7306 J. Org. Chem. 1994, 59, 7306-7315

A New and Efficient Preparation of Cyclic Carbodiimides from Bis(iminophosphoranes) and the System Boc_2O/DMAP

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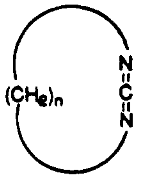
Received May 17, 1994⊗

A one-pot synthesis of cyclic carbodiimides which involves reaction of *C,C*-bis(aryliminophosphoranes) connected by aliphatic bridges with Boc_2O in the presence of DMAP is described. The method is also applicable when a heteroatom such as oxygen or nitrogen is incorporated into the tether connecting the two aromatic rings. A conformation study has been carried out on carbodiimide **23a**, which posseses a central nine-membered ring, using ^1H NMR spectroscopy and semiempirical as well as molecular mechanics calculations.

Although an enormous variety of heterocumulenes are known, only a few have been incorporated in strained rings.[1] Carbodiimides are the best known among strained heterocumulenes, and they have been the subject of spectroscopic studies in an attempt to examine the configurational stability of nitrogen in the NCN linkage.[2] The two main approaches for the preparation of cyclic carbodiimides involve either formation of the carbodiimide group into a preformed ring or ring expansion involving an exocyclic nitrogen functionality. The first approach, which is based on the dehydrosulfurization of cyclic thioureas with mercuric oxide[3] or triphenylphosphane in the presence of carbon tetrachloride and triethylamine,[4] allows the preparation of dibenzo[*e,g*][1,3]diazonine, 1,3-diazacyclonona-1,2-diene, and coronands with two carbodiimide groups, though in most cases they had not been isolated in a pure state. On the basis of the second approach the modified Tiemann rearrangement on cyclic amidoxime *O*-methanesulfonates has been used to synthesize cycloalkylenecarbodiimides **1** and 4,5,6,7-tetrahydrobenzo[1,3]diazonine.[5] 1,3-Diazacycloocta-1,2-diene (**1**, $n = 5$) proved to be the smallest isolable structure; this compound easily oligomerized and was undistillable. Several very labile seven-membered ring carbodiimides have been prepared and spectroscopically identified by flash vacuum pyrolysis of heteroaromatic azides at elevated temperatures.[6]



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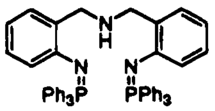
n = 5,6,7,10,11



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Continuing our interest on the preparation and synthetic applications of functionalized carbodiimides, we have shown that bis(iminophosphoranes) are valuable building blocks for the preparation of bis(carbodiimides) which undergo a plethora of heterocyclization reactions via multistep processes to give complex nitrogen-containing heterocyclic systems.[7] In this context, we have recently reported that bis(iminophosphoranes) type **2** react with aromatic isocyanates to give directly ($6 + n$) ($n = 5$, 6, 7, and 8) rigid bicyclic guanidines.[8]

In this paper we describe an easy and efficient preparation of cyclic carbodiimides of varying ring size and complexity, starting from appropriate *C,C*-bis(iminophosphoranes), in which both iminophosphorane groups are directly linked to different aromatic rings, by reaction with Boc_2O. This new annulation approach has suprisingly been found to be useful in the construction of medium- and large-membered cyclic carbodiimides.

Results and Discussion

It has been reported[9] that a wide range of nitrogen compounds can be converted to the corresponding *tert*-butoxycarbonyl (Boc) derivatives under rather mild conditions using Boc_2O as reagent and 4-(dimethylamino)pyridine (DMAP) as catalyst. So, at first it was of interest to study the behavior of simple iminophosphoranes toward the combination Boc_2O/DMAP. Thus, iminophosphorane **3** derived from 1-naphthylamine reacted with a equiv of Boc_2O in the presence of DMAP in dry dichloromethane at room temperature to give bis(1-naphthyl)carbodiimide (**4**) in 64% yield. Likewise, iminophosphorane **5** under the same reaction conditions

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⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1994.

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provided the N-protected carbodiimide **6** in 71% yield. However, iminophosphorane **7** derived from *o*-azidobenzylamine reacted with an excess of Boc$_2$O in the presence of DMAP under the aforementioned conditions to give the cyclic compound **8** in 75% yield (Scheme 1). At first these results could be explained by the fact that Boc$_2$O slowly decomposes to 2-methyl-2-propanol, isobutene, and two molecules of carbon dioxide,[10] so it seemed likely that the formation of carbodiimides **4**, **6** and compound **8** could involve an aza Wittig reaction between the iminophosphorane group and carbon dioxide resulting from the decomposition of Boc$_2$O to give an isocyanate as intermediate which eventually underwent either intermolecular aza Wittig-type reaction with a second molecule of starting iminophosphorane to give carbodiimides **4** and **6** or intramolecular nucleophilic attack of the amino group on the central carbon atom of the isocyanate to give the cyclic compound **8**. However, when the reactions between iminophosphoranes **5** and **7** with Boc$_2$O were carried out without DMAP, the corresponding *N*-Boc-protected iminophosphoranes were isolated as the only reaction products. So, the DMAP catalyst must play an unusual role to generate an unstable carbamic carbonic anhydride[11] which on standing at room temperature underwent a four-center rearrangement with loss of carbon dioxide avoiding side reactions.

Scheme 1

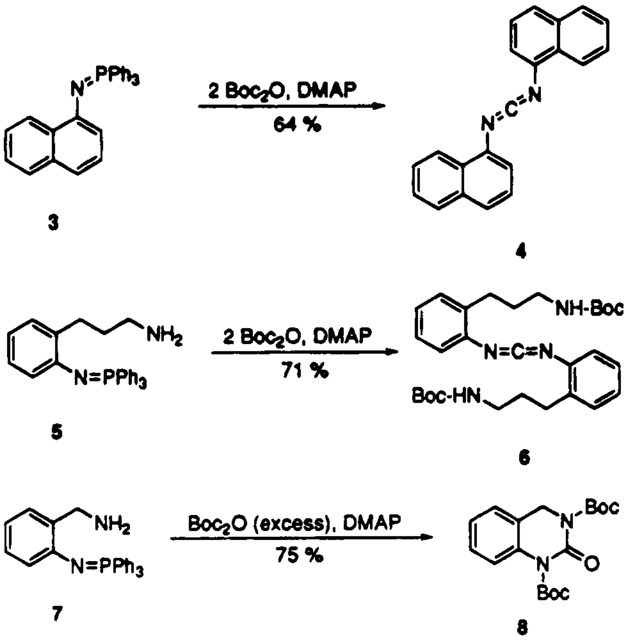
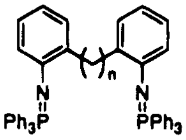


Table 1. Yield and Method of Preparation of Bis(iminophosphoranes) 9–11 and 14

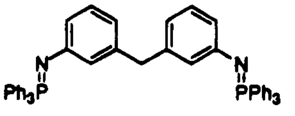
compd no.	yield (%)	method[a]
9a	85	A
9b	88	B
9c	92	A
9d	85	A
10	93	A
11	64	B
14a	68	B
14b	93	A
14c	83	B
14d	70	A

[a] For explanation of methods A and B see text.

Having established that the reaction of iminophosphoranes with the system Boc$_2$O/DMAP provides carbodiimides, it was decided that the next logical step in the development of this chemistry would be to study the intramolecular version of this process using bis(iminophosphoranes) in order to prepare the otherwise not readily available cyclic carbodiimides. Towards this end, the previously unreported bis(iminophosphoranes) **9–11** and **14** were prepared either by Staudinger reaction of the corresponding bis(azide) with triphenylphosphane (method A) or by treatment of the bis(amine) with dibromotriphenylphosphorane in the presence of triethylamine (method B) (Table 1). On the other hand, bis(iminophosphoranes) **12** were easily prepared by condensation of the appropriate (*o*-azidophenyl)alkylamine with *o*-azidobenzaldehyde, reaction with triphenylphosphane, and further reduction with sodium borohydride.[8] Bis(iminophosphorane) **13a** was prepared in 72% overall yield by the following sequence: (a) condensation of *o*-azidocinnamaldehyde[12] with *o*-azidocinnamylamine,[13] (b) Staudinger reaction with triphenylphosphane; and (c) reduction with sodium borohydride. Bis(iminophosphorane) **13b** was obtained in 67% yield from **13a** by treatment with BocN$_3$. Finally, reaction of 2–(2-azidophenyl)ethanol[14] with *N*-chlorosuccinimide and dimethyl sulfide in dichloromethane and further treatment of the resulting bis(azide) with triphenylphosphane fur-



9a (n = 0)
9b (n = 1)
9c (n = 2)
9d (n = 4)



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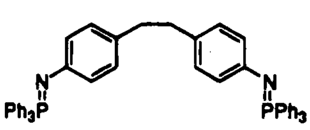

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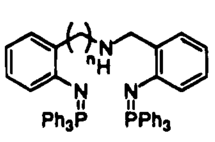
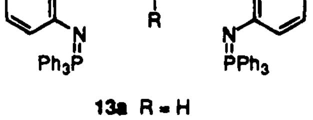
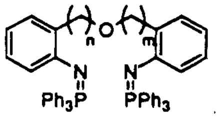


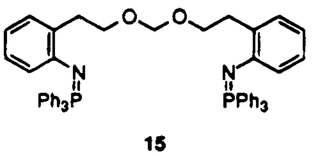
12a (n = 1)
12b (n = 2)
12c (n = 3)



13a R = H
13b R = Boc



14a (n = m = 0)
14b (n = m = 1)
14c (n = 1, m = 0)
14d (n = 1, m = 2)



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(13) Prepared from the commercially available *o*-nitrocinnamaldehyde by a six-step sequence in 49% yield: (a) reduction with sodium borohydride (99%); (b) reduction with sodium borohydride/Pd (98%); (c) diazotization followed by azidation (82%); (d) reaction with *N*-chlorosuccinimide/dimethyl sulfide (96%); (e) treatment with potassium phthalimide (91%); and (f) hydrazinolysis (70%).

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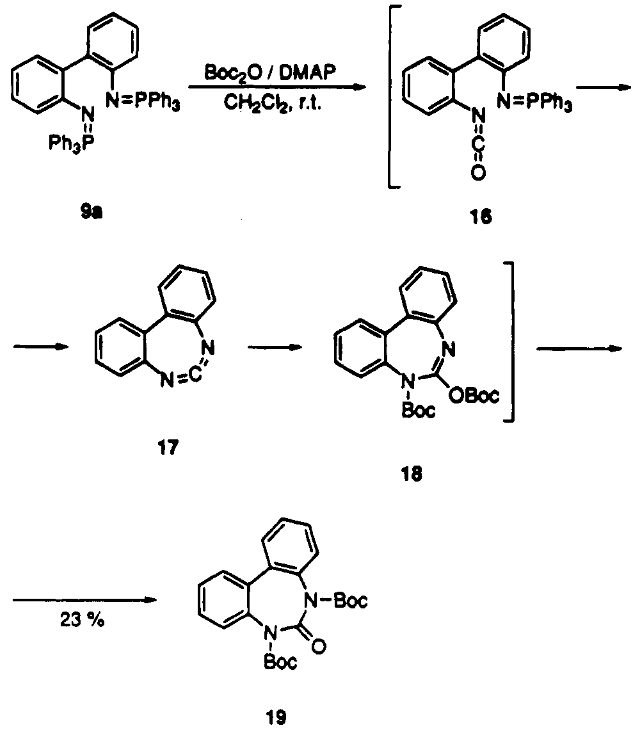
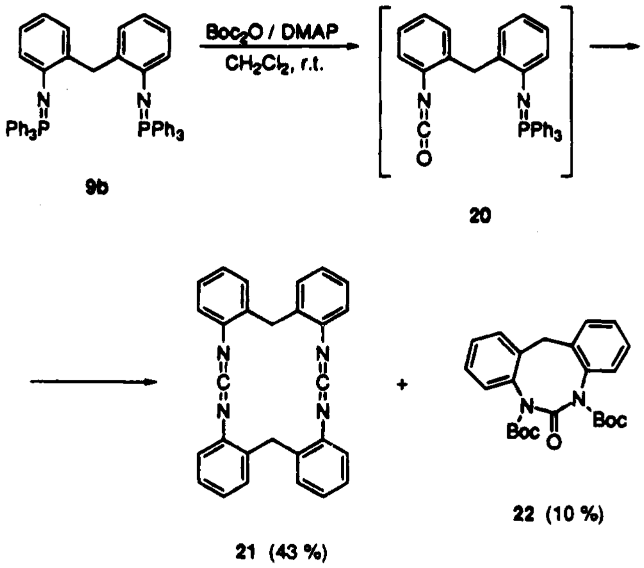
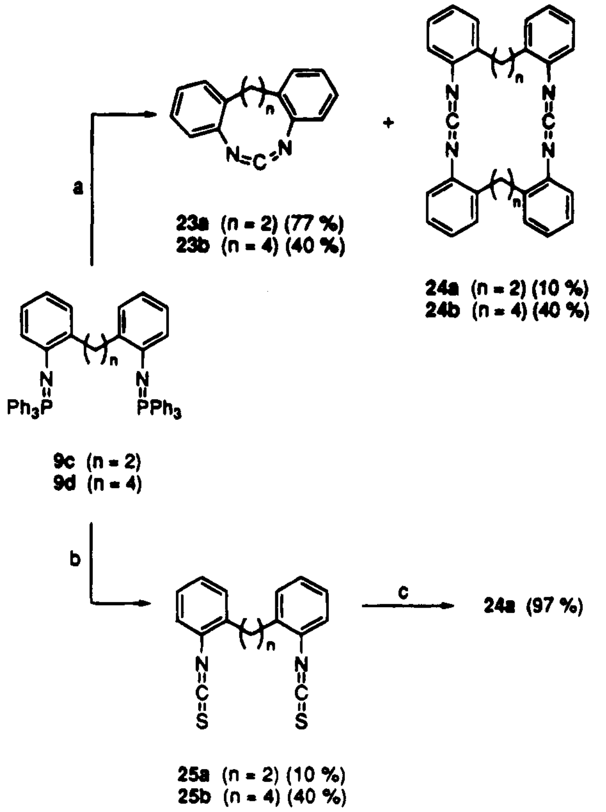
Scheme 2



Scheme 3



Scheme 4[a]



[a] Reagents and conditions: (a) Boc$_2$O (2 equiv), DMAP, CH$_2$Cl$_2$, rt; (b) CS$_2$ (20 equiv), C$_6$H$_6$, reflux; (c) **9c** (1 equiv), C$_6$H$_6$, reflux.

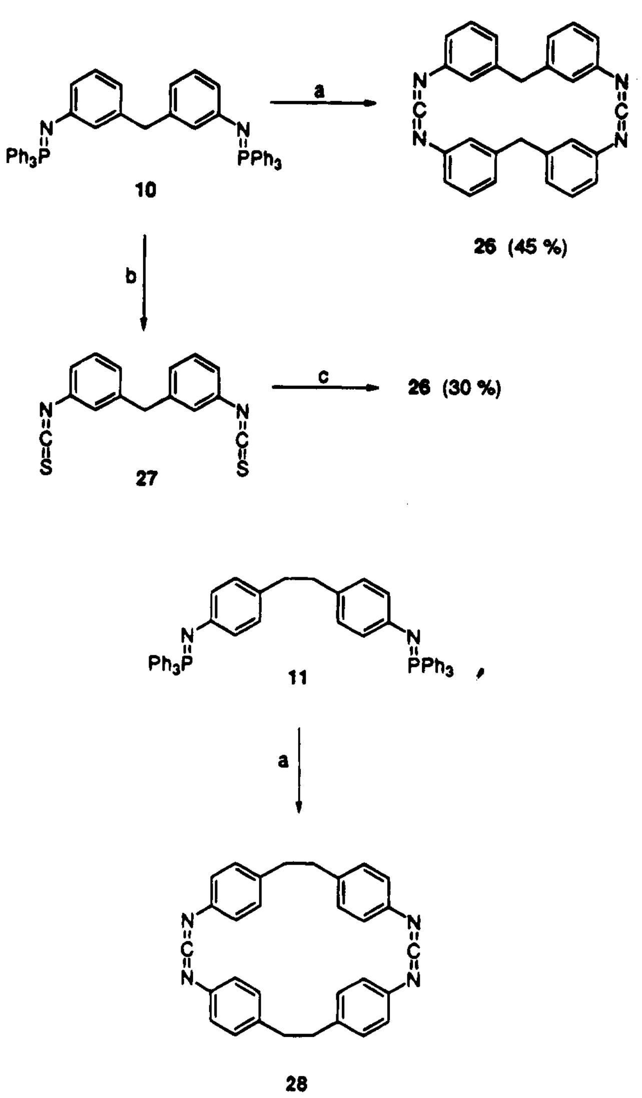
nished the bis(iminophosphorane) **15** in an overall yield of 20%.

Bis(iminophosphorane) **9a** reacted with 2 equiv of Boc$_2$O in the presence of 1 equiv of DMAP in dry dichloromethane at room temperature to give the tricyclic compound **19** in 23% yield. A tentative mechanism for this conversion could involve initial conversion of one iminophosphorane group of the starting material **9a** into an isocyanate function to give the intermediate **16** which underwent an intramolecular aza Wittig-type reaction to afford the highly reactive carbodiimide **17**, which reacted with the second equivalent of Boc$_2$O to give a isourea **18** which, under the reaction conditions, rearranged to the final product **19** (Scheme 2).

Bis(iminophosphorane) **9b** reacted with the Boc$_2$O/DMAP system under the same reaction conditions to give the cyclic bis(carbodiimide) **21** as major product (43%) and the tricyclic compound **22** as minor product (10%). Probably, the conversion **9b** → **21** + **22** takes place through the intermediate **20** bearing two reactive groups for the aza Wittig reaction, which undergoes either intermolecular aza Wittig-type reaction to give **21** or intramolecular condensation followed by addition of the second equivalent of Boc$_2$O to give **22** (Scheme 3).

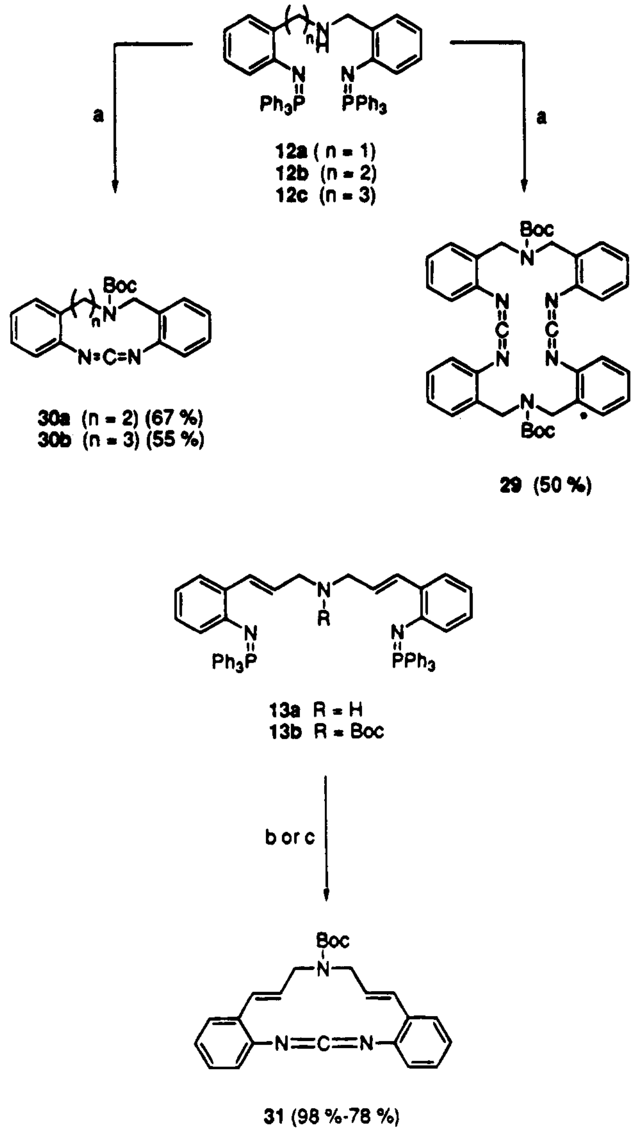
Bis(iminophosphorane) **9c** reacted with the Boc$_2$O/DMAP system to give 6,7-dihydrodibenzo[*d*,*h*][1,3]diazonine (**23a**), isolated as crystalline solid after chromatographic purification in 77% yield, accompanied by a minor amount of the bis(carbodiimide) **24a** (10%). However, the related bis(iminophosphorane) **9d** provided a 1:1 mixture of the carbodiimide **23b** and bis(carbodiimide) **24b**. It is worth noticing that earlier attempts to prepare **23a** were unsuccessful.[5] Bis(carbodiimide) **24a** was prepared by a two-step route: reaction of bis(iminophosphorane) **9c** with carbon disulfide led to the bis(isothiocyanate) **25a** in 93% yield, which reacted in aza Wittig-type fashion with **9c** to afford the cyclic bis(carbodiimide) **24a** as a crystalline solid in 97% yield, high-dilution techniques not being mandatory to favor the **24a** formation. Attempts to prepare the cyclic bis(carbodiimide) **24b** using this route failed. Thus, bis(isothiocyanate) **25b**, available from **9d** and carbon disulfide in 92% yield, reacted with **9d** in benzene at reflux temperature to give **24b** in disappointing yield (less than 10%). The reaction of bis(iminophosphorane) **9c** with carbon dioxide led to a mixture of **23a** (major component), **24a**, and the corresponding bis(isocyanate) (Scheme 4). On the other hand, the bis(iminophosphoranes) **10** and **11** reacted with Boc$_2$O/DMAP to give the macrocyclic bis(carbodiimides) **26** and **28** as crystalline solids in 45% and 84% yield. Bis(carbodiimide) **26** was also obtained in 30% yield by reaction of bis(isothiocyanate) **27** with 1 equiv of **10** (Scheme 5).

Scheme 5[a]



[a] Reagents and conditions: (a) Boc_2O (2 equiv), DMAP, CH_2Cl_2, rt; (b) CS_2 (20 equiv), C_6H_6, reflux; (c) **10** (1 equiv), C_6H_6, reflux.

Scheme 6[a]



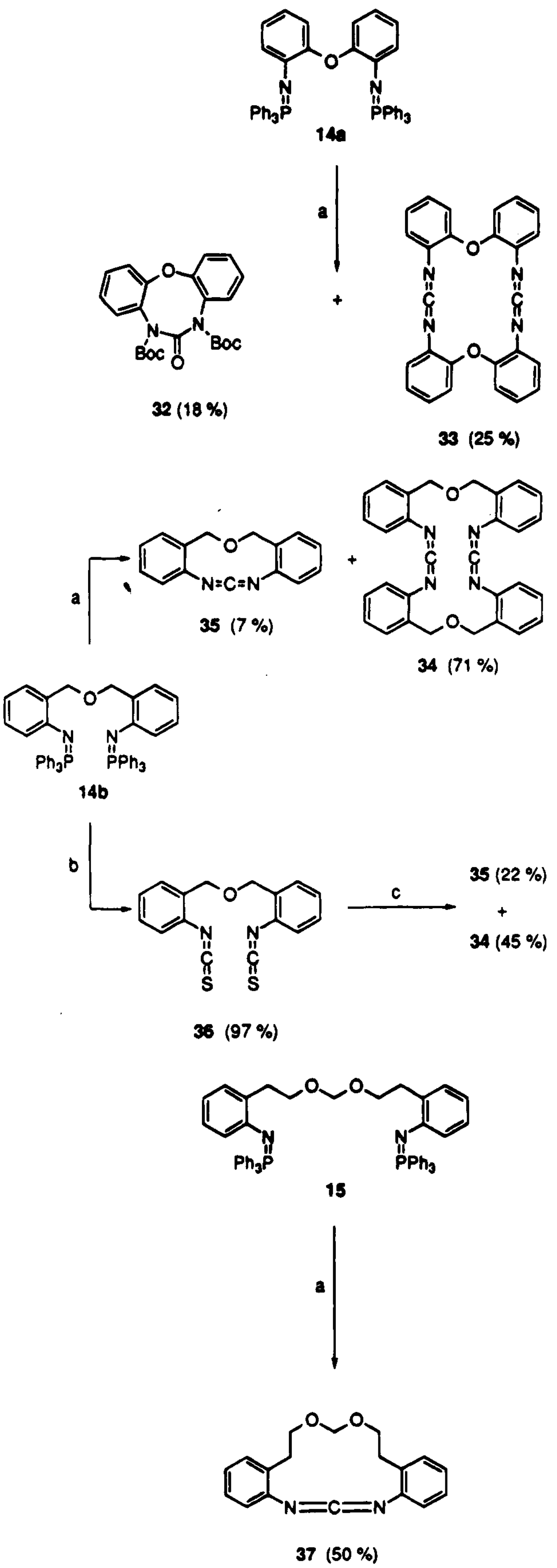
[a] Reagents and conditions: (a) Boc_2O (excess), DMAP, CH_2Cl_2, rt; for **13a**; (b) Boc_2O (2 equiv), DMAP, CH_2Cl_2, rt; for **13b**; (c) Boc_2O (excess), DMAP, CH_2Cl_2, rt or CO_2, C_6H_6, 70 °C, sealed tube.

The incorporation of a heteroatom into the tether connecting the two aromatic rings has also been examined. Bis(iminophosphorane) **12a** reacted with an excess of Boc_2O in the presence of DMAP in dry dichloromethane at room temperature to give the 20-membered bis(carbodiimide) **29** in 50% yield. The *N*-Boc-protected bis(iminophosphorane) derived from **12a** also reacted either with Boc_2O/DMAP or carbon dioxide to give **29** in low yields (16−20%), whereas with carbon disulfide led to the corresponding bis(isothiocyanate). However, bis(iminophosphoranes) **12b** and **12c** under the same conditions afforded the cyclic carbodiimides **30a** and **30b** in 67% and 55% yields, respectively. On the other hand, bis(iminophosphorane) **13a** reacted with 2 equiv of Boc_2O in the presence of DMAP under the same reaction conditions to give the cyclic carbodiimide **31** as a viscous oil in 45% yield. Better results were obtained starting from the bis(iminophosphorane) **13b**, available from **13a** and $BocN_3$ in 67% yield. In this case, the reaction with a slight excess of Boc_2O under the above-mentioned conditions led to **31** in almost quantitative yield (98%). Compound **13b** also reacted with carbon dioxide in dry benzene at 70 °C in a sealed tube to give **31** in 78% yield. Similarly, reaction with carbon disulfide in benzene at reflux temperature also led to **31**, albeit in low yield (15%) (Scheme 6). It is worth noticing that the reaction of **13a** with carbon dioxide yielded a complex mixture in which the cyclic carbodiimide **31** could not be detected. When the reaction between bis(iminophosphoranes) **12a**, **12c**, **13a**, and **13b** and Boc_2O was carried out without DMAP, the corresponding *N*-Boc-protected bis(iminophosphoranes) were isolated as the only reaction products.

The presence of an oxygen atom into the tether connecting the two aromatic rings did not affect the general behavior observed in bis(iminophosphoranes) type **9** and **12**. Thus, bis(iminophosphorane) **14a** reacted with Boc_2O/DMAP to give the tricyclic compound **32** along with the bis(carbodiimide) **33**, which were isolated in moderate yields as crystalline solids after chromatographic separation. The related bis(iminophosphorane) **14b** provided the cyclic bis(carbodiimide) **34** in excellent yield (70%) together with the cyclic carbodiimide **35** albeit in very low yield (7%). These carbodiimides could also be obtained from the bis(isothiocyanate) **36**, prepared in excellent yield (97%) from the bis(iminophosphorane) **14b** and carbon disulfide, by aza Wittig-type reaction with **14b**. In this reaction the cyclic carbodiimide **35** was isolated in yield somewhat higher (22%) than from **14b** and the system Boc_2O/DMAP, whereas the cyclic bis-

(carbodiimide) **34** was obtained in lower yield (45%) with respect to the direct formation from **14b**. Bis(iminophosphoranes) **14c** and **14d** led to complex mixtures in which at least three different types of carbodiimides could be detected by ^{1}H-NMR analysis of the crude, although all attempts to isolate some pure material by chromatography were unsuccessful. Finally, the related bis(iminophosphorane) **15** led directly to the cyclic carbodiimide **37** in 50% yield as the only reaction product (Scheme 7).

Scheme 7^{a}



^{a}a Reagents and conditions: (a) Boc_2O (2 equiv), DMAP, CH_2Cl_2, rt; (b) CS_2 (20 equiv), C_6H_6, reflux; (c) **14c** (1 equiv), C_6H_6, reflux.

In general all cyclic carbodiimides and bis(carbodiimides) were isolated as stable crystalline solids after chromatographic separation, except the *N*-Boc-protected carbodiimides **29–31**, which were isolated as viscous oils. In solution they can be kept for several months without change. The IR carbodiimide band ranged from 2129 cm^{-1} for **23a** (nine-membered ring) to 2186 cm^{-1} for **31** (14-membered ring). The lower value in **23a** is probably due to a weakening of the heterocumulene band as a result of an increased strain on the N=C=N moiety.

The ^{1}H and ^{13}C NMR, spectra of cyclic carbodiimides showed the expected signals for the bridges and aromatic rings, except the *N*-Boc-protected carbodiimides **29** and **31** which showed temperature-dependent signals. In the ^{1}H NMR spectrum of **29** the multiplet centered at δ 4.59–4.65 appeared as four signals at 273 K and as two signals at 233 K. Likewise, when the ^{1}H NMR spectrum of **31** is carried out at temperature below to 263 K the multiplet centered at δ 4.10–4.22 appears now as two doublets, and the multiplet centered at 6.13–6.25 appears as two double-triplets. In addition, the broad signals appearing in the ^{13}C NMR spectrum of **31** are split when the spectrum is recorded at 243 K.

Theoretical Calculations and ^{1}H NMR Study of 6,7-Dihydrodibenzo[d,h][1,3]diazonine (23a). The conformational study of this compound has been approached simultaneously by theoretical methods and by ^{1}H NMR spectroscopy. Both molecular mechanics[15] and semiempirical calculations (AM1)[16] led to the same conformation for the fully optimized geometry which is represented in Figure 1 using the PLUTO program.[17] The dihedral angles and the corresponding vicinal $^{3}J(^{1}H, ^{1}H)$ coupling constants[18] are reported in Table 2; Table 3 contains interatomic distances corresponding to the AM1-optimized geometry. The system is very rigid and no interconversion (nitrogen and/or ring inversion) is possible.

The geometry of Figure 1 corresponds in ^{1}H NMR to an AA'BB' system for the ethane bridge and to two identical ABCD systems for the aromatic protons. The ethane part obtained at 500 MHz in acetone at room temperature (near 298 K) is represented in Figure 2 (top). It can be seen that the low-field part of the spectrum is broader than the high-field part probably due to a small coupling with some aromatic protons. On the other hand, the aromatic part shows that the low-field triplet of doublets (at 7.25 ppm, necessarily H6 or H7) is of much lower intensity than the other similar multiplet due to the above-mentioned small coupling constant. The aromatic proton which shows this coupling must be H6(H6') since a COSY experiment [$^{3}J(^{1}H,^{1}H)$ ortho couplings] established the sequence 7.32 ppm (d,d) ↔ 7.25 ppm (t,d), ↔ 7.12 ppm (t,d) ↔ 7.00 ppm (d,d), i.e., 7.32 [H5(H5')], 7.25 [H6(H6')], 7.12 [H7(H7')], and 7.00 [H8(H8')]. The

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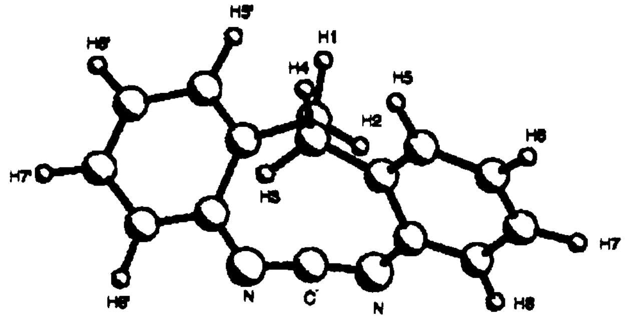

Figure 1. View of the AM1 optimized geometry of compound **23a**.

Table 2. Coupling Constants (in Hz) and Dihedral Angles, Φ, Obtained by Theoretical Methods

	MM2		AM1	
fragment	$J(^1H-^1H)$	ϕ (deg)	$J(^1H-^1H)$	ϕ
H1,H3	6.75	134	6.53	132.8
H1,H4	10.41	−20	10.79	−17.32
H2,H3	2.40	112	2.40	111.64
H2,H4	6.75	−134	6.75	−132.83

decoupling of aromatic protons results in a spectrum [Figure 2 (bottom)] for the ethane part totally symmetric as expected for an AA′BB′ system.

A NOESY experiment shows a correlation spot for the aromatic proton at 7.32 ppm [H5(H5′)] and the AA′ part of the system centered at 3.15 ppm. This result, together with the calculated distances of Table 3, allows us to identify the AA′ part is belonging to H1 and H4. Consequently, the small coupling constant between aromatic and aliphatic BB′ protons involves H2−H6′ and H3−H6, and it is related to the $^5J(^1H,^1H)$ "zig−zag path" coupling constant.[19]

The analysis, using the PANIC86 program,[20] of the decoupled spectrum of Figure 2 (bottom) yields the parameters of Table 4. Using the Altona generalization of the Karplus equation,[18] the following dihedral angles are obtained: H1−H3 138°, H1−H4 0°, H2−H3 106°, and H2−H4 −138°, values in excellent agreement with the calculated values of Table 2 taking into account small oscillations about the equilibrium geometry. These small oscillations have very low activation energy which explains why even at 183 K no modification of the spectrum obtained at 298 K is observed.

Concluding Remarks

The work described in this paper shows for the first time that easily available *C,C*-bis(aryliminophosphoranes) undergo an intramolecular aza Wittig reaction by the action of the system Boc_2O/DMAP to afford the otherwise not readly available cyclic carbodiimides with variable substituents and ring size. Although aza Wittig reactions have recently been utilized in the synthesis of five-, six-, and even seven-membered nitrogen heterocycles, the present result is the first example of utilization for the synthesis of large-membered heterocycles.

Experimental Section

General Methods. All melting points were obtained 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 Varian Unity 300 apparatus (^1H at 299.95 MHz and ^{13}C at 74.43 MHz), and chemical shifts are expressed in parts per million (δ) relative to tetramethylisilane. The signals were assigned by DEPT-135 and ^{13}C gate-decoupled spectra, as well as by COSY-45 and $^1H-^{13}C$ 2D heteronuclear correlation experiments. ^{31}P NMR spectra were observed at 121.42 MHz, and chemical shifts are referenced to 85% H_3PO_4. The mass spectra were carried out on a VG-Autospec L-SIMS spectrometer, and in the FAB mode *m*-nitrobenzyl alcohol was used as matrix. Elemental analyses were recorded on an Eager 200 instrument.

The ^1H NMR spectra of compound **23a** were recorded on a Varian UNITY-500 spectrometer operating at 499.84 MHz, using [$^2H_6$]acetone as solvent. The spectra were acquired using 3660 Hz spectral width digitized with 32 K data points with a pulse width of 12 ms (90° flip angle). Digital resolution for the real part was ±0.2 Hz. Gaussian multiplication was used prior to Fourier transform. Variable-temperature experiments were carried out in the same conditions. The temperature was varied in the range 193−298 K.

The phase-sensitive NOESY experiment on compound **23a** was performed at 298 K. The spectral widths were 3660 Hz in both domains, a relaxation delay of 2.0 s, a mixing time of 500 ms, and 256 increments with 1024 data points each. Zero filling of the F1 dimensions produced a 1024 × 1024 data matrix after 2D Fourier transform.

The number of data points, number of increments and the spectral widths of the COSY spectrum were the same as those in the NOESY spectrum. A relaxation delay of 1 s was used.

The ^1H-NMR iterative analysis of the spectrum was performed using the PANIC program.[20]

Materials. 1-[(Triphenylphosphoranylidene)amino]naphthalene[21] (**3**) and bis(iminophosphoranes)[8] **12** were prepared as described in the literature. The previously unreported iminophosphoranes **5** and **7** were prepared in 86% and 93% yield, respectively, from triphenylphosphane and 3-(*o*-azidophenyl)propylamine[8] or 2-azidobenzylamine.

Reaction of Iminophosphoranes 3 and 5 with Boc_2O/DMAP. To a solution of iminophosphorane **3** or **5** (0.74 mmol) in 10 mL of dry dichloromethane were added Boc_2O (0.32 g, 1.48 mmol) and DMAP (0.09 g, 0.74 mmol). The reaction mixture was stirred at room temperature under nitrogen for 48 h, the solvent was removed under reduced pressure, and the resulting material was purified by column chromatography (silica gel, *n*-hexane/diethyl ether 1:1) to give either bis(1-naphthyl)carbodiimide[22] (**4**) (64%) as a viscous oil or carbodiimide **6**: yield 71%; oil; IR (neat) 3358, 2146, 1693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (s, 18H), 1.82 (m, 4H), 2.75 (t, 4H, *J* = 7.6 Hz), 3.11−3.23 (m, 4H), 4.81 (br s, 2H), 7.05−7.23 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.4, 29.3, 30.7, 40.2, 79.0, 124.9, 125.6, 127.5, 130.2, 134.0, 135.8, 136.7, 156.0; mass spectrum *m/z* (relative intensity) 508 (M^+, 5), 57 (100). Anal. Calcd for $C_{29}H_{40}N_4O_4$; C, 68.48; H, 7.93; N, 11.01. Found: C, 68.15; H, 8.17; N, 10.85.

Reaction of Iminophosphorane 7 with Boc_2O/DMAP. To a solution of iminophosphorane **7** (0.25 g, 0.65 mmol) in 10 mL of dry dichloromethane were added Boc_2O (1.00 g, 4.58 mmol) and DMAP (0.079 g, 0.65 mmol). The mixture was stirred at room temperature under nitrogen for 12 h, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, diethyl ether/*n*-hexane 7:3) and further recrystallization from *n*-hexane to give **8**: yield 75%; mp 127−129 °C; IR (Nujol) 1789, 1727, 1297, 1138 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 9H), 1.58 (s, 9H), 4.71 (s, 2H), 7.16 (td, 1H, *J* = 7.4, 1.2 Hz), 7.22 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.32 (td, 1H, *J* = 7.7, 1.6 Hz), 7.55 (dd, 1H, *J* = 8.1, 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 27.8, 28.0, 45.3, 83.8, 84.5, 120.4, 125.0, 125.3, 126.1, 128.1, 136.0, 149.5, 150.7, 151.6; mass spectrum *m/z* (relative intensity) 348 (M^+, 5), 192 (40), 57 (100). Anal. Calcd for $C_{18}H_{24}N_2O_5$; C, 62.05; H, 6.94; N, 8.04. Found: C, 61.87; H, 7.12; N, 7.88.

2,2′-Diazidobiphenyl. To a solution of 2,2′-diaminobiphenyl[23] (1.32 g, 9.88 mmol) cooled at 0 °C in 70 mL of 2 N

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Table 3. Interatomic Distances Corresponding to the AM1 Optimized Geometry (Figure 1)

fragment	H1,H5	H2,H5	H3,H5	H4,H5	H1,H5′	H2,H5′	H3,H5′	H4,H5′
d(Å)	3.42	3.70	3.62	2.33	2.33	3.62	3.70	3.42

Table 4. Values of the PANIC Analysis of the Ethane Fragment. Chemical Shifts in ppm and Coupling Constants in Hz

atom	δ	error	fragment	$J(^1H-^1H)$	error
H1 (H4)	3.129	0.027	H1,H2 (H3,H4)	−15.56	0.044
H2 (H3)	3.200	0.028	H1,H3 (H2,H4)	7.58	0.042
			H1,H4	11.97	0.063
			H2,H3	1.52	0.061

HCl was added dropwise a solution of sodium nitrite (2.07 g, 30 mmol) in 15 mL of water. The resultant solution was stirred at 0 °C for 1 h. Then, a solution of sodium azide (2.66 g, 41 mmol) in 15 mL of water was added dropwise and allowed to warm at room temperature. The mixture was stirred at that temperature for 12 h. The yellow precipitated solid was collected by filtration, washed with water (3 × 10 mL), and air-dried to give 2,2′-diazidobiphenyl (2.05 g, 88%) as pale yellow crystals, mp 69–70 °C (from ethanol). Anal. Calcd. for $C_{12}H_8N_6$: C, 61.01; H, 3.41; N, 35.57. Found: C, 60.89; H, 3.31; N, 35.29.

Following this procedure the following azides were prepared:

1,2-Bis(2-azidophenyl)ethane. From 1,2-bis(2-aminophenyl)ethane;[24] yield 67%; mp 104–106 °C; colorless prisms (dichloromethane). Anal. Calcd for $C_{14}H_{12}N_6$: C, 63.63; H, 4.58; N, 31.80. Found: C, 63.41; H, 4.69; N, 32.13.

1,4-Bis(2-azidophenyl)butane. From (*E,E*)-1,4-bis(2-nitrophenyl)buta-1,3-diene[25] by catalytic hydrogenation with Pd on charcoal (95%) and further diazotation followed by azidation: yield 93%; mp 75–77 °C; colorless prisms (*n*-hexane). Anal. Calcd for $C_{16}H_{16}N_6$: C, 65.74; H, 5.52; N, 28.75. Found: C, 65.55; H, 5.57; N, 28.82.

Bis(3-azidophenyl)methane. From bis(3-aminophenyl)methane:[24] yield 98%; oil. Anal. Calcd for $C_{13}H_{10}N_6$: C, 62.39; H, 4.03; N, 33.58. Found: C, 62.55; H, 3.91; N, 33.70.

General Procedure for the Preparation of Bis(iminophosphoranes) 9a, 9c, 9d, and 10. To a well-stirred solution of the appropriate diazide (2,2′-diazido)biphenyl, 1,2-bis(2-azidophenyl)ethane, 1,4-bis(2-azidophenyl)butane (4.50 mmol), or bis(3-azidophenyl)methane in 15 mL of dry diethyl ether was added triphenylphosphane (2.34 g, 8.93 mmol). The reaction mixture was stirred at room temperature for 8 h. The separated solid was collected by filtration, washed with diethyl ether (2 × 10 mL), air-dried, and recrystallized from the adequate solvent.

9a: yield 85%; 259–260 °C; yellow crystals (dichloromethane/*n*-hexane). Anal. Calcd for $C_{48}H_{38}N_2P_2$: C, 81.80; H, 5.43; N, 3.97. Found: C, 81.63; H, 5.31; N, 3.79.

9c: yield 92%; mp 275–277 °C; colorless prisms (dichloromethane). Anal. Calcd for $C_{50}H_{42}N_2P_2$: C, 81.95; H, 5.78; N, 3.82. Found: C, 82.18; H, 5.55; N, 3.61.

9d: yield 85%; mp 218–220 °C; colorless prisms (chloroform). Anal. Calcd for $C_{52}H_{46}N_2P_2$: C, 82.08; H, 6.09; N, 3.68. Found: C, 81.87; H, 5.83; N, 3.73.

10: yield 93%; mp 133–135 °C; colorless prisms (diethyl ether). Anal. Calcd for $C_{49}H_{40}N_2P_2$: C, 81.88; H, 5.61; N, 3.90. Found: C, 82.03; H, 5.69; N, 3.81.

Preparation of Bis(iminophosphoranes) 9b and 11. Bromine (0.79 g, 4.94 mmol) in 5 mL of dry benzene was added dropwise to a stirred solution of triphenylphosphane (1.30 g, 4.94 mmol) in 20 mL of the same solvent at 0 °C under nitrogen. The mixture was stirred for 1 h and then allowed to warm to room temperature. A solution of 2,2′-diaminodiphenylmethane[26] or 1,2-bis(4-aminophenyl)ethane (2.47 mmol) and triethylamine (1.00 g, 9.88 mmol) in 20 mL of dry benzene was added; after 5 h of heating under reflux, triethylammonium bromide was deposited and separated by filtration. The filtrate was concentrated to dryness, and the residual material was slurried with diethyl ether (2 × 10 mL) and recrystallized from the adequate solvent.

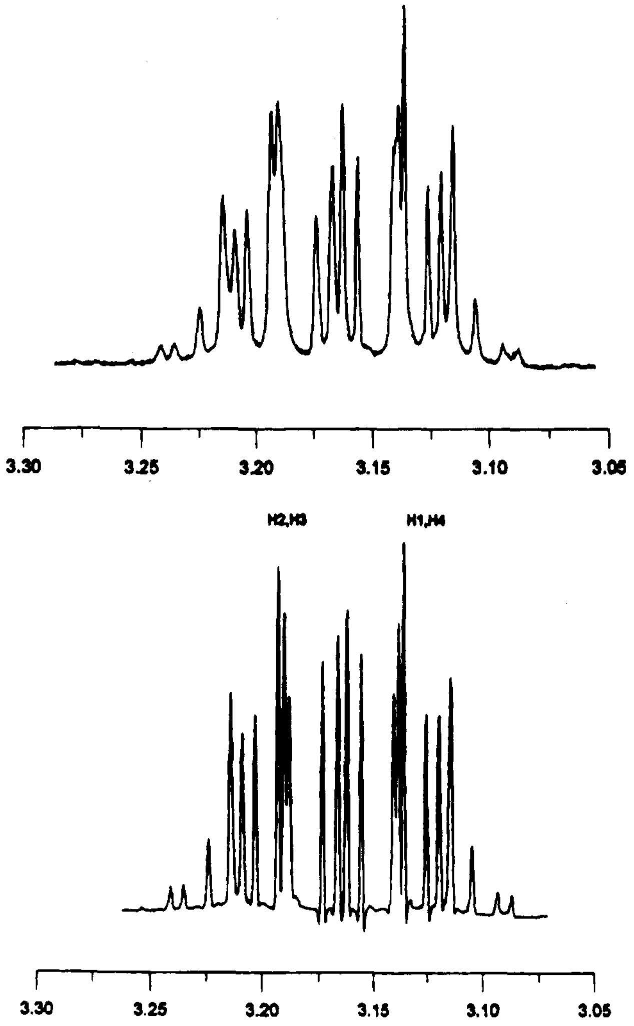

Figure 2. AA′BB′ part of the ^1H NMR spectra of compound **23a**: (top) normal spectrum; (bottom) spectrum obtained after proton decoupling of the aromatic protons.

9b: yield 88%; mp 211–212 °C; pale yellow crystals (diethyl ether). Anal. Calcd for $C_{49}H_{40}N_2P_2$: C, 81.88; H, 5.61; N, 3.90. Found: C, 81.68; H, 5.50; N, 3.73.

11: yield 64%; mp 162–164 °C; pale yellow crystals (dichloromethane). Anal. Calcd for $C_{50}H_{42}N_2P_2$: C, 81.95; H, 5.78; N, 3.82. Found: C, 82.10; H, 5.65; N, 3.89.

Preparation of Bis(iminophosphorane) 13a. A mixture of 2-azidocinnamaldehyde (0.97 g, 5.6 mmol) and 2-azidocinnamylamine (0.98 g, 5.6 mmol) in 20 mL of dry dichloromethane was stirred at room temperature, in the presence of $MgSO_4$ and Na_2SO_4, for 6 h until the band corresponding to the carbonyl group disappeared in the IR of the mixture. After filtration, the solvent was removed from the filtrate under reduced pressure and the residual material was dissolved in 15 mL of dry dichloromethane. Then a solution of triphenylphosphane (2.39 g, 9.12 mmol) in 15 mL of dry diethyl ether was added. The resultant mixture was stirred at room temperature for 3 h and then concentrated to dryness. The crude was dissolved in 20 mL of dry dichloromethane and 20 mL of anhydrous methanol and cooled at 0 °C. Sodium borohydride (0.38 g, 10 mmol) was added, the mixture was stirred at that temperature for 30 min, and then additional sodium borohydride (0.38 g, 10 mmol) was added and stirring was continued at room temperature for 1 h. The solvent was

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(24) Commercially available.

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removed under reduced pressure, and the solid residue was treated with cold water (2 × 20 mL), filtered, washed with cold water (3 × 15 mL), and recrystallized from diethyl ether to give **13a**: yield 72%; mp 96–98 °C; yellow crystals. Anal. Calcd for $C_{54}H_{47}N_3P_2$: C, 81.08; H, 5.92; N, 5.25. Found: C, 80.89; H, 5.79; N, 5.10.

Preparation of Bis(iminophosphorane) 13b. To a cooled (0 °C) solution of bis(iminophosphorane) **13a** (0.40 g, 0.50 mmol) in 5 mL of dimethyl sulfoxide was added dropwise a solution of *tert*-butyl azidoformate (0.36 g, 2.50 mmol) in 2 mL of dry diethyl ether. The reaction mixture was stirred at room temperature for 16 h, and then 10 mL of dichloromethane and 5 mL of water were added and stirring was continued for 10 min. The organic layer was separated, washed with water (2 × 25 mL), dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the crude product was chromatographed (silica gel, *n*-hexane/ethyl acetate 1:1) and recrystallized from benzene to give **13b**: yield 67%; mp 86–88 °C; yellow prisms. Anal. Calcd for $C_{59}H_{55}N_3O_2P_2$: C, 78.73; H, 6.16; N, 4.67. Found: C, 78.59; H, 6.01; N, 4.53.

Preparation of Bis(iminophosphoranes) 14a and 14c. To a well-stirred mixture of 2,2′-dinitrodiphenyl ether[27] (2.00 g, 7.68 mmol) and tin (7.75 g) in 40 mL of ethanol was added 60 mL of 35% hydrochloric acid. The resultant mixture was refluxed for 30 min. After cooling, the suspension was filtered and 60 mL of 50% aqueous NaOH was added. The precipitate was separated and the filtrate was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with water (3 × 10 mL), dried over $MgSO_4$, and concentrated to dryness. The crude product was purified by chromatography (silica gel, diethyl ether) to give **2,2′-diaminodiphenyl ether** in 79% yield as a viscous oil. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.05; H, 6.07; N, 13.78.

Reaction of 2,2′-diaminodiphenyl ether with dibromotriphenylphosphorane, as described for the preparation of bis(iminophosphoranes) **9b** and **11**, provided compound **14a**: yield 68%; mp 124–126 °C; pale yellow crystals (diethyl ether). Anal. Calcd for $C_{48}H_{38}N_2OP_2$: C, 79.99; H, 5.31; N, 3.89. Found: C, 80.23; H, 5.41; N, 3.78.

In a similar manner starting from 2,2′-diaminobenzylphenyl ether[28] bis(iminophosphorane) **14c** was prepared.

14c: yield 83%; mp 191–192 °C; pale yellow crystals (diethyl ether). Anal. Calcd for $C_{49}H_{40}N_2OP_2$: C, 80.09; H, 5.49; N, 3.81. Found: C, 80.13; H, 5.44; N, 3.69.

Bis(2,2′-diazidobenzyl) Ether. A mixture of 2-azidobenzyl alcohol (0.81 g, 5.46 mmol), 2-azidobenzyl chloride (1.83 g, 10.9 mmol), and tetrabutylammonium bromide (0.88 g, 2.7 mmol) in 11 mL of 50% aqueous NaOH and 13 mL of benzene was well stirred at room temperature for 6 h. Then, 12 mL of diethyl ether and 12 mL of water were added and stirring was continued for 15 min. The organic layer was separated, washed with water (3 × 15 mL), dried over $MgSO_4$, and concentrated to dryness. The residue was purified by chromatography (silica gel, diethyl ether/*n*-hexane (10:1) to give the **bis(2,2′-diazidobenzyl) ether** in 80% yield: mp 85–87 °C; pale yellow prisms (diethyl ether). Anal. Calcd for $C_{14}H_{12}N_6O$: C, 59.99; H, 4.32; N, 29.98. Found: C, 59.73; H, 4.28; N, 29.91.

2-Azidobenzyl 2-(2-Azidophenyl)ethyl Ether. A mixture of 2-(2-azidophenyl)ethanol[14] (0.50 g, 3.07 mmol), 2-azidobenzyl chloride (1.02 g, 6.13 mmol), and tetrabutylammonium bromide (0.49 g, 1.53 mmol) in 6 mL of 50% aqueous NaOH and 8 mL of benzene was vigorously stirred at room temperature for 20 h. Then, 8 mL of water was added, and stirring was continued for 15 min. The organic layer was separated, washed with water (3 × 10 mL), extracted with diethyl ether (3 × 20 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by chromatography (silica gel, *n*-hexane/diethyl ether 20:1) to give **2-azidobenzyl 2-(2-azidophenyl)ethyl ether** in 85% yield as a viscous oil. Anal. Calcd for $C_{15}H_{14}N_6O$: C, 61.22; H, 4.79; N, 28.55. Found: C, 61.12; H, 4.73; N, 28.49.

1,7-Bis(2-azidophenyl)-3,5-dioxaheptane. To a cooled suspension of *N*-chlorosuccinimide (3.34 g, 25 mmol) in 40 mL of dry dichloromethane was added dimethyl sulfide (1.74 g, 28 mmol) under nitrogen. The mixture was cooled at −15 °C, and a solution of (2-azidophenyl)ethanol (0.97 g, 5.95 mmol) in 50 mL of dry dichloromethane was added dropwise. The reaction mixture was stirred and allowed to warm at room temperature. Then, 50 mL of aqueous ammonium chloride was added, and the resultant solution was extracted with dichloromethane (3 × 20 mL), dried over $MgSO_4$, and concentrated to dryness. The crude was purified by chromatography (silica gel, *n*-hexane/diethyl ether 9:1) to give **1,7-bis(2-azidophenyl)-3,5-dioxaheptane**, yield 37%, as a viscous oil. Anal. Calcd for $C_{17}H_{18}N_6O_2$: C, 60.34; H, 5.36; N, 24.84. Found: C, 60.17; H, 5.21; N, 24.75.

Preparation of Bis(iminophosphoranes) 14b, 14d, and 15. These compounds were obtained following the method described for bis(iminophosphoranes) **9a**, **9c** and **9d**.

14b: yield 93%; mp 173–175 °C; pale yellow prisms (diethyl ether). Anal. Calcd for $C_{50}H_{42}N_2OP_2$: C, 80.20; H, 5.65; N, 3.74. Found: C, 79.99; H, 5.72; N, 3.64.

14d: yield 70%; mp 194–196 °C; colorless crystals (diethyl ether). Anal. Calcd for $C_{51}H_{44}N_2OP_2$: C, 80.30; H, 5.81; N, 3.67. Found: C, 80.43; H, 5.69; N, 3.72.

15: yield 50%; mp 56–58 °C; pale yellow crystals (diethyl ether/*n*-hexane). Anal. Calcd for $C_{58}H_{48}N_2O_2P_2$: C, 78.89; H, 6.00; N, 3.47. Found: C, 78.92; H, 5.81; N, 3.41.

Reaction of Bis(iminophosphoranes) 9 with the System Boc_2O/DMAP. General Procedure. To a solution of the appropriate bis(iminophosphorane) **9** (0.71 mmol) in 20 mL of dry dichloromethane were added Boc_2O (0.31 g, 1.40 mmol) and DMAP (0.086 g, 0.71 mmol). The reaction mixture was stirred under nitrogen at room temperature for 12 h. The solvent was removed under reduced pressure, and the residual material was chromatographed.

19: silica gel, *n*-hexane/ethyl acetate 1:1; yield 23%; mp 155–157 °C; colorless prisms (*n*-hexane/diethyl ether); IR (Nujol) 1761, 1727, 1308, 1217, 1147 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 18H), 7.43–7.48 (m, 4H), 7.51–7.54 (m, 2H), 7.59–7.62 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.9, 83.6, 128.2, 128.3, 128.5, 128.8, 134.0, 135.6, 151.4, 154.3; HRMS (EI) M$^+$ 410.1841, theor 410.1842. Anal. Calcd for $C_{23}H_{26}N_2O_5$: C, 67.30; H, 6.38; N, 6.82. Found: C, 67.19; H, 6.31; N, 6.80.

21: silica gel, *n*-hexane/diethyl ether 7:3; yield 43%; mp 207–209 °C, colorless prisms (*n*-hexane/diethyl ether); IR (Nujol) 2143, 1484, 1451 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.22 (s, 4H), 6.62–6.67 (m, 4H), 6.79–6.84 (m, 4H), 6.91–6.98 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 34.5, 125.2, 125.4, 127.7, 130.0, 131.9, 134.0, 136.9; HRMS (EI) M$^+$ 412.1681, theor 412.1688. Anal. Calcd for $C_{28}H_{20}N_4$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.51; H, 4.74; N, 13.37.

22: silica gel, *n*-hexane/diethyl ether 7:3; yield 10%; mp 159–161 °C; pale yellow crystals (*n*-hexane/diethyl ether); IR (Nujol) 1784, 1740, 1723, 1335 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 18H), 3.96 (s, 2H), 7.24–7.28 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.0, 36.8, 83.5, 127.3, 127.8, 128.0, 130.5, 132.6, 137.3, 150.9, 153.3; HRMS (EI) M$^+$ 424.1984, theor 424.1998. Anal. Calcd for $C_{24}H_{28}N_2O_5$: C, 67.91; H, 6.65; N, 6.60. Found: C, 67.79; H, 6.61; N, 6.44.

23a: silica gel, *n*-hexane/dichloromethane 1:1; yield 77%; mp 140–142 °C; colorless prisms (*n*-hexane/chloroform); IR (Nujol) 2129, 1597, 1574, 1449 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.94–3.07 (m, 2H), 3.23–3.36 (m, 2H), 6.99–7.25 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 32.6, 123.9, 125.4, 128.1, 130.4, 134.5, 135.5, 138.5; HRMS (EI) M$^+$ 220.0990, theor 220.1000. Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.93; H, 5.27; N, 12.62.

23b: silica gel, *n*-hexane/dichloromethane 1:1; yield 40%; mp 134–136 °C; colorless prisms (chloroform); IR (Nujol) 2154, 1595, 1484, 1266 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.58–1.63 (m, 4H), 2.82–2.86 (m, 4H), 6.97–7.12 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 29.0, 30.4, 124.0, 125.7, 127.1, 130.8, 133.6, 137.4, 137.8; HRMS (EI) M$^+$ 248.1307, theor 248.1313. Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28. Found: C, 82.13; H, 6.33; N, 11.35.

24a: silica gel, *n*-hexane/dichloromethane 1:1; yield 10%; mp 234–235 °C; colorless prisms (chloroform); IR (Nujol) 2169, 1574, 1482, 1183 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.99 (s, 8H), 7.04–7.09 (m, 4H), 7.12–7.21 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 34.0,

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125.0, 125.2, 127.3, 130.2, 132.3, 135.5, 137.7; HRMS (EI) M$^+$ 440.2009, theor 440.2001. Anal. Calcd for $C_{30}H_{24}N_4$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.63; H, 5.55; N, 12.88.

24b: silica gel, *n*-hexane/dichloromethane 1:1; yield 40%; mp 145–147 °C; colorless prisms (chloroform); IR (Nujol) 2155, 1575, 1483 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.58–1.63 (m, 8H), 2.63–2.68 (m, 8H), 6.98–7.15 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 30.6, 32.2, 124.9, 125.3, 127.0, 130.1, 132.3, 136.9, 137.1; HRMS (EI) M$^+$ 496.2613, theor 496.2627. Anal. Calcd for $C_{34}H_{32}N_4$: C, 82.22; H, 6.49; N, 11.28. Found: C, 82.01; H, 6.33; N, 11.12.

Preparation of Bis(isothiocyanates) 25 and 27. To a suspension of the appropriate bis(iminophosphorane) **9c**, **9d**, or **10** (1.36 mmol) in 30 mL of dry benzene was added an excess of carbon disulfide (3 mL), and the resultant mixture was stirred under nitrogen at reflux temperature for 2 h. After cooling, the solvent was removed under reduced pressure and the crude material was chromatographed (silica gel, *n*-hexane/dichloromethane 1:1) to give the corresponding bis(isothiocyanate) **25**.

25a: yield 93%; mp 142–143 °C; colorless prisms (chloroform); IR (Nujol) 2097, 1454, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.99 (s, 4H), 7.19–7.21 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 33.1, 126.6, 127.6, 127.7, 130.0, 130.4, 135.4, 137.1; mass spectrum *m/z* (relative intensity) 296 (M$^+$, 6), 148 (100). Anal. Calcd for $C_{16}H_{12}N_2S_2$: C, 64.84; H, 4.08; N, 9.45. Found: C, 64.66; H, 3.85; N, 9.27.

25b: yield 92%; oil; IR (neat) 2097, 1484, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67–1.73 (m, 4H), 2.70–2.76 (m, 4H), 7.17–7.21 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 29.8, 32.2, 126.4, 127.1, 127.5, 129.9, 130.0, 135.3, 138.9; mass spectrum *m/z* (relative intensity) 324 (M$^+$, 55), 162 (65), 149 (100). Anal. Calcd for $C_{18}H_{16}N_2S_2$: C, 66.63; H, 4.97; N, 8.63. Found: C, 66.49; H, 4.81; N, 8.50.

27: yield 85%; mp 72–74 °C; colorless prisms (diethyl ether/*n*-hexane); IR (Nujol) 2131, 1594, 1471, 1381 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 2H), 7.00 (s, 2H), 7.06–7.09 (m, 4H), 7.28 (t, 2H, J = 7.9Hz); ^{13}C NMR ($CDCl_3$) δ 41.1, 124.0, 126.1, 128.0, 129.9, 131.6, 135.5, 141.9; mass spectrum *m/z* (relative intensity) 282 (M$^+$, 73), 224 (100), 190 (45). Anal. Calcd for $C_{15}H_{10}N_2S_2$: C, 63.80; H, 3.57; N, 9.92. Found: C, 63.97; H, 3.42; N, 9.79.

Preparation of Bis(carbodiimides) 24a and 26. To a solution of bis(isothiocyanate) **25a** (0.20 g, 0.67 mmol) in 25 mL of dry benzene was added the bis(iminophosphorane) **9c** (0.49 g, 0.67 mmol). The mixture was stirred under nitrogen at reflux temperature for 24 h. After cooling, the solvent was removed under reduced pressure and the residue was chromatographed (silica gel, *n*-hexane/dichloromethane 4:1) to give **24a** in 97% yield. By using this method the reaction of bis(iminophosphorane) **9d** and the bis(isothiocyanate) **25b** provided a mixture of the cyclic carbodiimide **23b** (7% yield) and the bis(carbodiimide) **24b** (4% yield), and the reaction of the bis(iminophosphorane) **10** and the bis(isothiocyanate) **27** provided the bis(carbodiimide) **26** in 30% yield.

Preparation of Bis(carbodiimides) 26 and 28. To a suspension of the appropriate bis(iminophosphorane) **10** or **11** (0.69 mmol) in 20 mL of dry dichloromethane were added Boc_2O (0.30 g, 1.39 mmol) and DMAP (0.083 g, 0.69 mmol). The resultant mixture was stirred under nitrogen at room temperature for 12 h. The solvent was removed under reduced pressure, the resulting material was either chromatographed (silica gel, *n*-hexane/dichloromethane 1:1) to give the carbodiimide **26** or suspended in 10 mL of anhydrous ethanol, and the solid was separated by filtration, air-dried, and recrystallized from dichloromethane to give **28**.

26: 45% yield; mp 210–212 °C; colorless prisms (chloroform); IR (Nujol) 2139, 1588, 1485, 1239 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 4H), 6.91–6.96 (m, 8H), 7.04–7.08 (m, 4H), 7.23 (td, 4H, J = 7.4, 0.7 Hz); ^{13}C NMR ($CDCl_3$) δ 41.4, 121.9, 124.5, 126.4, 129.7, 135.9, 136.5, 142.3; HRMS (EI) M$^+$ 412.1691, theor 412.1688. Anal. Calcd for $C_{28}H_{20}N_4$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.34; H, 4.71; N, 13.67.

28: 84% yield; mp 104–106 °C; pale yellow crystals (dichloromethane); IR (Nujol) 2146, 2101, 1547, 1501 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.87 (s, 8H), 6.98–7.12 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 37.3, 124.1, 129.6, 135.7, 136.3, 138.9; HRMS (EI) M$^+$ 440.2005, theor 440.2001. Anal. Calcd for $C_{30}H_{24}N_4$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.61; H, 5.35; N, 12.60.

Reaction of Bis(iminophosphoranes) 12 with the System Boc$_2$O/DMAP. General Procedure. To a solution of the appropriate bis(iminophosphorane) **12** (0.33 mmol) in 10 mL of dry dichloromethane were added Boc_2O (0.50 g, 2.30 mmol) and DMAP (0.04 g, 0.33 mmol). The resultant solution was stirred under nitrogen at room temperature for 12 h. The solvent was removed under reduced pressure and the resulting material was purified by chromatography (silica gel, *n*-hexane/diethyl ether 7:3) to give the carbodiimides **29** and **30**, respectively, as oils.

29: yield 50%; IR (neat) 2152, 1693, 1580, 1410 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 9H), 4.59–4.65 (m, 4H), 7.07–7.52 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.7, 45.4, 80.2, 125.2, 125.7, 128.4, 129.4, 130.5, 132.8, 136.8, 156.4; HRMS (FAB$^+$) M$^+$ + 1 671.3333, theor 671.3346. Anal. Calcd for $C_{40}H_{42}N_6O_4$: C, 71.62; H, 6.31; N, 12.53. Found: C, 71.48; H, 6.18; N, 12.38.

30a: yield 67%; IR (neat) 2152, 1693, 1597, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 9H), 2.93 (t, 2H, J = 8.3 Hz), 3.47 (t, 2H, J = 8.3 Hz), 4.55 (s, 2H), 7.03–7.33 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.6, 32.7, 47.9, 48.5, 80.2, 123.1, 125.1, 125.6, 126.2, 128.0, 129.1, 131.4, 131.8, 132.1, 134.6, 136.5, 139.5, 155.2; HRMS (EI) M$^+$ 349.1779, theor 349.1790. Anal. Calcd for $C_{21}H_{23}N_3O_2$: C, 72.18; H, 6.63; N, 12.03. Found: C, 71.96; H, 6.48; N, 12.15.

30b: yield 55%; IR (neat) 2153, 1689, 1599 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9H), 1.78–1.89 (m, 2H), 2.58–2.64 (m, 2H), 3.33 (t, 2H, J = 7.1 Hz), 7.06–7.30 (m, 7H), 7.42 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 28.6, 30.7, 32.0, 48.1, 48.3, 79.9, 124.2, 124.9, 125.2, 125.9, 127.3, 129.0, 130.5, 131.3, 131.5, 132.6, 136.4, 137.3, 138.5, 156.0; HRMS (EI) M$^+$ 363.1938, theor 363.1947. Anal. Calcd for $C_{22}H_{25}N_3O_2$: C, 72.70; H, 6.93; N, 11.56. Found: C, 72.61; H, 7.15; N, 11.38.

Preparation of the Bis(carbodiimide) 31. Method A. Bis(iminophosphorane) **13a** treated with the system Boc_2O/DMAP under the same conditions used for the preparation of carbodiimides **23** led to the cyclic carbodiimide **31** in 45% yield. **Method B.** Bis(iminophosphorane) **13b** treated with the system Boc_2O/DMAP under the same conditions used for the preparation of carbodiimides **30** provided **31** in 93% yield. **Method C.** To a solution of the bis(iminophosphorane) **13b** (0.30 g, 0.33 mmol) in 20 mL of dry toluene was added an excess of solid carbon dioxide. The mixture was heated in a glass sealed tube at 70 °C for 16 h. After cooling, the solvent was removed under reduced pressure and the remaining material was chromatographed (silica gel, *n*-hexane/ethyl acetate 1:1) to give **31** in 78% yield.

31: viscous oil; IR (neat) 2186, 1693, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 9H), 4.10–4.22 (m, 4H), 6.13–6.25 (m, 2H), 6.81 (d, 2H, J = 15.7 Hz), 7.07–7.24 (m, 4H), 7.22 (td, 2H, J = 7.6, 1.6 Hz), 7.42 (dd, 2H, J = 7.6, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 28.5, 48.5, 80.1, 124.4, 125.3, 127.3, 128.5, 128.9, 129.6, 130.9, 135.5, 155.2; HRMS (EI) M$^+$ 387.1942, theor 387.1947. Anal. Calcd for $C_{24}H_{25}N_3O_2$: C, 74.39; H, 6.50; N, 10.34. Found: C, 74.52; H, 6.35; N, 10.19.

Reaction of Bis(iminophosphoranes) 14a, 14b and 15 with the System Boc$_2$O/DMAP. General Procedure. The reaction of compounds **14a**, **14b**, and **15** with the system Boc_2O/DMAP were carried out under the same conditions as described for bis(iminophosphoranes) **9**.

32: 18%; mp 160–162 °C, colorless crystals (*n*-hexane/diethyl ether); IR (Nujol) 1789, 1727, 1489, 1314 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 18H), 7.14–7.27 (m, 6H), 7.36 (dd, 2H, J = 7.6, 0.8 Hz); ^{13}C NMR ($CDCl_3$) δ 27.9, 83.7, 122.0, 125.2, 127.8, 128.8, 131.6, 149.8, 150.3, 152.9; HRMS (EI) M$^+$ 426.1781, theor 426.1791. Anal. Calcd for $C_{23}H_{26}N_2O_6$: C, 64.78; H, 6.15; N, 6.57. Found: C, 64.59; H, 6.02; N, 6.40.

33: 25%; mp 182–184 °C; colorless prisms (*n*-hexane/diethyl ether); IR (Nujol) 2137, 1485, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.80 (dd, 4H, J = 7.3, 1.0 Hz), 6.99–7.12 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 118.1, 124.4, 125.8, 126.3, 129.5, 135.7, 151.6; HRMS (EI) M$^+$ 416.1268, theor 416.1273. Anal. Calcd for $C_{26}H_{16}N_4O_2$: C, 74.99; H, 3.87; N, 13.45. Found: C, 75.05; H, 3.81; N, 13.33.

34: 71%; mp 217–218 °C; colorless prisms (chloroform); IR (Nujol) 2157, 1608, 1585, 1489 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.69

(s, 8H), 7.07–7.22 (m, 12H), 7.36 (d, 4H, J = 7.5 Hz); ^{13}C NMR (CDCl$_3$) δ 69.1, 125.0, 125.4, 128.9, 129.8, 132.5, 137.0 one quaternary carbon atom was not observed; HRMS (EI) M$^+$ 472.1884, theor 472.1899. Anal. Calcd for $C_{30}H_{24}N_4O_2$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.09; H, 5.03; N, 11.73.

35: 7%; mp 147–149 °C; colorless prisms (chloroform); IR (Nujol) 2146, 1602, 1518, 1404 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.73 (s, 4H), 6.95 (d, 2H, J = 7.7 Hz), 7.01 (dd, 2H, J = 7.4, 0.6 Hz), 7.08–7.22 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 73.2, 124.3, 125.1, 129.5, 129.7, 131.7, 137.7, 139.8; HRMS (EI) M$^+$ 236.0941, theor 236.0950. Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.20; H, 5.05; N, 11.79.

37: 50% yield; mp 86–88 °C; pale yellow prisms (n-hexane/diethyl ether); IR (Nujol) 2163, 1602, 1580, 1489, 1105 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ 3.09 (t, 4H, J = 7.4 Hz), 3.86 (t, 4H, J = 7.4 Hz), 4.70 (s, 2H), 7.07–7.21 (m, 8H); ^{13}C NMR (CDCl$_3$) δ 33.2, 68.5, 96.0, 125.0, 125.6, 127.6, 130.3, 130.7, 133.3, 137.1; HRMS (EI) M$^+$ 294.1363, theor 294.1368. Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.54; H, 5.99; N, 9.41.

Preparation of the Bis(isothiocyanate) 36. This compound was prepared from bis(iminophosphorane) **14b** by the procedure described for the preparation of bis(isothiocyanate) **25**. Compound **36**: 97% yield; oil; IR (neat) 2084, 1602, 758 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.68 (s, 4H), 7.20–7.31 (m, 6H), 7.48–7.51 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 69.1, 126.4, 127.5, 129.1, 129.7, 130.0, 134.1, 136.1; mass spectrum m/z (relative intensity) 312 (M$^+$, 5), 164 (32), 77 (100). Anal. Calcd for $C_{16}H_{12}N_2S_2O$: C, 61.52; H, 3.87; N, 8.97. Found: C, 61.47; H, 3.71; N, 8.79.

Reaction of compound **36** with the bis(iminophosphorane) **14b**, under the same conditions described for the preparation of **24a**, provided a mixture of **34** and **35**, which after chromatographic separation were isolated in 45% and 22% yield, respectively.

Acknowledgment. We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica (project no. PB92-0984). One of us (P.S.A.) also thanks the Conserjería de Educación de la Comunidad Autónoma de Murcia for a studentship.

Supplementary Material Available: Spectroscopic data (IR, NMR, MS) for seven bis(azides), 2,2′-diaminophenyl ether, and bis(iminophosphoranes) **9a–d**, **10**, **11**, **13a**, **13b**, **14a–d**, and **15** (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.