# Preparation and Intramolecular Cyclization of Bis(carbodiimides). Synthesis and X-ray Structure of 1,3-Diazetidine-2,4-diimine Derivatives

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Aza-Wittig reactions of bis(iminophosphorane) **1** derived from 2,2′-diazidobiphenyl with aromatic isocyanates provided dibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepine derivatives **2** in moderate yields. Similar results can be achieved from the reaction of 2,2′-bis(isothiocyanato)biphenyl **4** with aryliminophosphoranes. Treatment of bis(isothiocyanate) **4** with arylamines and further dehydrosulfurization of the resulting bis(thioureas) leads to the seven-membered ring guanidines **8**. *N*-2-(2′-Azido)biphenyl-*N*′-arylcarbodiimides **13** react with 1 equiv of triphenylphosphane to give zwitterionic compounds **15**, which undergo either hydrolytic cleavage to afford the guanidines **8** or react with 1 equiv of aromatic isocyanates to provide **2**. Cross-experiments suggest that the conversion **15** → **2** takes place through a nonisolable bis(carbodiimide) that undergoes an intramolecular [2 + 2] cycloaddition at the final step. The reaction of bis(iminophosphorane) **1** with an excess of carbon dioxide leads to a mixture of the tricyclic 1,3-diazetidine derivative **6** and the 14-membered cyclic bis(carbodiimide) **23**, which decomposes by thermal treatment. Compound **6** can also be obtained along with the seven-membered cyclic urea derivatives **24** from the reaction of bis(iminophosphorane) **1** with the carbon dioxide source $Boc_2O$/DMAP system. A comprehensive mechanistic scheme for the aza-Wittig reactions studied is conveniently presented. The molecular and crystal structures of 1-(4-methoxyphenyl)-2-(4-methoxyphenyl)iminodibenzo[*d*,*f*]-1,3-diazetidino-[1,2-*a*]diazepine (**2c**) and [*a*,*c*]bis[dibenzo[*d*,*f*][1,3]diazepino]-1,3-diazetidine (**6**) have been determined by X-ray analysis.

Despite its apparent simplicity, the [2 + 2] cyclodimerization of carbodiimides is rare.[1] In the intermolecular version, it has only been briefly reported that acyclic aliphatic or aromatic carbodiimides undergo cyclodimerization either by heating[2] or under catalytic conditions, tri-*n*-butylphosphane[3] or tetrafluoroboric acid,[4] to give 1,3-diazetidine-2,4-diimines together with other products such as trimeric and polymeric materials. Steric and electronic effects seem to play a role in the [2 + 2] cycloaddition of carbodiimides. Thus, in the first example described of a [2 + 2] cycloaddition reaction involving two unsymmetrically substituted carbodiimides with inverse electron demand only one regioisomer was obtained and all attempts to trap the postulated ionic intermediate failed.[5] In this context, we have described the regioselective formation of (*Z*,*Z*)-1,3-diazetidine-2,4-diimines[6] by [2 + 2] cycloaddition of *N*-heteroaryliminophosphoranes and aromatic isocyanates; when aliphatic isocyanates were used, intermediate betaines, arising from a [2 + 2] cycloaddition between the iminophosphorane and the initially formed carbodiimide, were isolated, which in turn were converted into the corresponding 1,3-diazetidine-2,4-diimines by the action of a second equivalent of isocyanate.[7]

Strained cyclic carbodiimides, obtained either by thermal ring expansion of heteroarylnitrenes[8] or by dehydrosulfurization of cyclic thioureas,[9] are extremely unstable compounds that undergo rapid oligomerization to give, besides other products, the corresponding 1,3-diazetidine-2,4-diimines.

To gain further insight namely into the almost unexplored area of the intramolecular [2 + 2] cycloaddition of bis(carbodiimides), we studied the preparation of several acyclic and cyclic bis(carbodiimides) and their applications to the preparation of the otherwise not readily available 1,3-diazetidine-2,4-diimine ring system.[10] Our approach to the preparation of bis(carbodi-

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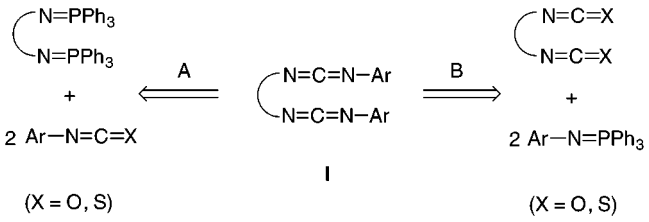
imides) is based on the aza-Wittig reaction of *C*,*C*-bis(iminophosphoranes), which has proven to be useful for the synthesis of macrocyclic carbodiimides.[11]

## Results and Discussion

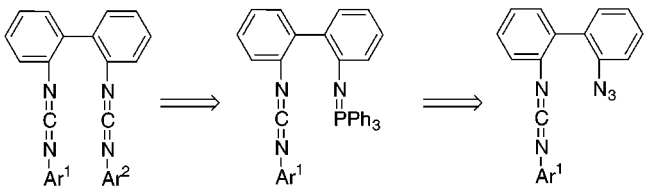
At first, we tried the preparation of bis(carbodiimides) type **I** by two different ways. The first one (route A) involves aza-Wittig reaction of the appropriate bis(iminophosphorane) with 2 equiv of isocyanate or isothiocyanate, whereas the second way (route B) is based on the reaction of a bis(isocyanate) or bis(isothiocyanate) with 2 equiv of aryliminophosphorane.



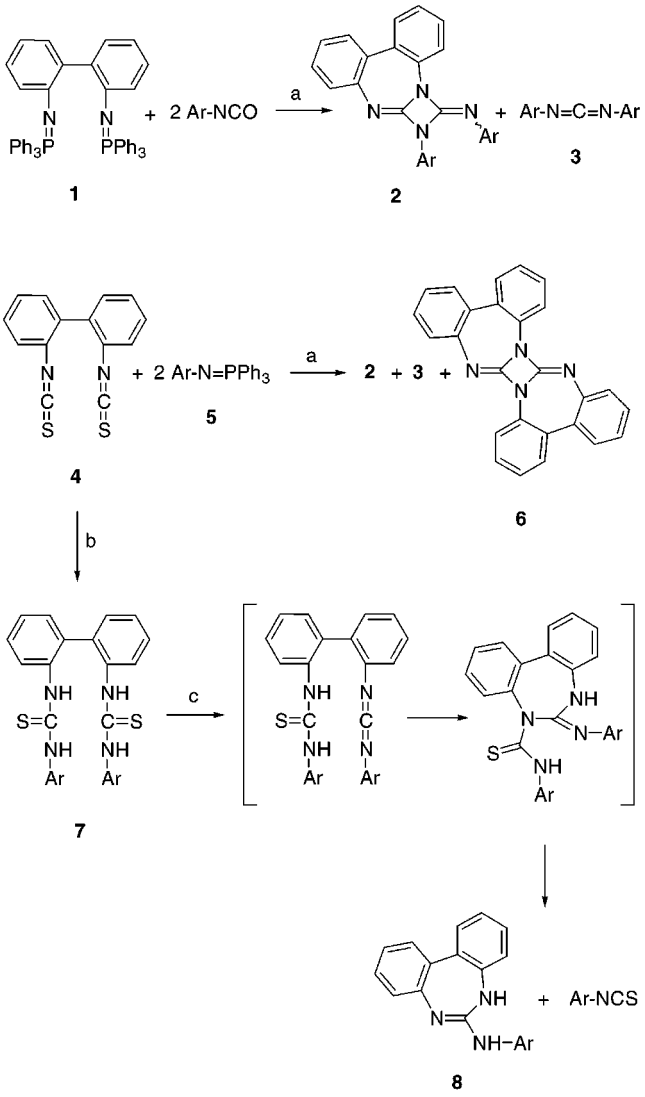

The reaction of the bis(iminophosphorane) **1**, readily available from 2,2′-diazidobiphenyl and triphenylphosphane, with 2 equiv of aromatic isocyanates in benzene at reflux temperature provided a mixture of the corresponding 1-aryl-2-aryliminodibenzo[*d*,*f*]-1,3-diazetidino-[1,2-*a*]diazepine **2** (22−40%) and diarylcarbodiimide **3** (24−43%), which were readily separated by column chromatography. In regard to route B, the reaction of bis(isothiocyanate) **4**, readily available in 67% yield from the reaction of 2,2′-diaminobiphenyl with thiocarbonyl dichloride, with 2 equiv of aryliminophosphorane **5** in dry benzene at reflux temperature led to a mixture of **2** (20−64%), diarylcarbodiimide **3** (3−42%), and the diazetidine **6** albeit in very low yield (2−6%).

Another attempt to prepare bis(carbodiimides) of type **I** by dehydrosulfurization of the bis(thioureas) **7**, prepared from the bis(isothiocyanate) **4** and aromatic amines, failed, and only the corresponding guanidines **8** could be isolated in 21−45% yields (Scheme 1). This conversion can be rationalized by initial dehydrosulfurization of only one thiourea group to give a thioureidocarbodiimide intermediate, which undergoes ring closure by nucleophilic attack of one NH group of the remaining thiourea function on the central carbon atom of the carbodiimide moiety, followed by elimination of 1 equiv of isothiocyanate.

A slight modification of these routes, which involves the sequential formation of the two heterocumulenic moieties, is outlined below. This approach, which is based on the stepwise formation of the two carbodiimide functions by two independent aza-Wittig reactions, would allow the access to bis(carbodiimides) of type **I** bearing two different *N*-aryl substituents. Keeping in mind the above results, the use of this kind of bis(carbodiimides) would give rise to diazetidine[1,2-*a*]diazepines **2** in which the two aryl groups are different.




**Scheme 1**[a]




[a] Reagents and conditions: (a) $C_6H_6$, reflux; (b) $ArNH_2$ (2 equiv), DMF, rt; (c) $CH_2Cl_2$, $PPh_3/Et_3N/CCl_4$, reflux or $C_6H_6$, HgO, reflux.

2-Amino-2′-azidobiphenyl **9** was used as starting material for the preparation of the 2-azido-2′-heterocumulenic biphenyls **10**, **11**, and **13**. Compound **9** was prepared by the two-step sequence: diazotization followed by azidation of 2-amino-2′-phthalimidobiphenyl led to 2-azido-2′-phthalimidobiphenyl in 93% yield, which was converted into **9** in 97% yield by reaction with hydrazine hydrate. Treatment of **9** with thiocarbonyl dichloride in the presence of potassium carbonate[12] provided **10** in 77% yield, whereas the reaction with bis(trichloromethyl)-carbonate (triphosgene) in the presence of triethylamine[13] led to the corresponding isocyanate **11** in 57% yield. *N*-2-(2′-Azido)biphenyl-*N*′-arylcarbodiimides **13** were prepared by the two-step sequence: reaction of **9** with aryl isothiocyanates to give the thioureas **12** (90−91% yield), which were subsequently dehydrosulfurized with yellow HgO affording **13** (44−48% yield) (Scheme 2).

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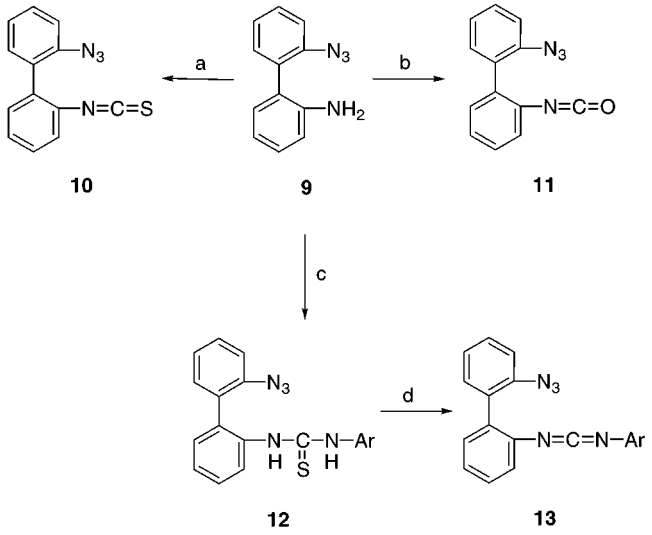
**Scheme 2**[a]




[a] Reagents and conditions: (a) $CsCl_2$, $K_2CO_3$, $CHCl_3/H_2O$, rt; (b) $Cl_3CCO_3CCl_3$, $Et_3N$, $C_6H_6$, reflux; (c) ArNCS, DMF, rt; (d) yellow HgO, $MgSO_4$, $C_6H_6$, reflux.

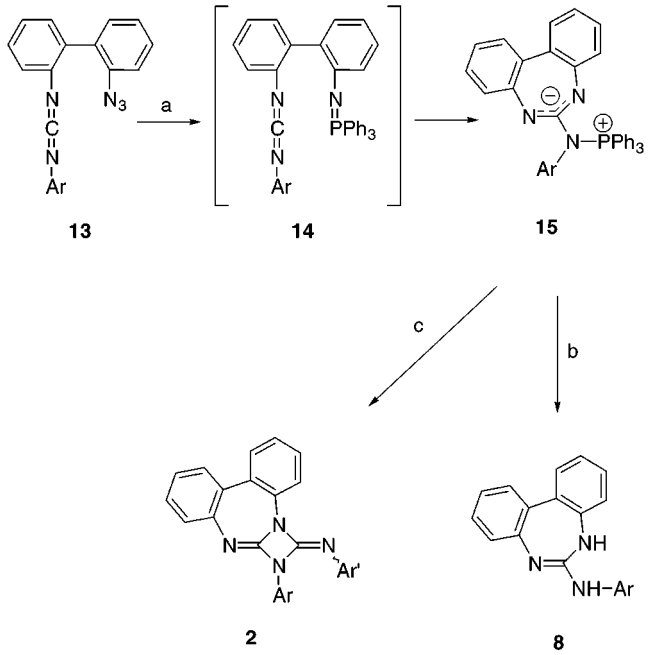
When carbodiimides **13** were treated with 1 equiv of triphenylphosphane at room temperature, the corresponding zwitterionic compounds **15** were isolated as crystalline solids. These compounds, probably arising from the initial formation of the iminophosphorane **14** and further nucleophilic attack of the nitrogen atom of the iminophosphorane moiety on the central carbon atom of the carbodiimide fragment,[14] underwent hydrolytic cleavage easily to afford the guanidines **8** and triphenylphosphane oxide. Due to their ability to undergo hydrolysis, the NMR spectra of compounds **15** could not be recorded. However, when compounds **15** were submitted to react with 1 equiv of isocyanate at room temperature, the 1,3-diazetidino[1,2-*a*]diazepines **2** were isolated in modest yields (Scheme 3).

The first indication of a diazetidine structure in compounds **2** was obtained from EI-mass spectrometry: all these compounds showed that the molecular ion-peak had very low intensity, the base peak being the one corresponding to the fragment [ArNCNAr]; $^1H$ and $^{13}C$ NMR spectra clearly showed two sets of signals for the two aryl groups. An X-ray structure determination of compound **2c** (Ar = 4-$H_3COC_6H_4$) revealed the proposed structure and the (*Z*)-configuration of the exocyclic C−N double bond.

Although the isolation of compound **6** by gas-phase pyrolysis of 2-azidophenanthridine has been briefly reported,[8] no data of this compound are available. The IR spectrum showed a strong absorption band at $\nu = 1697$ $cm^{-1}$ due to the C−N double bonds and is in good agreement with the previously reported values for this kind of ring.[6a,14b,15] The EI-mass spectrum showed the molecular ion peak at low intensity, with the fragment appearing at $m/z = 192$ ($M^+/2$) being the base peak. An X-ray structure determination of compound **6** confirmed the proposed structure.

Selected geometrical parameters for compounds **2c** and **6** are listed in Table 2 according to the numbering scheme

**Scheme 3**[a]




[a] Reagents and conditions: (a) $PPh_3$, $Et_2O$, rt; (b) workup ($H_2O$); (c) Ar−N=C=O, $CH_2Cl_2$, rt.

shown in Figure 1. Molecules in **6** are located on inversion centers; therefore, there is only half a molecule in the asymmetric unit. In both compounds, the N(2) atoms have a distorted tetrahedral environment (sum of angles around N(2): $\Sigma N(2) = 324.7(2)$ and $338.1(2)°$ for **2c** and **6**, respectively) while the hybridization of the N(4) atoms is $sp^2$ [$\Sigma N(4) = 359.1(3)°$]. This behavior is reflected, mainly in **2c**, in a remarkable elongation of all bond distances involving N(2). In **2c**, the four-membered ring and the phenyl substituent at N(4) are coplanar, which indicates an extension of the delocalized $\pi$-bonding system across both rings aided by the C−H···N intramolecular interactions (Table 2). These facts are also supported by the structure of the few related compounds previously reported and retrieved from the Cambridge Structural Database[16] that present a seven-membered ring fused to the diazetidine one (CSD refcode: SOZCAL[14a]). The $sp^2$ hybridization of the N atoms of the diazetidine ring is observed when they are bonded to phenyl rings as in FAHVAL,[6a] while the $sp^3$ hybridization is presented with cyclohexane rings, HIHTUM.[17] The methoxy groups in **2c** are almost in the plane of their benzene rings. C−H···N intramolecular interactions are also present in **6** (Table 2).

According to the Cano and Foces-Foces treatment[18] the conformation of the seven-membered rings of both compounds can be described as distorted boat-sofas, more puckered in **2c** than in **6** (experimental puckering amplitudes and phases angles in Table 2 vs q1 = 0 Å, q3/q2 = 0.555 and $\Phi 2 = 270$, $\Phi 3 = 90°$ for the undistorted conformation).

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(18) Cano, F. H.; Foces-Foces, C. *THEOCHEM* **1983**, *94*, 209.

**Table 1. Crystal Analysis Parameters at Room Temperature**

| | **2c** | **6** |
|---|---|---|
| crystal data | | |
| formula | $C_{28}H_{22}N_4O_2$ | $C_{26}H_{16}N_4$ |
| crystal habit | colorless, hexagonal plate | colorless, hexagonal prism |
| crystal size (mm) | 0.20 × 0.20 × 0.13 | 0.67 × 0.27 × 0.27 |
| symmetry | monoclinic, *I*2/*a* | orthorhombic, *Pbca* |
| unit cell determination: | least-squares fit from 80 reflections ($\theta$ < 45°) | least-squares fit from 50 reflections reflections ($\theta$ < 45°) |
| unit cell dimens (Å, deg) | *a* = 21.8604(4)<br>*b* = 14.0153(6)<br>*c* = 14.5155(6)<br>90, 92.814(4), 90 | *a* = 19.2780(11)<br>*b* = 13.8770(7)<br>*c* = 6.9601(2)<br>90, 90, 90 |
| packing: *V* (Å$^3$), *Z* | 4441.9(4), 8 | 1862.0(2), 4 |
| $D_c$ (g/cm$^3$), *M*, *F*(000) | 1.335, 446.51, 1872 | 1.371, 384.44, 800 |
| $\mu$ (cm$^{-1}$) | 6.90 | 6.53 |
| experimental data | | |
| technique: | four circle diffractometer, Philips PW1100, bisecting geometry graphite-oriented monochromator. $\omega/2\theta$ scans detector apertures 1 × 1°. 1 min/reflection Cu Kα radiation, 1.5° scan width and $\theta_{max}$ = 65° | |
| no. of reflections: | | |
| independent | 3769 | 1579 |
| obsd [2$\sigma$(*I*) criterion] | 3017 | 1459 |
| standard reflections: | two reflections every 90 min | |
| | 4.0% decay | no variation |
| solution and refinement | | |
| solution | direct methods: Sir92 | |
| refinement | least-squares on $F_o$, full matrix | |
| parameters: | | |
| no. of variables | 395 | 169 |
| degrees of freedom | 2622 | 1290 |
| ratio of freedom | 7.6 | 8.6 |
| final shift/error | 0.001 | 0.001 |
| H atoms | from difference synthesis | |
| weighting scheme | empirical as to give no trends in $\langle w\Delta^2F\rangle$ vs $\langle\|F_o\|\rangle$ and $\langle\sin\theta/\lambda\rangle$ | |
| max thermal value (Å$^2$) | U33[C(27)] = 0.109(3) | U22[C(15)] = 0.099(1) |
| final $\Delta F$ peak (e Å$^{-3}$) | 0.20 | 0.14 |
| final *R* and $R_w$ | 0.039, 0.042 | 0.046, 0.052 |

The structure of compounds **8** was established from their spectroscopic ($^1$H and $^{13}$C NMR, and IR) data.

To clarify the somewhat complex mechanistic scheme needed to describe the aza-Wittig reactions of the bis(iminophosphorane) **1** with isocyanates and of the bis(isothiocyanate) **4** with *N*-aryliminophosphoranes, we have divided the presentation of the reaction sequences into two schemes. In Scheme 4, the formation of diazetidine **6** and diarylcarbodiimides **3** is considered. In Scheme 5, the mechanism of the formation of diazetidines **2** and guanidines **8** is illustrated.

In Scheme 4 we address the question of how compound **6** is formed. A tentative mechanism could involve initial "abnormal" aza-Wittig reaction[19] between bis(iminophosphorane) **1** and the first equivalent of isocyanate to give the corresponding *N*-aryliminophosphorane and the highly reactive intermediate isocyanate−iminophosphorane **16**. Formation of diarylcarbodiimide **3** can be explained by aza-Wittig reaction of the *N*-aryliminophosphorane with the second equivalent of isocyanate. Intramolecular aza-Wittig reaction in compound **16** would lead to the cyclic seven-membered carbodiimide **18**, which under the reaction conditions undergoes a [2 + 2] cyclodimerization to give **6**. The reaction of bis(isothiocyanate) **4** and *N*-aryliminophosphoranes takes place by the same course, through the intermediate **17**, to give **3** and **6**, respectively. Support for the intermediates **16** and **17** as precursors of the diazetidine **6** was found in the treatment of the azidoisocyanate **10** or azidoisothiocyanate **11** with 1 equiv of triphenylphosphane at room temperature, which led to a complex mixture from which only the diazetidine **6** could be isolated in low yield (5%).

In Scheme 5, the iminophosphorane **14**, a nucleophilic phosphorus−nitrogen ylide, initially formed from the Staudinger reaction of **13** with triphenylphosphane or from the intermediates **16** or **17** with *N*-aryliminophosphoranes, attacks the central carbon atom of the carbodiimide moiety to give the zwitterionic compound **15**. This compound reacts with the second equivalent of isocyanate across the negative endocyclic nitrogen atom to give the adduct **19**, which can be considered as an extended ylide or betaine. This compound collapses to form an oxadiazaphosphorine **20**, which disappears by a pericyclic reaction to form triphenylphosphane oxide and the bis(carbodiimide) **21**, which in turn undergoes an intramolecular [2 + 2] cycloaddition to give **2**. The results obtained from the reaction of **15** with an aromatic isocyanate bearing a different substituent at the aromatic ring (Scheme 3) support the idea that the bis(carbodiimide) **21** is formed from **20** by triphenylphosphane oxide extrusion. Thus, the reaction of **15** (Ar = 4-$H_3CC_6H_4$) with 1 equiv of 4-methoxyphenylisocyanate at room temperature led to a mixture of two isomeric diazetidines **2f** and **2g** in 28% and 12% yield, respectively, while the reaction of **15** (Ar = 4-$H_3COC_6H_4$) with 1 equiv of 4-tolyl isocyanate under the same conditions afforded a mixture of the same diazetidines, now in 38% and 16%, respectively. The fact that two diazetidines are formed in both cross-experiments in almost the same ratio (1.5 vs 1.7) points to the bis(carbodiimide) **21** as a common intermediate for both compounds.

The next step of this study was the preparation of a well-defined model system, such as bis(carbodiimide) **23** (Scheme 6), in which the two carbodiimide portions could

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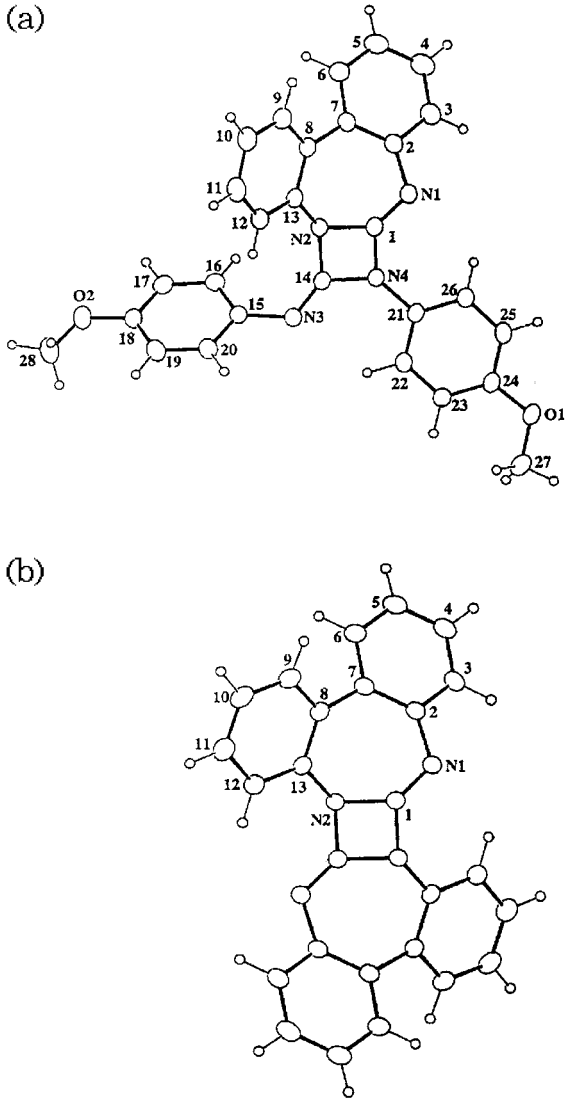



**Figure 1.** Molecular structures of (a) compound **2c** and (b) compound **6** showing the numbering system and the displacement parameters drawn at the 30% probability level. In **6**, the two halves of the molecule are related by a symmetry center at (1/2, 0, 1/2).

be rigidly fixed in an adequate arrangement to promote an intramolecular [2 + 2] cycloaddition.

Attempts to prepare the cyclic bis(carbodiimide) **23** either by intermolecular aza-Wittig reaction between the bis(iminophosphorane) **1** and the bis(isothiocyanate) **4** or by dehydrosulfurization of the bis(thiourea) **22**, available from **4** and 2,2′-diaminobiphenyl, with a wide variety of reagents failed, and only the diazetidine **6** could be isolated in low yields (3−7%). However, the reaction of **1** with an excess of carbon dioxide in dry benzene at 70 °C in a sealed tube afforded a mixture of diazetidine **6** (28% yield) and the desired bis(carbodiimide) **23** in low yield (6%). Compound **23**, which was isolated as a crystalline solid, was fully characterized by its spectroscopic (IR, $^1$H and $^{13}$C NMR) data and FAB-mass spectrum. The thermal treatment of compound **23** led to a complex mixture from which the diazetidine **6** was not detected. This result clearly indicates that the formation of diazetidine **6** takes place through a [2 + 2] cyclodimerization of the highly reactive carbodiimide intermediate **18** and does not occur by intramolecular [2 + 2] cycloaddition of the bis-

**Table 2. Selected Geometrical Parameters (Å, deg)**

| compound | **2c** | **6** |
|---|---|---|
| C(1)−N(2) | 1.440(2) | 1.426(2) |
| N(2)−C(14)/C(1′) | 1.457(2) | 1.419(2) |
| N(2)−C(13) | 1.431(2) | 1.426(2) |
| C(1)−N(4) | 1.392(2) | |
| C(14)−N(4) | 1.405(2) | |
| N(4)−C(21) | 1.415(2) | |
| C(1)−N(2)−C(13) | 114.7(1) | 122.3(1) |
| C(13)−N(2)−C(14) | 123.0(1) | 127.7(1) |
| C(1)−N(2)−C(14) | 87.0(1) | 88.8(1) |
| C(1)−N(4)−C(14) | 90.9(1) | |
| C(14)−N(4)−C(21) | 133.9(2) | |
| C(1)−N(4)−C(21) | 134.3(2) | |
| N(1)−C(1)−N(2)−C(13) | −56.5(3) | −46.1(2) |
| C(1)−N(2)−C(13)−C(8) | 57.0(2) | 40.8(2) |
| N(2)−C(13)−C(8)−C(7) | −3.2(3) | 10.5(2) |
| C(13)−C(8)−C(7)−C(2) | −37.3(3) | −39.7(2) |
| C(8)−C(7)−C(2)−N(1) | 7.6(3) | 3.9(2) |
| C(7)−C(2)−N(1)−C(1) | 30.2(3) | 31.8(2) |
| C(2)−N(1)−C(1)−N(2) | −3.7(3) | −7.5(2) |
| N(2)−C(14)−N(3)−C(15) | 3.7(4) | |
| C(19)−C(18)−C(1)−C(27) | 3.1(3) | |
| C(14)−N(3)−C(15)−C(16) | 38.6(3) | |
| C(14)−N(4)−C(21)−C(22) | −1.6(3) | |
| C(23)−C(24)−C(2)−C(28) | −12.5(3) | |

| conformational parameters (see text): | **2c** | **6** |
|---|---|---|
| q1/q2/q3 (Å) | 1.5(2), 44.5(2), 23.3(2) | 0.9(1), 41.6(1), 12.0(1) |
| Φ1/Φ2/Φ3 (°) | −35.5(62), 275.8(2), 83.3(4) | −11.9(68), 269.9(2), 70.5(5) |

| hydrogen interactions | **2c** | | **6** | |
|---|---|---|---|---|
| | X−H | H···Y | X···Y | X−H···Y |
| compound **2c** | | | | |
| C(26)−H(26)···N(1) | 0.99(2) | 2.56(2) | 3.219(3) | 124(2) |
| C(22)−H(22)···N(3) | 0.99(2) | 2.46(2) | 3.138(2) | 125(2) |
| Compound **6** | | | | |
| C(12)−H(12)···N(1)-(1 − *x*, − *y*, 1 − *z*) | 0.99(2) | 2.54(2) | 3.195(2) | 124(1) |

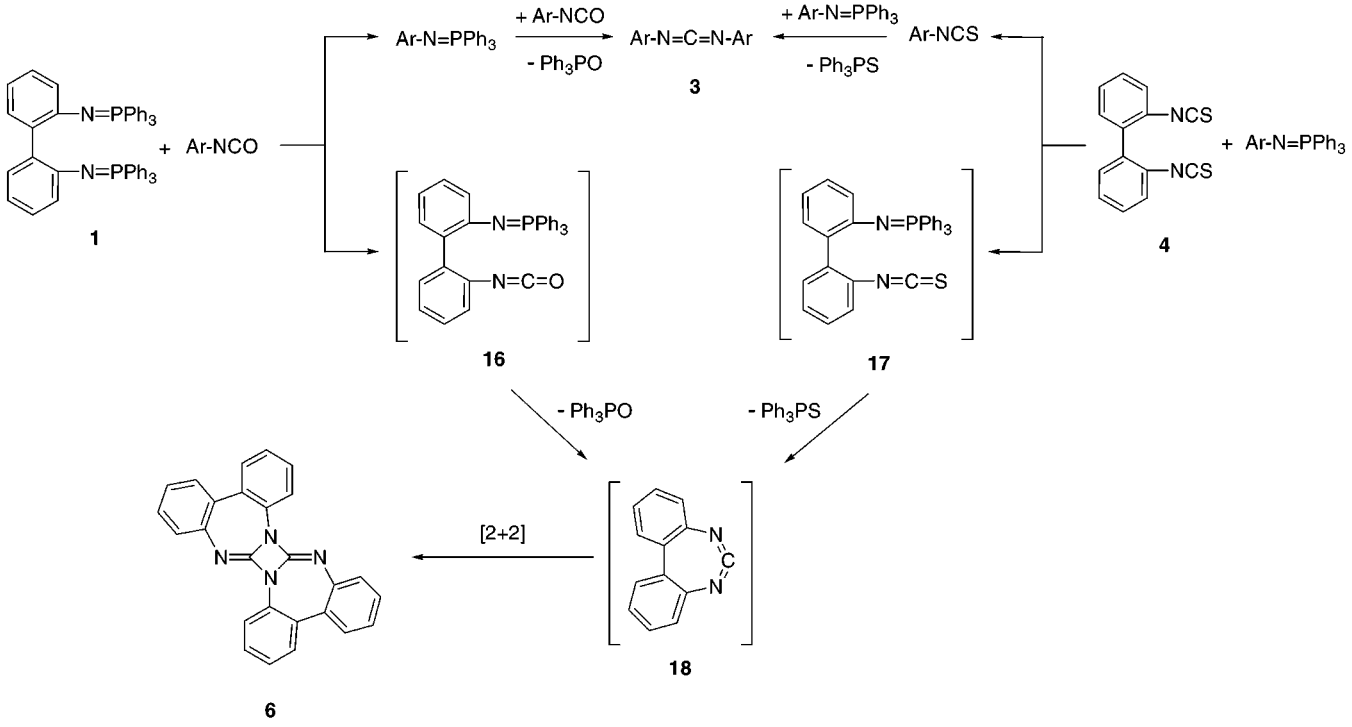
(carbodiimide) **23**. Further proof is offered by the isolation of the *N*-Boc-protected cyclic urea **24** (28%) and diazetidine **6** (8%) from the reaction of **1** with the carbon dioxide source $Boc_2O$/DMAP system. Compound **24** is most likely, formed by addition of 1 equiv of $Boc_2O$ to the intermediate **18** and further rearrangement of the resulting isourea.

The reason the cyclic bis(carbodiimide) **23**, in contrast to the acyclic bis(carbodiimides) **21**, does not undergo intramolecular [2 + 2] cycloaddition may arise from the geometric constrain imposed by the two biphenyl rings, which does not allow the appropriate approximation and/or disposition of the two carbodiimide moieties.

## Concluding Remarks

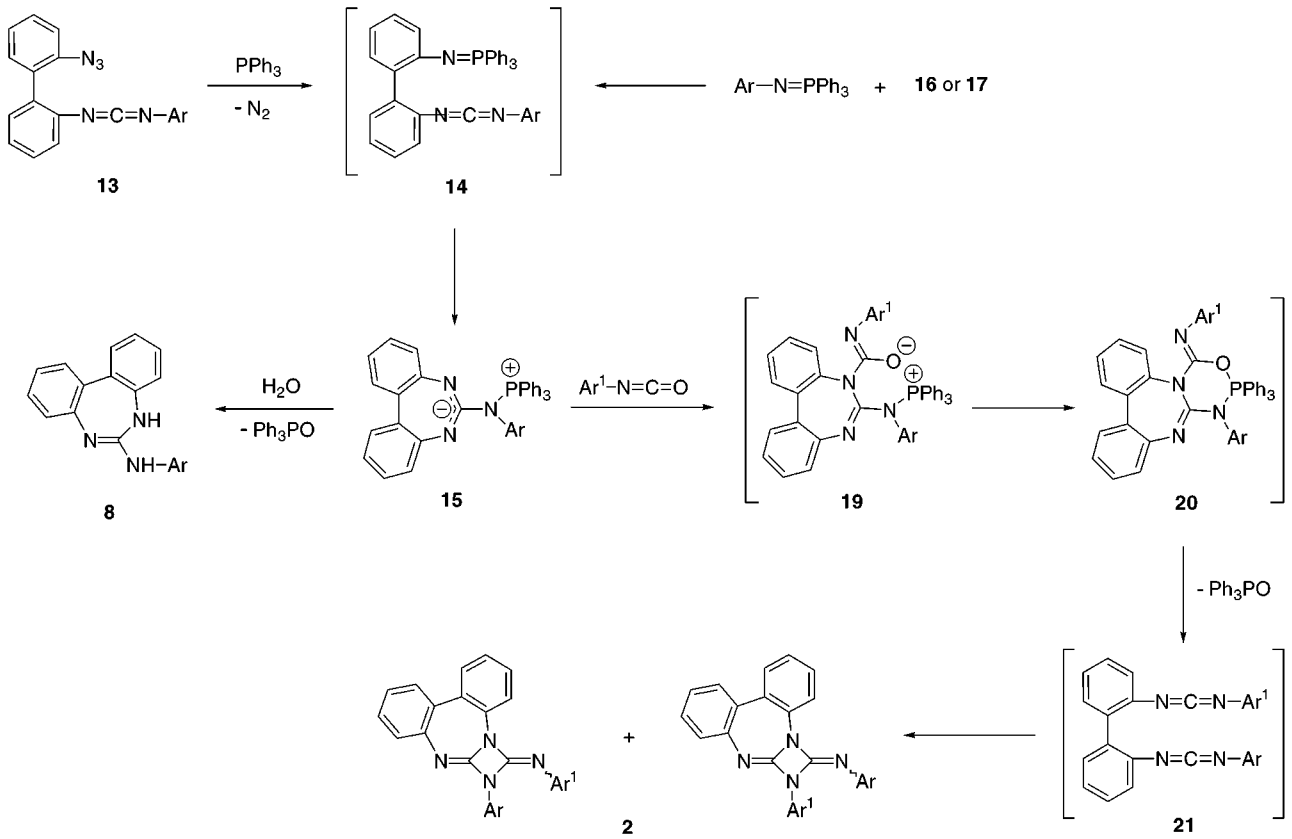
The rich chemistry displayed in the aza-Wittig reaction of *C*,*C*-bis(iminophosphoranes) deserves further study in different systems. In the present case, we have shown that the bis(iminophosphorane) derived from the rigid system 2,2′-diazidobiphenyl reacted with isocyanates to give the four-membered ring 1,3-diazetidine-2,4-diimines through a complex reaction pathway involving as a final step an intramolecular [2 + 2] cycloaddition of a bis(carbodiimide). In an analogous reaction pathway, the reaction of 2,2′-bis(isothiocyanato)biphenyl with aryliminophosphoranes also leads to 1,3-diazetidine-2,4-diimines. Isolation of a seven-membered ring guanidine intermedi-

**Scheme 4**[a]




[a] Probable mechanism for the formation of the diazetidine **6**.

**Scheme 5**[a]



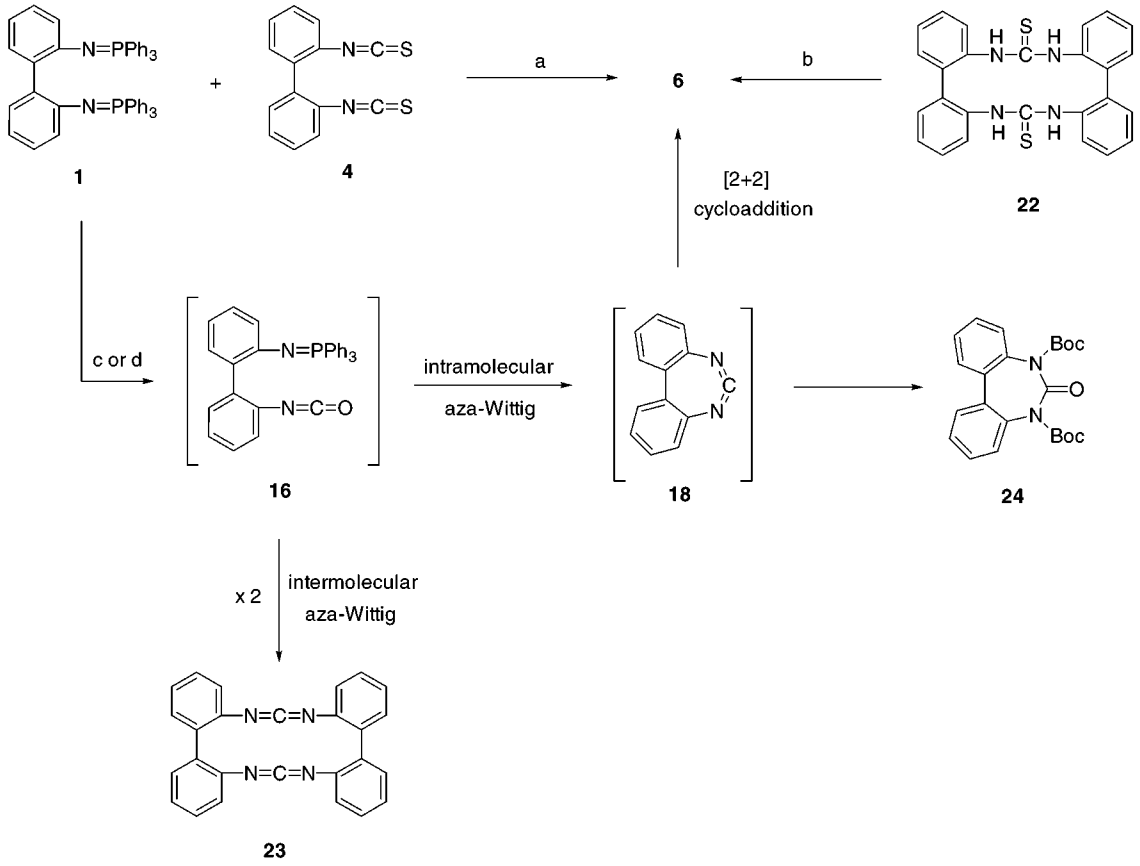

[a] Mechanism for the formation of diazetidines **2**.

ate and further conversion into a 1,3-diazetidine-2,4-diimine, as well as cross experiments, strongly support the proposed mechanism.

## Experimental Section

**General Methods.** General experimental conditions and spectroscopic instrumentation used have been described.[11]

**Scheme 6**[a]




[a] Reagents and conditions: (a) $C_6H_6$, reflux; (b) $PPh_3/Et_3N/CCl_4$; or diethyl azodicarboxylate/$PPh_3$; or yellow HgO/$MgSO_4$; (c) excess $CO_2$ solid, $C_6H_6$, 70 °C, sealed tube; (d) $Boc_2O$/DMAP, $CH_2Cl_2$, rt.

**X-ray Analysis.** The experimental details and the most relevant parameters are in Table 1. The structures were solved by direct methods, SIR92.[20] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included as isotropic. Most of the calculations were performed on a DEC3000-300X workstation using the XTAL[21] system, PESOS,[22] and PARST.[23] The atomic scattering factors were taken from the *International Tables for X-ray Crystallography*, Vol. IV.[24]

**Materials.** 2,2′-Bis[(triphenylphosphoranylidene)amino]-biphenyl (**1**) was prepared from 2,2′-diazidobiphenyl as we have described previously.[11] 2,2′-Diaminobiphenyl,[25] 2,2′-diazidobiphenyl,[26] *N*-(4-tolyl)-,[27] *N*-(4-methoxyphenyl)-,[27] *N*-(1-naphthyl)-,[28] and *N*-(4-dimethylaminophenyl)iminotriphenylphosphorane,[27] and 2-amino-2′-phthalimidobiphenyl[29] were prepared as described in the literature.

**2,2′-Bis(isothiocyanato)biphenyl (4).** To a well-stirred solution of 2,2′-diaminobiphenyl (2.5 g, 0.014 mol) in 35 mL of $CHCl_3$ and cooled at 0 °C were added simultaneously and dropwise a solution of $K_2CO_3$ (7.49 g, 0.054 mol) in 40 mL of water and a solution of thiophosgene (3.12 g, 0.027 mol) in 35 mL of $CHCl_3$. The reaction mixture was allowed to warm at room temperature and stirred for 2.5 h. Then, the organic layer was separated, washed with water (3 × 50 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting material was purified by chromatography (silica gel, *n*-hexane/dichloromethane 7:3) to give **2,2′-bis(isothiocyanato)biphenyl** (**4**) in 65% yield as a colorless semisolid: mp 32−34 °C (lit.[30] 33−36 °C); IR (Nujol) 2087 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.30−7.48 (m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 126.5, 127.4, 129.6, 130.6, 131.0, 134.9, 136.0; mass spectrum *m*/*z* (relative intensity) 268 ($M^+$, 60). Anal. Calcd for $C_{14}H_8N_2S_2$: C, 62.66; H, 3.00; N, 10.44. Found: C, 62.84; H, 2.88; N, 10.53.

***N*-(2,4-Dimethoxyphenyl)iminotriphenylphosphorane (5b).** To a solution of triphenylphosphane (1.7 g, 6.53 mmol) in 20 mL of dry benzene under nitrogen at 0 °C was added dropwise a solution of $Br_2$ (1.05 g, 6.53 mmol) in 10 mL of the same solvent. The resulting mixture was stirred for 1 h and allowed to warm at room temperature. Then, a solution of 2,4-dimethoxyaniline (1 g, 6.53 mmol) and triethylamine (1.3 g, 13.1 mmol) in 15 mL of dry benzene was added dropwise. After the addition was completed, the reaction mixture was heated at reflux temperature for 5 h, the precipitated triethylammoniun bromide was separated by filtration, the solvent was removed under reduced pressure, the resulting material was treated with dry diethyl ether, and the precipitated solid was collected by filtration, air-dried, and recrystallized from chloroform/*n*-hexane to give **5b** in 73% yield: mp 195−197 °C; pale yellow prisms (chloroform/*n*-hexane); IR (Nujol) 1436, 1105 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.43 (s, 3H), 3.58 (s, 3H), 6.18 (dd, 1H, $J$ = 8.6, 2.9 Hz), 6.45 (d, 1H, $J$ = 2.9 Hz), 6.60 (dd,

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1H, $J$ = 8.6, 1.1 Hz), 7.33−7.46 (m, 9H), 7.68−7.79 (m, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.3, 55.6, 102.1, 110.2 (d, $^3J_{C-P}$ = 7.6 Hz), 111.8, 128.3 (d, $^3J_{C-P}$ = 11.9 Hz), 131.2 (d, $^4J_{C-P}$ = 2.8 Hz), 132.4 (d, $^1J_{C-P}$ = 100.1 Hz), 132.4 (d, $^2J_{C-P}$ = 9.8 Hz), 141.5 (d, $^2J_{C-P}$ = 2.4 Hz), 147.5 (d, $^3J_{C-P}$ = 2.9 Hz), 154.1 (d, $^4J_{C-P}$ = 1.7 Hz); mass spectrum *m*/*z* (relative intensity) 413 ($M^+$, 23), 183 (100). Anal. Calcd for $C_{26}H_{24}NO_2P$: C, 75.53; H, 5.85; N, 3.39. Found: C, 75.40; H, 5.69; N, 3.53.

**General Procedure for the Preparation of 1-Aryl-2-aryliminodibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepines (2). Method A.** To a solution of 2,2′-bis(isothiocyanato)biphenyl (**4**) (0.35 g, 1.3 mmol) in 30 mL of dry benzene was added the corresponding aryliminophosphorane **5** (2.6 mmol). The reaction mixture was stirred and heated at reflux temperature under nitrogen for 8−20 h. The solvent was removed under reduced pressure, and the remaining material was chromatographed on a silica gel column using the appropriate eluent. By this procedure, the following compounds (**2a**−**e**) were prepared, and the diazetidine **6** was also isolated in low yield (2−6%):

**1-(4-Tolyl)-2-(4-tolyl)iminodibenzo[*d*,*f*]-1,3-diazetidino-[1,2-*a*]diazepine (2a):** silica gel, *n*-hexane/dichloromethane 7:3; 37% yield; mp 184−186 °C; colorless prisms (*n*-hexane); IR (Nujol) 1687 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.28 (s, 3H), 2.33 (s, 3H), 6.27−6.48 (m, 1H), 7.00−7.44 (m, 13H), 7.84−8.05 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 20.2, 21.1, 117.3, 118.8, 123.2, 124.9, 125.7, 127.6, 128.2, 128.7, 128.9, 129.5, 130.0, 131.2, 131.5, 132.7, 133.3, 134.5, 134.8, 141.4, 141.7, 142.2, 143.8, 151.3; mass spectrum *m*/*z* (relative intensity) 414 ($M^+$, 5) 222 (100). Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 81.00; H, 5.46; N, 13.54.

**1-(2,4-Dimethoxyphenyl)-2-(2,4-dimethoxyphenyl)iminodibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepine (2b):** silica gel, *n*-hexane/dichloromethane 1:1; 62% yield; mp 121−122 °C; colorless prisms (ethanol); IR (Nujol) 1702, 1681 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.58 (s, 9H), 3.64 (s, 3H), 6.37−6.73 (m, 6H), 7.07−7.29 (m, 6H), 7.39−7.46 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.7, 55.8, 55.9, 56.0, 108.9, 109.9, 111.6, 112.1, 113.7, 115.3, 116.0, 122.2, 124.9, 125.6, 127.6, 127.9, 128.7, 128.8, 131.2, 131.7, 132.9, 133.8, 142.9, 143.8, 144.2, 145.3, 149.2, 152.1, 153.0, 153.3; mass spectrum *m*/*z* (relative intensity) 506 ($M^+$, 9), 314 (100). Anal. Calcd for $C_{30}H_{26}N_4O_4$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.64; H, 5.37; N, 10.93.

**1-(4-Methoxyphenyl)-2-(4-methoxyphenyl)iminodibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepine (2c):** silica gel, *n*-hexane/dichloromethane 1:1; 53% yield; mp 162−164 °C; colorless prisms (*n*-hexane); IR (Nujol) 1670 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.75 (s, 3H), 3.80 (s, 3H), 6.31−6.38 (m, 1H), 6.79−7.46 (m, 14H), 7.94−8.02 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.4, 55.5, 114.2, 114.6, 117.5, 120.2, 124.6, 124.9, 125.6, 127.5, 128.3, 128.8, 128.9, 131.2, 131.5, 132.6, 137.0, 141.4, 142.4, 143.8, 151.5, 156.7, 157.1, one quaternary carbon atom was not observed; mass spectrum *m*/*z* (relative intensity) 446 ($M^+$, 25), 254 (100). Anal. Calcd for $C_{28}H_{22}N_4O_2$: C, 75.32; H, 4.97; N, 12.55. Found: C, 75.16; H, 5.08; N, 12.73.

**1-(1-Naphthyl)-2-(1-naphthyl)iminodibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepine (2d):** silica gel, *n*-hexane/dichloromethane 7:3; 20% yield; mp 172−173 °C; colorless prisms (diethyl ether); IR (Nujol) 1690 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 6.57−7.72 (m, 20H), 8.15−8.29 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 116.4, 116.9, 123.5, 123.9, 124.6, 124.9, 125.2, 125.8, 126.0, 126.1, 126.5, 126.6, 127.7, 128.0, 128.7, 129.0, 129.1, 129.3, 129.5, 131.6, 131.6, 131.7, 132.8, 134.0, 134.1, 139.8, 142.6, 143.6, 144.0, 152.3, three methine carbon atoms and two quaternary carbon atoms were not observed; mass spectrum *m*/*z* (relative intensity) 486 ($M^+$, 19), 294 (100). Anal. Calcd for $C_{34}H_{22}N_4$: C, 83.93; H, 4.56; N, 11.51. Found: C, 83.78; H, 4.43; N, 11,-78.

**1-[4-(Dimethylamino)phenyl]-2-[4-(dimethylamino)-phenyl]iminodibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepine (2e):** silica gel, dichloromethane; 64% yield; mp 121−123 °C dec; pale yellow prisms (chloroform/*n*-hexane); IR (Nujol) 1687, 1677 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.88 (s, 6H), 2.93 (s, 6H), 6.35−6.49 (m, 1H), 6.63 (d, 2H, $J$ = 8.7 Hz), 6.71−6.77 (m, 2H), 7.00−7.45 (m, 9H), 7.82−7.97 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 40.7, 40.8, 112.8, 113.1, 117.6, 120.4, 124.6, 124.7, 125.2, 125.7, 127.3, 128.3, 128.7, 128.7, 131.1, 131.2, 132.6, 133.3, 140.4, 142.8, 144.2, 148.1, 152.2, one quaternary carbon atom was not observed; mass spectrum *m*/*z* (relative intensity) 472 ($M^+$, 9), 280 (100). Anal. Calcd for $C_{30}H_{28}N_6$: C, 76.24; H, 5.97; N, 17.78. Found: C, 76.40; H, 5.75; N, 17.85.

**[*a*,*c*]Bis[dibenzo[*d*,*f*][1,3]diazepino]-1,3-diazetidine (6):** 2−6% yield; mp 324−325 °C; colorless prisms (dichloromethane); IR (Nujol) 1708 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.12−7.44 (m, 7H), 7.96 (dd, 1H, $J$ = 8.0, 1.3 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 115.9, 125.8, 126.8, 127.9, 128.8, 129.0, 129.2, 131.4, 132.0, 133.1, 142.0, 143.6, 149.1; mass spectrum *m*/*z* (relative intensity) 384 ($M^+$, 11), 192 (100). Anal. Calcd for $C_{26}H_{16}N_4$: C, 81.23; H, 4.19; N, 14.57. Found: C, 81.37; H, 3.95; N, 14.68.

**Method B.** To a solution of 2,2′-bis[(triphenylphosphoranylidene)amino]biphenyl (**1**) (0.55 g, 0.78 mmol) in 25 mL of dry benzene was added the corresponding aryl isocyanate (1.6 mmol). The resulting mixture was heated at reflux temperature under nitrogen for 8−20 h. The solvent was removed under reduced pressure, and the residual material was chromatographed on a silica gel column with *n*-hexane/dichloromethane 7:3 as eluent. Using this procedure the following compounds were prepared:

**2a:** 40% yield.

**2d:** 22% yield.

**2,2′-Bis[*N*-(4-methoxyphenyl)thioureido-*N*′-yl]biphenyl (7c).** 4-Methoxyaniline (0.46 g, 3.72 mmol) was added to a solution of 2,2′-bis(isothiocyanato)biphenyl (0.5 g, 1.86 mmol) in 20 mL of dry dimethylformamide. The resulting mixture was stirred at room temperature under nitrogen for 12 h. Then, the reaction mixture was poured into water/ice, and the precipitated solid was collected by filtration, air-dried, and recrystallized from chloroform to give **7**: 87% yield; mp 191−193 °C; colorless prisms (chloroform); IR (Nujol) 3159, 1520 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.74 (s, 6H), 6.71 (d, 4H, $J$ = 9.0 Hz), 6.80 (d, 4H, $J$ = 9.0 Hz), 7.15 (dd, 2H, $J$ = 7.6, 1.4 Hz), 7.27 (t, 2H, $J$ = 7.8 Hz), 7.41 (td, 2H, $J$ = 7.6, 1.6 Hz), 7.56 (s, broad, 2H), 7.74 (d, 2H, $J$ = 7.8 Hz), 8.12 (s, broad, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.5, 115.0, 126.7, 127.8, 128.2, 128.3, 128.4, 130.1, 134.9, 136.8, 158.9, 180.6; mass spectrum *m*/*z* (relative intensity) 268 (9), 108 (100). Anal. Calcd for $C_{28}H_{26}N_4O_2S_2$: C, 65.35; H, 5.09; N, 10.89. Found: C, 65.18; H, 5.22; N, 11.02.

**2-[4-(Methoxyphenyl)amino]dibenzo[*d*,*f*][1,3]diazepine (8c).** This compound was obtained from the dehydrosulfurization reactions of the bis(thiourea) **7c** employing procedures a and c, which will be described in the following text for the dehydrosulfurization of the bis(thiourea) **22**. After chromatography (silica gel, *n*-hexane/ethyl acetate 1:1), the guanidine **8c** (45 and 21% yield, respectively) and 4-methoxyphenyl isothiocyanate were isolated. **8c**: 45% yield; mp 244−245 °C; colorless prisms (chloroform); IR (Nujol) 3348, 1665 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.81 (s, 3H), 6.89−6.93 (m, 6H), 7.14−7.31 (m, 6H), 7.47 (dd, 2H, $J$ = 7.3, 1.8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.1, 115.1, 120.6, 124.1, 124.7, 128.8, 129.4, 130.6, 140.5, 155.9, 157.9; mass spectrum *m*/*z* (relative intensity) 315 ($M^+$, 100), 108 (66). Anal. Calcd for $C_{20}H_{17}N_3O$: C, 76.16; H, 5.44; N, 13.33. Found: C, 76.02; H, 5.27; N, 13.15.

**2-Azido-2′-phthalimidobiphenyl.** To a stirred solution of 2-amino-2′-phthalimidobiphenyl (6.3 g, 20 mmol) in 74 mL of 2 N HCl cooled at 0 °C was added dropwise a solution of $NaNO_2$ (1.66 g, 24 mmol) in 30 mL of water. The reaction mixture was stirred at 0 °C for 45 min, and then a solution of $NaN_3$ (2.75 g, 42 mmol) in 40 mL of water was added. The reaction mixture was allowed to warm at room temperature for 5 h. The precipitated solid was collected by filtration, air-dried, and chromatographed (silica gel, *n*-hexane/ethyl acetate 1:1) to give **2-azido-2′-phthalimidobiphenyl** in 93% yield: mp 154−156 °C; white prisms (dichloromethane); IR (Nujol) 2135, 1717 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.03−7.82 (m); $^{13}$C NMR ($CDCl_3$) $\delta$ 118.7, 123.6, 124.7, 129.0, 129.1, 129.2, 130.2, 130.4, 131.0, 131.6, 131.7, 134.2, 137.3, 137.6, 167.1; mass spectrum *m*/*z* (relative intensity) 315 ($M^+$, 100). Anal. Calcd for $C_{20}H_{12}N_4O_2$: C, 70.58; H, 3.55; N, 16.46. Found: C, 70.64; H, 3.21; N, 16.55.

**2-Amino-2′-azidobiphenyl (9).** To a solution of 2-azido-2′-phthalimidobiphenyl (6.65 g, 19.6 mmol) in 300 mL of tetrahydrofuran and 46 mL of ethanol was added 9.18 g (0.15 mol) of 80% $N_2H_4 \cdot H_2O$. The reaction mixture was stirred overnight at room temperature. The precipitated solid was separated by filtration, the solvent was removed under reduced pressure, and the resulting material was purified by chromatography (silica gel, *n*-hexane/ethyl acetate 7:3) to give **2-amino-2′-azidobiphenyl** (**9**) in 98% yield: colorless semisolid; mp 31−32 °C (lit.[31] mp 32−33 °C).

**2-Azido-2′-isothiocyanatobiphenyl (10).** To a solution of 2-amino-2′-azidobiphenyl (0.42 g, 1.99 mmol) in 25 mL of chloroform cooled at 0 °C were added dropwise a solution of potasium carbonate (0.55 g, 4 mmol) in 15 mL of water and simultaneously a solution of thiophosgene (0.23 g, 4 mmol) in 15 mL of chloroform. The reaction mixture was allowed to warm at room temperature for 4 h. The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting material was purified by chromatography (silica gel, *n*-hexane/dichloromethane 1:1) to give **10** in 77% yield: pale yellow oil; IR (neat) 2121, 1583 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.22−7.38 (m, 7H), 7.43−7.52 (m, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 118.6, 122.5, 124.9, 125.7, 127.2, 129.0, 129.4, 130.0, 131.1, 131.6, 136.0, 138.6, one quaternary carbon atom was not observed; mass spectrum *m*/*z* (relative intensity) 252 ($M^+$, 98), 251 (100). Anal. Calcd for $C_{13}H_8N_4S$: C, 61.89; H, 3.20; N, 22.22. Found: C, 61.25; H, 3.27; N, 22.94.

**2-Azido-2′-isocyanatobiphenyl (11).** Triethylamine (1 g, 9.84 mmol) and triphosgene (0.33 g, 1.1 mmol) were added to a solution of 2-amino-2′-azidobiphenyl (0.69 g, 3.28 mmol) in 45 mL of dry benzene. The reaction mixture was heated under nitrogen at reflux temperature for 3 h. Then, the solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel, *n*-hexane/dichloromethane 1:1) to give **11** in 57% yield: pale yellow oil; IR (neat) 2266, 2126 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.13−7.38 (m, 7H), 7.43−7.53 (m, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 118.6, 124.7, 124.8, 125.0, 125.7, 129.1, 129.8, 130.0, 131.0, 132.3, 134.4, 138.6, one quaternary carbon atom was not observed; mass spectrum *m*/*z* (relative intensity) 236 ($M^+$, 7), 182 (100). Anal. Calcd for $C_{13}H_8N_4O$: C, 66.08; H, 3.42; N, 23.73. Found: C, 66.25; H, 3.33; N, 24.02.

**Preparation of the Azidothioureas 12.** To a solution of 2-amino-2′-azidobiphenyl (2 g, 9.52 mmol) in 20 mL of dry dimethylformamide was added 9.52 mmol of 4-tolyl- or 4-methoxyphenyl isothiocyanate. The reaction mixture was stirred under nitrogen for 24 h and then poured into water/ice and extracted with dichloromethane. The organic layer was separated, washed well with $H_2O$, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residual material was purified by chromatography (silica gel, *n*-hexane/ethyl acetate 7:3) to give compounds **12a** and **12c**, respectively.

***N*-[2-(2′-Azido)biphenyl]-*N*′-4-tolylthiourea (12a):** 91% yield; mp 167−168 °C; white prisms; IR (nujol) 3353, 3159, 2142, 1536 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.36 (s, 3H), 6.92 (d, 2H, $J$ = 8.2 Hz), 7.04 (d, 1H, $J$ = 8.1 Hz), 7.13−7.35 (m, 6H), 7.38−7.47 (m, 2H), 7.79−7.86 (m, 2H), 8.1 (s, broad, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.1, 117.6, 125.4, 126.2, 127.0, 127.8, 128.5, 129.4, 130.1, 130.3, 130.8, 132.0, 133.4, 134.2, 135.7, 137.1, 137.9, 180.2; mass spectrum *m*/*z* (relative intensity) 331 (5), 106 (100). Anal. Calcd for $C_{20}H_{17}N_5S_2$: C, 61.36; H, 4.38; N, 17.89. Found: C, 61.22; H, 4.50; N, 17.77.

***N*-[2-(2′-Azido)biphenyl]-*N*′-(4-methoxyphenyl)thiourea (12c):** 90% yield; mp 185−187 °C; yellow prisms (chloroform/*n*-hexane); IR (nujol) 3342, 2126, 1541 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.83 (s, 3H), 6.85 (d, 2H, $J$ = 8.9 Hz), 6.96 (d, 2H, $J$ = 8.9 Hz), 7.06 (d, 1H, $J$ = 8.0 Hz), 7.14−7.47 (m, 6H), 7.67 (s, 1H), 7.81 (s,1H), 7.88 (d, 1H, $J$ = 7.8 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 55.5, 114.8, 114.9, 117.7, 125.4, 126.9, 127.6, 128.3, 128.5, 129.4, 130.2, 130.8, 132.1, 134.1, 135.8, 137.2, 159.1, 180.7; mass spectrum *m*/*z* (relative intensity) 375 ($M^+$, 2), 108 (100). Anal. Calcd for $C_{20}H_{17}N_5OS_2$: C, 58.95; H, 4.20; N, 17.19. Found: C, 59.07; H, 4.04; N, 17.28.

**Preparation of the Azidocarbodiimides 13.** A mixture of the corresponding azidothiourea **12a** or **12c** (4 mmol), yellow HgO (1.73 g, 8 mmol), and anhydrous magnesium sulfate (1.15 g, 9.6 mmol) in 30 mL of dry benzene was heated at reflux temperature under nitrogen for 4 h. After cooling, the reaction mixture was filtered over Celite and the filtrate concentrated to dryness. The resulting material was chromatographed on a silica gel column using the appropriate eluent to give the azidocarbodiimides **13a** and **13c**, respectively.

***N*-[2-(2′-Azido)biphenyl]-*N*′-(4-tolyl)carbodiimide (13a):** silica gel, *n*-hexane/dichloromethane 3:2; 68% yield; pale yellow oil; IR (neat) 2142, 1503 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.28 (s, 3H), 6.79 (d, 2H, $J$ = 8.2 Hz), 6.99−7.38 (m, 10H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.0, 118.4, 123.8, 124.7, 124.8, 125.3, 129.1, 129.4, 129.9, 130.1, 130.6, 131.1, 131.6, 133.9, 135.0, 135.6, 136.9, 138.4; mass spectrum *m*/*z* (relative intensity) 325 ($M^+$, 27), 152 (100). Anal. Calcd for $C_{20}H_{15}N_5$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.97; H, 4.78; N, 21.34.

***N*-[2-(2′-Azido)biphenyl]-*N*′-(4-methoxyphenyl)carbodiimide (13c):** silica gel, *n*-hexane/dichloromethane 7:3; 44% yield; yellow oil; IR (neat) 2136, 1504 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.77 (s, 3H), 6.75 (d, 2H, $J$ = 9.1 Hz), 6.83 (d, 2H, $J$ = 9.1 Hz), 7.06−7.14 (m, 2H), 7.17−7.36 (m, 6H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 55.6, 114.6, 118.4, 124.7, 125.0, 125.3, 129.1, 129.4, 130.7, 130.9, 131.1, 131.6, 133.9, 133.9, 137.1, 138.5, 157.2, one methine carbon atom was not observed; mass spectrum *m*/*z* (relative intensity) 341 ($M^+$, 19), 152 (100). Anal. Calcd for $C_{20}H_{15}N_5O$: C, 70.37; H, 4.43; N, 20.52. Found: C, 70.55; H, 4.48; N, 20.63.

**Reaction of the Betaines 15 with Aryl Isocyanates.** The betaines **15a** and **15c** were prepared by the following procedure and were used without purification in the next step. Triphenylphosphane (0.23 g, 0.89 mmol) was added to a solution of azidocarbodiimides **15a** or **15c** (0.89 mmol) in 7 mL of dry diethyl ether. The reaction mixture was stirred under nitrogen for 3 h. The resulting betaines precipitated from the reaction medium and were collected by filtration and dried under nitrogen.

To a solution of the corresponding isocyanate (0.23 mmol) in 5 mL of dry dichloromethane under nitrogen was added the betaine (0.23 mmol). The resulting mixture was stirred at room temperature for 16 h, the solvent was removed under reduced pressure, and the remaining material was chromatographed on a silica gel column using the appropriate eluent. From the reaction of betaine **15c** with 4-methoxyphenyl isocyanate, the diazetidine **2c** was isolated in 35% yield. From the reactions of the betaines **15a** and **15c** with 4-methoxyphenyl and 4-tolyl isocyanates, respectively, were isolated diazetidines **2f** and **2g**.

**1-(4-Tolyl)-2-(4-methoxyphenyl)iminodibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepine (2f):** silica gel, *n*-hexane/dichloromethane 1:1; 28 or 38% yield, respectively; colorless oil; IR (neat) 1682 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.34 (s, 3H), 3.75 (s, 3H), 6.28−6.39 (m, 1H), 6.81 (d, 2H, $J$ = 8.7 Hz), 6.91−7.45 (m, 11H), 7.91−8.03 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.1, 55.5, 114.6, 117.5, 118.6, 124.6, 124.9, 125.6, 127.6, 128.3, 128.8, 128.9, 129.5, 131.2, 131.4, 132.6, 133.3, 134.4, 137.1, 141.2, 142.3, 143.9, 151.4, 157.1; mass spectrum *m*/*z* (relative intensity) 430 ($M^+$, 44), 238 (100). Anal. Calcd for $C_{28}H_{22}N_4O$: C, 78.12; H, 5.15; N, 13.01. Found: C, 78.01; H, 5.27; N, 12.78.

**1-(4-Methoxyphenyl)-2-(4-tolyl)iminodibenzo[*d*,*f*]-1,3-diazetidino[1,2-*a*]diazepine (2g):** silica gel, *n*-hexane/dichloromethane 1:1; 12 or 16% yield respectively; colorless oil; IR (neat) 1687 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.28 (s, 3H), 3.80 (s, 3H), 6.28−6.44 (m, 1H), 6.90−7.45 (m, 13H), 7.89−8.05 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.0, 55.5, 114.2, 117.2, 120.4, 123.1, 124.9, 125.6, 127.5, 128.2, 128.7, 128.9, 130.0, 130.9, 131.3, 131.4, 132.5, 132.7, 134.7, 141.4, 141.9, 143.8, 151.4, 156.8; mass spectrum *m*/*z* (relative intensity) 430 ($M^+$, 47), 238 (100). Anal. Calcd for $C_{28}H_{22}N_4O$: C, 78.12; H, 5.15; N, 13.01. Found: C, 76.95; H, 5.60; N, 13.71.

**Reaction of Azides 10 and 11 with Triphenylphosphane.** To a solution of azide **10** (0.16 g, 0.62 mmol) in 15 mL of dry benzene was added triphenylphosphane (0.16 g, 0.62

(31) Murat, S.; Tsuji, H.; Tomioka, H. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 895.

mmol). The reaction mixture was stirred under nitrogen and heated at reflux temperature for 24 h. The solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel, *n*-hexane/dichloromethane 1:1) to give the diazetidine **6** in 4% yield.

To a solution of 2-azido-2′-isocyanatobiphenyl (**11**) (4 g, 1.7 mmol) in 25 mL of dry dichloromethane was added triphenylphosphane (0.44 g, 1.7 mmol). The reaction mixture was stirred under nitrogen at room temperature for 8 h. The solvent was removed under reduced pressure, and the residual material was chromatographed (silica gel, *n*-hexane/dichloromethane 1:1) to give the diazetidine **6** in 5% yield.

**Reaction of 2,2′-Bis[(triphenylphosphoranylidene)-amino]biphenyl (1) with 2,2′-Bis(isothiocyanato)biphenyl (4).** A mixture of bis(iminophosphorane) **1** (2 g, 2.84 mmol) and bis(isothiocyanate) **4** (0.76 g, 2.84 mmol) in 50 mL of dry benzene was heated under nitrogen at reflux temperature for 24 h. Then, the solvent was removed under reduced pressure, and the residual material was chromatographed (silica gel, *n*-hexane/dichloromethane 7:3) to give the diazetidine **6** in 4% yield.

**Bis(thiourea) 22.** To a solution of 2,2′-diaminobiphenyl (0.3 g, 1.6 mmol) in 80 mL of dry dimethylformamide was added dropwise for 2 h a solution of 2,2′-bis(isothiocyanato)biphenyl (0.44 g, 1.6 mmol) in 45 mL of the same solvent. The reaction mixture was stirred for 20 h at room temperature and was heated at reflux temperature for 2 h. Then the reaction mixture was poured into water/ice. The precipitated solid was collected by filtration, washed with water, and air-dried to give the bis(thiourea) **22** in 85% yield: mp 208−210 °C; white prisms; IR (Nujol) 3154, 1595 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.08 (dd, 4H, $J$ = 7.7, 1.0 Hz), 7.16−7.34 (m, 8H), 7.41 (dd, 4H, $J$ = 7.5, 1.5 Hz), 10.08 (s, 4H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 121.5, 125.5, 128.8, 129.2, 130.7, 130.0, 141.0, 193.7; mass spectrum *m*/*z* (relative intensity) 452 ($M^+$, 4), 168 (100). Anal. Calcd for $C_{26}H_{20}N_4S_2$: C, 69.01; H, 4.46; N, 12.39. Found: C, 68.83; H, 4.59; N, 12.50.

**Dehydrosulfurization of Bis(thiourea) 22. Method A.** To a suspension of bis(thiourea) **22** (0.3 g, 0.66 mmol) in 50 mL of dry dichloromethane were added triphenylphosphane (0.38 g, 1.5 mmol), triethylamine (0.15 g, 1.5 mmol) and carbon tetrachloride (0.22 g, 1.5 mmol). The stirred reaction mixture was heated under nitrogen at reflux temperature for 24 h. The precipitated solid was collected by filtration, washed with water, air-dried, and identified as the starting bis(thiourea) (0.2 g). From the filtrate, the solvents were removed under reduced pressure, and the residual material was chromatographed on a silica gel column (*n*-hexane/dichloromethane 1:1) to give **[*a*,*c*]bis[dibenzo[*d*,*f*][1,3]diazepino]-1,3-diazetidine** (**6**) in 4% yield.

**Method B.** A solution of diethyl azodicarboxylate (0.12 g, 0.71 mmol) and triphenylphosphane (0.18 g, 0.71 mmol) in 30 mL of dry tetrahydrofuran was stirred for 20 h at room temperature under nitrogen, and then the bis(thiourea) **22** (0.16 g, 0.35 mmol) was added. The reaction mixture was stirred at the same temperature for 20 h. The solvent was removed under reduced pressure, and the resultant material was chromatographed (silica gel, *n*-hexane/dichloromethane 1:1) to give the diazetidine **6** in 3% yield and the starting bis(thiourea) (0.04 g).

**Method C.** Yellow HgO (1.2 g, 5.53 mmol) and magnesium sulfate (0.99 g) were added to a suspension of the bis(thiourea)-**22** (0.6 g, 1.38 mmol) in 60 mL of dry benzene. The reaction mixture was heated at reflux temperature under nitrogen for 3.5 days. After filtering over Celite and concentration to dryness, the resulting material was chromatographed on a silica gel column (*n*-hexane/dichloromethane 1:1) to give the diazetidine **6** in 7% yield.

**Reaction of 2,2′-Bis[(triphenylphosphoranylidene)-amino]biphenyl (1) with $CO_2$.** To a solution of 2,2′-bis-[(triphenylphosphoranylidene)amino]biphenyl (**1**) (1 g, 1.4 mmol) in 40 mL of dry benzene cooled to −78 °C was added an excess of solid carbon dioxide. The resulting mixture was introduced in a glass-sealed tube and heated at 70 °C for 5 h. The solvent was removed under reduced pressure, and the remaining material was chromatographed on a silica gel column (*n*-hexane/dichloromethane 1:1) to give bis(1,1′-biphenyl-2,2′-diyl)bis(carbodiimide) (**23**) and the diazetidine **6** in 6% and 28% yields, respectively.

**Bis(1,1′-biphenyl-2,2′-diyl)bis(carbodiimide) (23):** 6% yield; mp 205−207 °C; white prisms (dichloromethane); IR (Nujol) 2158, 1601 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 6.72−6.77 (m, 4H), 7.14−7.22 (m, 12H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 124.0, 125.1, 129.1, 130.6, 132.9, 134.2, 137.6; mass spectrum ($FAB^+$) (relative intensity) 385 ($M^+$ + 1, 100). Anal. Calcd for $C_{26}H_{16}N_4$: C, 81.23; H, 4.20; N, 14.57. Found: C, 81.18; H, 4.13; N, 14.69.

**Reaction of 2,2′-bis[(triphenylphosphoranylidene)-amino]biphenyl (1) with $Boc_2O$/DMAP.** $Boc_2O$ (0.43 g, 1.98 mmol) and DMAP (0.12 g, 0.99 mmol) were added to a solution of the bis(iminophosphorane) **1** (0.7 g, 0.99 mmol) in 40 mL of dry dichloromethane. The reaction mixture was stirred at room temperature under nitrogen for 24 h. The solvent was removed under reduced pressure, and the residual material was chromatographed on a silica gel column (*n*-hexane/dichloromethane 1:1) to give **1,3-bis-(*tert*-butoxycarbonyl)dibenzo[*d*,*f*][1,3]-diazepin-2-one**[11] (**24**) in 23% yield and the diazetidine **6** in 8% yield.

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**Supporting Information Available:** X-ray structure factors for compounds **2c** and **6** (12 pages). See any current masthead page for ordering and Internet access information.

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