed; mass spectrum, m/z (relative intensity) 527 (M^+, 100), 165 (55), 152 (40). Anal. Calcd for $C_{34}H_{29}N_3O_3$: C, 77.40; H, 5.54; N, 7.96. Found: C, 77.20; H, 5.31; N, 7.81.

Preparation of 5-(Ethoxycarbonyl)-7-methyl-3,3-diphenyl-2-(diphenylmethyl)benzo[*de*][1,6]naphthyridine (15). To a solution of the bis(iminophosphorane) 4 (1.29 g, 1.75 mmol) in 30 mL of dry toluene was added diphenylketene (0.68 g, 3.5

mmol). The reaction mixture was stirred at room temperature for 1 h and then heated in a sealed tube at 160 °C for 24 h. After cooling, the solvent was removed to dryness, and the residue was treated with 10 mL of ethanol. The separated solid was filtered and recrystallized to give **15**: yield 93%; mp 287 °C; colorless needles (ethyl acetate); IR (Nujol) 1707, 1277, 1033 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.26 (t, 3 H, J = 7.1 Hz), 2.63 (s, 3 H), 4.27 (q, 2 H, J = 7.1 Hz), 5.12 (s, 1 H), 6.99–7.33 (m, 20 H), 7.76 (d, 1 H, J = 7.5 Hz), 7.88 (d, 1 H, J = 7.5 Hz), 8.32 (s, 1 H); mass spectrum, m/z (relative intensity) 572 (M^+, 66), 167 (100). Anal. Calcd for $C_{40}H_{32}N_2O_2$: C, 83.89; H, 5.63; N, 4.89. Found: C, 83.87; H, 5.49; N, 4.81.

General Procedure for the Preparation of 2,3-Diaryl-5-(ethoxycarbonyl)-7-methyl-2,3-dihydro-1*H*-pyrido[2,3,4-*de*]quinazolines (17). To a stirred suspension of the bis(iminophosphorane) **4** (1.29 g, 1.75 mmol) in 25 mL of dry toluene was added at 80 °C a solution of the corresponding aldehyde (1.75 mmol) in the same solvent during 3 h, and the stirring was continued for 1 h. Afterwards, the solvent was removed under reduced pressure until 30 mL, and the appropriate isocyanate (1.75 mmol) was added. The new reaction mixture is stirred at room temperature for 30 min and then heated in a sealed tube at 160 °C for 16 h. After cooling, the solvent was removed under reduced pressure, and the residual material was purified by passing through a column of silica gel with *n*-hexane/ethyl acetate (7:3) as eluant.

17a: yield 36%; mp 105–107 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3323, 2225, 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, J = 7.1 Hz), 2.51 (s, 3 H), 3.70 (s, 3 H), 4.29 (dq, 1 H, J = 7.1, 11.5 Hz), 4.34 (dq, 1 H, J = 7.1, 11.5 Hz), 5.59 (s, 1 H), 6.00 (d, 1 H, J = 2.3 Hz), 6.64 (d, 1 H, J = 7.8 Hz), 6.75 (d, 2 H, J = 8.8 Hz), 7.16 (d, 2 H, J = 8.8 Hz), 7.25 (d, 1 H, J = 7.8 Hz), 7.39 (s, 4 H), 7.94 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.23, 18.17, 55.36, 61.37, 73.00, 110.01 (s), 110.72, 112.16 (s), 112.76, 114.16, 118.38 (s), 124.87 (s), 127.23, 128.69, 132.28, 132.74, 135.13 (s), 135.80 (s), 138.91 (s), 140.19 (s), 145.79 (s), 153.05 (s), 157.37 (s), 166.27 (s); mass spectrum, m/z (relative intensity) 464 (M^+, 100), 463 (41), 362 (86). Anal. Calcd for $C_{28}H_{24}N_4O_3$: C, 72.39; H, 5.21; N, 12.06. Found: C, 72.20; H, 5.15; N, 12.00.

18a: yield 20%; mp 115–116 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 2222, 1712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, J = 7.1 Hz), 2.54 (s, 3 H), 3.78 (s, 3 H), 4.30 (q, 2 H, J = 7.1 Hz), 6.83 (d, 2 H, J = 8.7 Hz), 7.14 (d, 2 H, J = 8.7 Hz), 7.35 (d, 1 H, J = 7.8 Hz), 7.51 (s, 4 H), 7.55 (d, 1 H, J = 7.8 Hz), 7.94 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.19, 18.55, 55.45, 61.36, 113.06 (s), 114.39, 115.58, 117.93 (s), 118.14 (s), 119.99, 129.21 (s), 129.67, 130.19 (s), 130.75, 131.87, 133.98, 135.90 (s), 139.71 (s), 141.59 (s), 141.70 (s), 153.02 (s), 154.87 (s), 159.32 (s), 165.63 (s); mass spectrum, m/z (relative intensity) 462 (M^+, 100), 461 (24), 387 (36). Anal. Calcd for $C_{28}H_{22}N_4O_3$: C, 72.71; H, 4.79; N, 12.11. Found: C, 72.62; H, 4.82; N, 12.00.

17b: yield 30%; mp 241–242 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3360, 1700, 1520, 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3 H, J = 7.1 Hz), 2.50 (s, 3 H), 4.33 (dq, 1 H, J = 7.1, 11.5 Hz), 4.39 (dq, 1 H, J = 7.1, 11.5 Hz), 5.90 (s, 1 H), 6.22 (d, 1 H, J = 3.1 Hz), 6.74 (d, 1 H, J = 7.7 Hz), 7.12 (t, 1 H, J = 7.1 Hz), 7.25–7.35 (m, 5 H), 7.56 (d, 2 H, J = 8.8 Hz), 7.97 (d, 2 H, J = 7.8 Hz), 7.99 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.27, 18.21, 61.59, 72.07, 111.71, 113.45, 123.82, 124.44, 128.34, 129.07, 133.08, 135.83 (s), 138.51 (s), 142.21 (s), 147.75 (s), 152.04 (s), 165.99 (s), five carbons were not observed; mass spectrum, m/z (relative intensity) 454 (M^+, 100), 453 (70), 332 (45). Anal. Calcd for $C_{26}H_{22}N_4O_4$: C, 68.71; H, 4.88; N, 12.33. Found: C, 68.63; H, 4.85; N, 12.21.

18b: yield 23%; mp 181–182 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 1698, 1547, 1350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (t, 3 H, J = 7.1 Hz), 2.55 (s, 3 H), 4.29 (q, 2 H, J = 7.1 Hz), 7.25–7.37 (m, 6 H), 7.55–7.58 (m, 3 H), 7.96 (s, 1 H), 8.06 (d, 2 H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 14.19, 18.64, 61.42, 115.71, 117.93 (s), 120.28, 123.30, 128.79, 129.34, 129.81, 130.12, 134.07, 135.98 (s), 137.64 (s), 141.67 (s), 147.89 (s), 152.85 (s), 154.25 (s), 165.68 (s), three carbons were not observed; mass spectrum, m/z (relative intensity) 452 (M^+, 100), 451 (15), 77 (80). Anal. Calcd for $C_{26}H_{20}N_4O_4$: C, 69.02; H, 4.45; N, 12.38. Found: C, 68.95; H, 4.37; N, 12.30.

17c: yield 47%; mp 198 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3364, 1701, 1513, 1342 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3 H, J = 7.1 Hz), 2.25 (s, 3 H), 2.49 (s, 3 H), 4.31 (dq, 1 H, J = 7.1, 11.3 Hz), 4.37 (dq, 1 H, J = 7.1, 11.3 Hz), 5.74 (s, 1 H), 6.11 (d, 1 H, J = 2.7 Hz), 6.66 (d, 1 H, J = 7.8 Hz), 7.03 (d, 2 H, J = 8.2 Hz), 7.19 (d, 2 H, J = 8.2 Hz), 7.23 (d, 1 H, J = 7.8 Hz), 7.51 (d, 2 H, J = 8.8 Hz), 7.93 (d, 2 H, J = 8.8 Hz), 7.96 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.28, 18.20, 20.96, 61.44, 72.18, 110.56 (s), 111.22, 113.07, 123.72, 124.67, 125.29 (s), 128.27, 129.52, 132.74, 135.18 (s), 135.88 (s), 138.51 (s), 139.75 (s), 140.10 (s), 147.63 (s), 147.94 (s), 152.42 (s), 166.22 (s); mass spectrum, m/z (relative intensity) 468 (M^+, 100), 467 (75), 346 (71). Anal. Calcd for $C_{27}H_{24}N_4O_4$: C, 69.22; H, 5.16; N, 11.96. Found: C, 69.15; H, 5.14; N, 11.87.

18c: yield 11%; mp 245–246 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 1702, 1524, 1352 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H, J = 7.1 Hz), 2.32 (s, 3 H), 2.56 (s, 3 H), 4.30 (q, 2 H, J = 7.1 Hz), 7.13 (s, 4 H), 7.37 (d, 1 H, J = 7.7 Hz), 7.57 (d, 3 H, J = 8.9 Hz), 7.96 (s, 1 H), 8.08 (d, 2 H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 14.23, 18.67, 21.34, 61.45, 115.68, 117.98 (s), 120.22, 123.35, 129.43, 129.99, 130.09, 134.06, 134.93 (s), 135.98 (s), 138.81 (s), 141.67 (s), 141.81 (s), 147.85 (s), 152.98 (s), 154.45 (s), 165.69 (s); mass spectrum, m/z (relative intensity) 466 (M^+, 100), 465 (17), 391 (43). Anal. Calcd for $C_{27}H_{22}N_4O_4$: C, 69.52; H, 4.75; N, 12.01. Found: C, 69.45; H, 4.69; N, 12.04.

17d: yield 35%; mp 244–245 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3320, 1705, 1506, 1348 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H, J = 7.1 Hz), 2.49 (s, 3 H), 3.71 (s, 3 H), 4.30 (dq, 1 H, J = 7.1, 11.7 Hz), 4.33 (dq, 1 H, J = 7.1, 11.7 Hz), 5.90 (s, 1 H), 6.11 (d, 1 H, J = 2.8 Hz), 6.69 (d, 1 H, J = 7.7 Hz), 6.75 (d, 2 H, J = 8.8 Hz), 7.18 (d, 2 H, J = 8.8 Hz), 7.24 (d, 1 H, J = 7.7 Hz), 7.48 (d, 2 H, J = 8.4 Hz), 7.92 (s, 1 H), 7.94 (d, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.25, 18.15, 55.38, 61.50, 72.78, 109.77 (s), 111.06, 112.86, 114.27, 123.67, 124.93 (s), 127.18, 128.33, 133.07, 134.70 (s), 135.63 (s), 139.04 (s), 139.59 (s), 147.59 (s), 147.67 (s), 152.78 (s), 157.49 (s), 166.03 (s); mass spectrum, m/z (relative intensity) 484 (M^+, 80), 483 (47), 362 (100). Anal. Calcd for $C_{27}H_{24}N_4O_5$: C, 66.93; H, 4.99; N, 11.56. Found: C, 66.85; H, 4.91; N, 11.50.

18d: yield 19%; mp 111–112 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 1720, 1617, 1520, 1345 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, J = 7.1 Hz), 2.54 (s, 3 H), 3.77 (s, 3 H), 4.30 (q, 2 H, J = 7.1 Hz), 6.83 (d, 2 H, J = 8.9 Hz), 7.16 (d, 2 H, J = 8.9 Hz), 7.34 (d, 1 H, J = 7.8 Hz), 7.55 (d, 1 H, J = 7.8 Hz), 7.57 (d, 2 H, J = 8.9 Hz), 7.94 (s, 1 H), 8.07 (d, 2 H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 14.18, 18.56, 55.40, 61.35, 114.38, 115.52, 117.91 (s), 120.14, 123.26, 129.18 (s), 130.02, 130.19 (s), 130.73, 133.95, 135.86 (s), 141.63 (s), 141.83 (s), 147.74 (s), 153.07 (s), 154.44 (s), 159.27 (s), 165.24 (s), one carbon was not observed; mass spectrum, m/z (relative intensity) 482 (M^+, 100), 407 (63). Anal. Calcd for $C_{27}H_{22}N_4O_5$: C, 67.21; H, 4.59; N, 11.61. Found: C, 67.15; H, 4.49; N, 11.58.

Reaction of 4 with Carbon Disulfide. To a solution of the bis(iminophosphorane) **4** (1.29 g, 1.75 mmol) in 30 mL of dry benzene was added carbon disulfide (10 mL). The reaction mixture was heated at reflux temperature for 12 h. After cooling, the solvent was removed under reduced pressure to dryness. The solid residue was extracted with dry *n*-hexane (3 × 50 mL). The extracts were mixed and the solvent was concentrated to dryness. The resulting material was chromatographed on a silica gel column eluting with *n*-hexane/ether (4:1).

19: yield 23%; mp 106–107 °C; colorless prisms (ether); IR (Nujol) 2113, 2007, 1721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (t, 3 H, J = 7.1 Hz), 2.37 (s, 3 H), 4.39 (q, 2 H, J = 7.1 Hz), 7.14 (dd, 1 H, J = 2.2, 8.2 Hz), 7.21 (d, 1 H, J = 8.2 Hz), 7.38 (s, 1 H), 7.77 (d, 1 H, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.30, 19.85, 63.15, 122.21 (s), 125.28, 127.05, 127.24, 129.42 (s), 131.74, 132.66 (s), 135.96 (s), 137.35 (s), 145.53 (s), 162.45 (s); mass spectrum, m/z (relative intensity) 304 (M^+, 38), 172 (47), 115 (100). Anal. Calcd for $C_{14}H_{12}N_2O_2S_2$: C, 55.24; H, 3.97; N, 9.20. Found: C, 54.27; H, 4.02; N, 9.29.

20: yield 41%; mp 102 °C; colorless prisms (ether); IR (Nujol) 2130, 2066, 1725, 1719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3 H, J = 7.1 Hz), 1.41 (t, 3 H, J = 7.1 Hz), 2.37 (s, 3 H), 2.38 (s, 3 H), 4.38 (q, 2 H, J = 7.1 Hz), 4.39 (q, 2 H, J = 7.1 Hz), 7.10 (dd, 1 H, J = 2.2, 8.1 Hz), 7.17–7.20 (m, 3 H), 7.26 (s, 1 H), 7.46 (s, 1 H), 7.96 (d, 1 H, J = 1.8 Hz), 8.06 (d, 1 H, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.32, 14.34, 19.63, 19.97, 62.90, 62.98, 120.95, 123.97,

124.69, 126.25, 126.31, 126.61, 127.65, 128.32, 128.91, 131.33, 131.61, 132.29, 133.82, 135.09, 135.49, 136.24, 137.11, 144.21, 162.79, 164.25, one carbon was not observed; mass spectrum, m/z (relative intensity) 533 (M^+, 19), 215 (52), 115 (100). Anal. Calcd for $C_{27}H_{24}N_4O_4S_2$: C, 60.88; H, 4.54; N, 10.52. Found: C, 60.59; H, 4.60; N, 10.29.

Reaction of 20 with [*N*-(4-Methylphenyl)imino]triphenylphosphorane. To a solution of **20** (0.53 g, 1 mmol) in 25 mL of dry toluene was added [*N*-(4-methylphenyl)imino]-triphenylphosphorane (1.10 g, 3 mmol). The reaction mixture was heated at reflux temperature for 3 h and afterwards at 150 °C in a sealed tube for 12 h. After cooling, the solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel column; *n*-hexane/ethyl acetate, 7:3) to give **5e** (48%) and **22**.

22: yield 51%; mp 243 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3267, 1719, 1439, 1336, 1111 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (t, 3 H, J = 7.1 Hz), 2.25 (s, 3 H), 2.41 (s, 3 H), 4.32 (q, 2 H, J = 7.1 Hz), 6.36 (s, 1 H, J = 7.8 Hz), 6.86 (d, 2 H, J = 8.3 Hz), 6.92 (d, 2 H, J = 8.3 Hz), 7.42–7.61 (m, 10 H), 7.71–7.82 (m, 7 H), 13.61 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.36, 18.96, 20.76, 60.95, 111.16, 115.97 (s, d, J_{P-C} = 19.9 Hz), 119.12 (d, J_{P-C} = 12.7 Hz), 119.73, 123.29 (s), 128.64 (s, d, J_{P-C} = 99.9 Hz), 128.82, 129.14 (d, J_{P-C} = 12.1 Hz), 130.22 (s), 130.68, 132.47 (d, J_{P-C} = 2.6 Hz), 132.81 (d, J_{P-C} = 9.8 Hz), 138.07 (s, d, J_{P-C} = 2.3 Hz), 138.66 (s, d, J_{P-C} = 2.9 Hz), 147.47 (s, d, J_{P-C} = 3.0 Hz), 155.67 (s, d, J_{P-C} = 1.5 Hz), 167.06 (s), one carbon was not observed; ^{31}P NMR ($CDCl_3$) δ 10.69; mass spectrum, m/z (relative intensity) 595 (M^+, 25), 183 (100), 108 (30). Anal. Calcd for $C_{38}H_{34}N_3O_2P$: C, 76.62; H, 5.75; N, 7.05. Found: C, 76.55; H, 5.71; N, 6.98.

Preparation of 5-(Ethoxycarbonyl)-3-(4-methylphenyl)-7-methyl-1*H*-pyrido[2,3,4-*de*]quinazoline-2-thione. To a solution of **22** (0.12 g, 0.2 mmol) in 10 mL of dry toluene was added carbon disulfide (1 mL). The mixture was heated at 140 °C in a sealed tube for 8 h. After cooling, the separated solid was isolated by filtration, dried, and recrystallized to give **23**: yield 68%; mp 299–300 °C; colorless prisms (toluene); IR (Nujol) 3296, 1698, 1169 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7.1 Hz), 2.44 (s, 3 H), 2.53 (s, 3 H), 4.27 (q, 2 H, J = 7.1 Hz), 7.06 (d, 1 H, J = 8.2 Hz), 7.27 (d, 2 H, J = 8.3 Hz), 7.38 (d, 2 H, J = 8.3 Hz), 7.44 (d, 1 H, J = 8.2 Hz), 7.98 (s, 1 H), 11.52 (s, 1 H), 11.52 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.02, 18.26, 21.50, 61.65, 109.40, 113.10 (s), 115.10, 127.85 (s), 128.78, 130.47, 133.56 (s), 133.76, 135.61 (s), 136.62 (s), 138.74 (s), 140.95 (s), 151.19 (s), 165.01 (s), 176.35 (s); mass spectrum, m/z (relative intensity) 377 (M^+, 67), 305 (100), 151 (29). Anal. Calcd for $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13. Found: C, 66.75; H, 5.00; N, 11.01.

Preparation of the Carbodiimide 21 (R = 4-$CH_3C_6H_4$). Procedure A. To a solution of the bis(iminophosphorane) **4** (1.29 g, 1.75 mmol) in 25 mL of dry methylene chloride was added at room temperature 4-methylphenyl isocyanate (0.23 g, 1.75 mmol) in the same solvent (25 mL) during 4–5 h. Afterwards, the solvent was removed under reduced pressure, the resulting material was dissolved in 30 mL of dry benzene, and carbon disulfide (10 mL) was added. The new reaction mixture was stirred at reflux temperature for 4 h. After cooling, the solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel column; *n*-hexane/ether, 4:1).

Procedure B. To a stirred solution of **19** (0.30 g, 1 mmol) in 20 mL of dry benzene at 50 °C was added dropwise a solution of [*N*-(4-methylphenyl)imino]triphenylphosphorane (0.36 g, 1 mmol) in the same solvent (20 mL), during 4 h, and the stirring was continued for 1 h. The solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel column; *n*-hexane/ether, 4:1).

21: yield 71% (procedure A), 65% (procedure B); viscous oil; IR (neat) 2135, 2021, 1727 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3 H, J = 7.1 Hz), 2.32 (s, 3 H), 2.35 (s, 3 H), 4.37 (q, 2 H, J = 7.1 Hz), 7.06–7.18 (m, 6 H), 7.44 (s, 1 H), 7.80 (d, 1 H, J = 2.1 Hz); mass spectrum m/z (relative intensity) 377 (M^+, 100), 345 (21), 91 (65). Anal. Calcd for $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13. Found: C, 66.73; H, 5.10; N, 11.01.

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Rearrangements of 1,6,7-Trisubstituted 2-Methyl-1,2,3,4-tetrahydroisoquinolinium 2-Methylides

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Chemical behavior of 1,6,7-trisubstituted 2-methyl-1,2,3,4-tetrahydroisoquinolinium 2-methylides **4** was investigated in fluoride-ion induced desilylation reaction of 1,6,7-trisubstituted 2-methyl-2-(trimethylsilyl)-methyl-1,2,3,4-tetrahydroisoquinolinium iodides **3**. The 1-nonsubstituted (**4a,b**) and 1-alkyl-substituted ylides (**4c,d**) gave mixtures of five products (**7–11**), but the 1-phenyl-substituted analogues (**4e,f**) yielded (*E*)- and (*Z*)-2,3-disubstituted 5-benzylidene-1,3-cyclohexadiene-6-spiro-3′-1′-methylpyrrolidines (*E*)-**5** and (*Z*)-**5** and 7,8-disubstituted 3-methyl-1-phenyl-2,3,4,5-tetrahydro-1*H*-3-benzazepines **6**. The mechanisms of the rearrangement are discussed.

Introduction

Ammonium ylide intermediates are usually produced by α-deprotonation of tetraorganoammonium salts under basic conditions, e.g., sodium amide in liquid ammonia.[1] However, it is difficult to prepare 2-methyl-1,2,3,4-tetrahydroisoquinolinium 2-methylides from 2,2-dimethyl-1,2,3,4-tetrahydroisoquinolinium salts because the α-deprotonation occurs on the 1-position in preference to the 2-methyl groups.[2] The ylide anions produced by fluoride-ion induced desilylation of trialkyl[(trimethylsilyl)-methyl]ammonium salts locate regioselectively on the

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