# Synthetic Applications of Bis(iminophosphoranes). An Efficient and General Route to Fully Unsaturated Azolo-Fused 1,3-Diazepines

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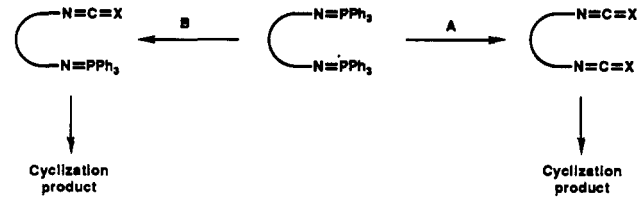
Recent years have witnessed a significant increase in the utilization of iminophosphoranes as valuable synthetic intermediates.[1] In particular, iminophosphoranes are versatile building blocks for the construction of nitrogen heterocycles, which constitute the backbone of various biologically active compounds[2] such as lavendamycin, eudistomin, aplysinopsine, and pimprinine. However, the chemistry of bis(iminophosphoranes) remains almost unexplored. Bis(iminophosphoranes) are expected to have synthetic potential as a result of their ability to react with reagents having two functionalities[3] or with two separate reagents with the same or different functionality[4] (Scheme I, mode A). The synthetic utility of the bis(iminophosphoranes) can be increased if the two iminophosphorane portions show different reactivity toward the same functionality. For example, after one aza Wittig-type reaction, the remaining iminophosphorane group could undergo cyclization across the heterocumulene and iminophosphorane moieties (Scheme I, mode B). In this context, we previously reported that *C,C*-bis(iminophosphoranes)[5] in which one iminophosphorane group is directly linked to an aromatic ring and the other is on a vinyl side chain at the ortho position undergo aza Wittig-type reactions with aromatic and aliphatic isocyanates to give iminophosphoranes derived from indoles or pyrrolo[2,3-*b*]indoles, respectively.[6] As a further extention of this methodology, we studied the behavior in aza Wittig-type reactions of *C,C*-bis(iminophosphoranes) in which the aromatic ring is replaced by a five-membered heterocyclic ring. This new annelation approach has surprisingly been found to be useful for the simultaneous formation of seven- and four-membered heterocyclic rings.

## Results and Discussion

Key bis(iminophosphorane) **2** was easily prepared in 55% overall yield from 5-azido-4-formyl-3-methyl-1*H*-pyrazole[7] by the following sequence of steps: (a) condensation of the formylpyrazole with ethyl azidoacetate at −25 °C in the presence of sodium ethoxide to afford **1** and (b) Staudinger reaction of **1** with triphenylphosphine at 0 °C. Aza Wittig-type reactions of bis(iminophosphorane) **2** with 1 equiv of aliphatic or aromatic isocyanates in toluene at room temperature lead directly to previously unreported pyrazolo[3,4-*d*][1,3]diazepines **3** in fair yields (53–70%). However, bis(iminophosphorane) **2** reacts with 2 equiv of aromatic isocyanates or isothiocyanates under the same conditions to give tricyclic 1,3-diazeto[1′,2′-*a*]-pyrazolo[3,4-*d*][1,3]diazepines **4** directly in 50–68% yields. Trace levels of compounds **3** (R = aryl) were detected in the reaction crudes. When 2 equiv of aliphatic isocyanates were used, the reaction product was found to be **3**, and no traces of the corresponding tricyclic compound **4** could be detected in the crude product[8] (Scheme II). The structures of compounds **3** were established from the spectroscopic ($^1$H and $^{13}$C NMR and IR) data. The ester absorptions in their IR spectra appeared between 1648 and 1699 cm$^{-1}$ and were clearly shifted to lower wavelength in comparison with the precursor bis-azide. In the $^1$H NMR spectra, the endocyclic NH proton also appeared a low field, which may be a consequence of hydrogen bonding that forms a five-membered ring chelate between the NH and the ethoxycarbonyl oxygen. This type of hydrogen bonding is analogous to that observed for 4-(ethoxycarbonyl)-3*H*-1,3-benzodiazepines.[9] In addition, in the $^{13}$C NMR spectra, coupling ($^3J_{CH}$ = 5.1 Hz) of the C-4 carbon atom with the endocyclic NH was observed. These facts strongly suggest that fused diazepines **3** are the 3H-isomers. For compounds **3a** and **3b**, the complexity of the signal for the remaining amino group suggested an exocyclic amino group. This hypothesis was confirmed by an X-ray diffraction analysis[10] carried out on a single crystal of compound **3b**. The $^1$H and $^{13}$C NMR spectra of compounds **4** indicated that the two aryl groups are nonequivalent. The two carbon atoms of the four-membered ring were assigned from fully proton-coupled spectra by their multiplicity, and the chemical shifts were in good agreement with the previously reported values for this kind of ring.[11] An X-ray structure determination[10] of compound **4b** confirmed the proposed structure.

**Scheme I**




(1) Barluenga, J.; Palacios, F. *Org. Prep. Proced. Int.* **1991**, *23*, 1. Gusar, N. I. *Russ. Chem. Rev.* **1991**, *60*, 146. Gololobov, Y. G.; Kasukin, L. *Tetrahedron* **1992**, *48*, 1353. Eguchi, S.; Matsushita, Y.; Yamashita, K. *Org. Prep. Proced. Int.* **1992**, *24*, 209.

(2) Molina, P.; Fresneda, P. M.; Cánovas, M. *Tetrahedron Lett.* **1992**, 2891. Molina, P.; Fresneda, P. M.; Almendros, P. *Tetrahedron Lett.* **1992**, 4491. Molina, P.; Fresneda, P. M.; Almendros, P. *Synthesis* **1993**, 54.

(3) Appel, R.; Volz, P. *Chem. Ber.* **1975**, *108*, 623. Katritzky, A. R.; Wrobel, L.; Savage, G. P. *J. Chem. Res. Synop.* **1990**, 330.

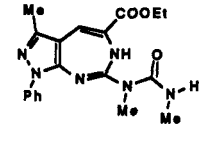
(4) (a) Molina, P.; Alajarín, M.; Vidal, A. *J. Chem. Soc., Chem. Commun.* **1992**, 295. (b) Molina, P.; Alajarín, M.; Vidal, A. *J. Org. Chem.* **1992**, *57*, 6703.

(5) We denote as *C,C*-bis(iminophosphoranes) those compounds where both iminophosphorane groups are placed either on an aromatic, a heteroaromatic, or an unsaturated carbon–carbon side chain.

(6) (a) Molina, P.; Arques, A.; Alías, A.; Vinader, M. V. *Tetrahedron Lett.* **1991**, 4401. (b) Molina, P.; Arques, A.; Alías, A.; Vinader, M. V.; Foces-Foces, M. C.; Hernández Cano, F. *Tetrahedron* **1992**, *48*, 3091.

(7) Molina, P.; Arques, A.; Vinader, M. V.; Becher, J.; Brondum, K. *J. Org. Chem.* **1988**, *53*, 4654.

(8) From the reaction of bis(iminophosphorane) **2** with 2 equiv of methyl isocyanate, the fused [1,3]diazepine (60%, mp 188–189 °C, red prisms) was isolated as the only reaction product. This compound probably arises from the addition of the second equiv of the methyl isocyanate to the exocyclic amino group of **3**.

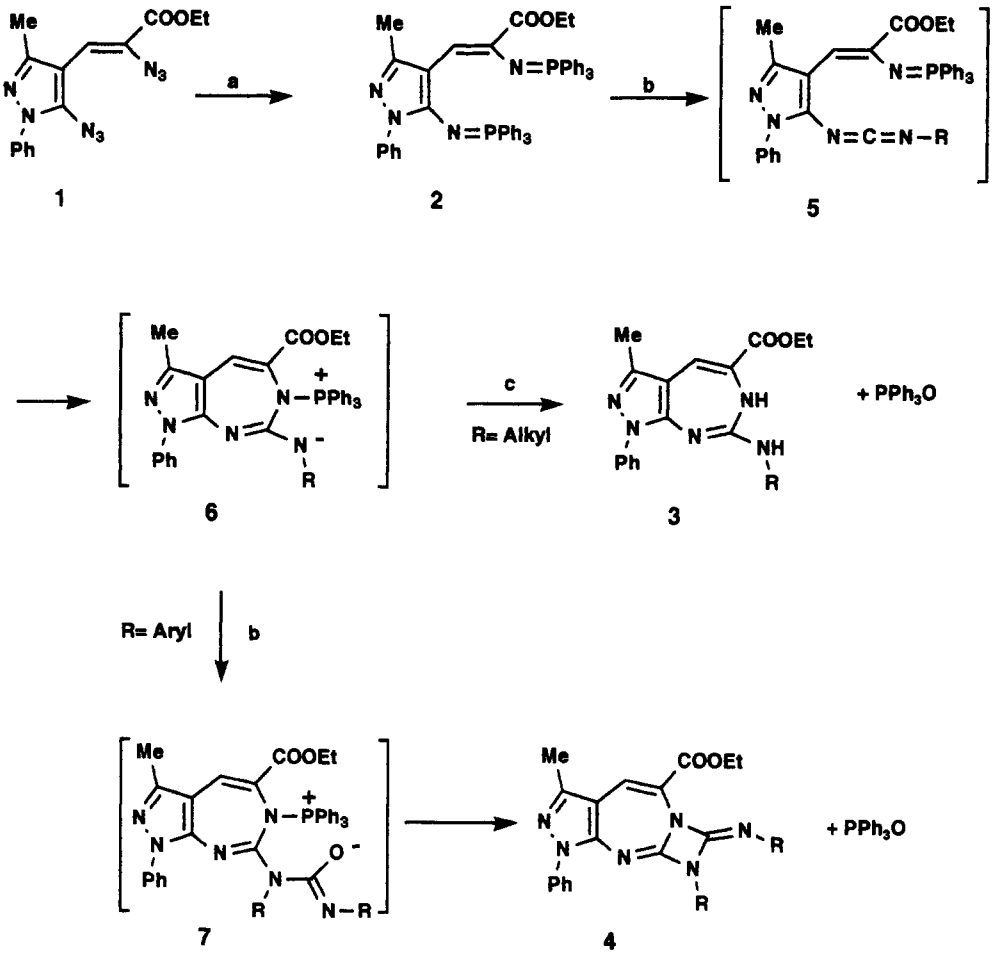



(9) Kurita, J.; Iwata, T.; Yasuite, S.; Tsuchiya, T. *J. Chem. Soc., Chem. Commun.* **1992**, 81.

(10) For a preliminary communication of a part of this work, see: Molina, P.; Arques, A.; Alías, A.; Foces-Foces, M. C.; Llamas-Saiz, A. L. *J. Chem. Soc., Chem. Commun.* **1992**, 424.

0022-3263/93/1958-5264$04.00/0 

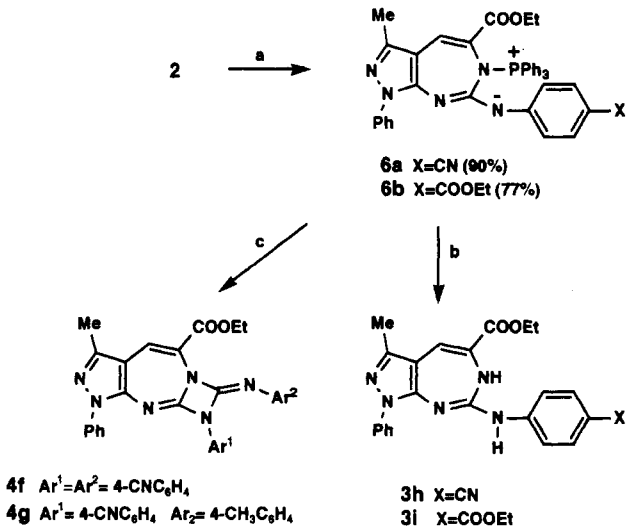
**Scheme II**[a]




[a] Reagents: (a) $PPh_3$, $CH_2Cl_2$, 0 °C; (b) RNCO, toluene, rt; (c) hydrolytic cleavage during the workup.

The formation of fused diazepines **3** and fused diazetidines **4** can be explained by an initial aza Wittig-type reaction between the iminophosphorane group directly linked to the heterocyclic ring and 1 equiv of the isocyanate to give carbodiimide **5**, which undergoes cyclization by nucleophilic attack of the nitrogen atom of the β-styryliminophosphorane-like cyclization by nucleophilic attack of the nitrogen atom of the β-styryliminophosphorane-like group on the central carbon atom of the carbodiimide moiety to give zwitterionic compound **6**. This compound either undergoes hydrolytic cleavage during the workup to give **3** or reacts with the second equiv of the isocyanate across the negative exocylic nitrogen atom to give **7**, which, by loss of triphenylphosphine oxide with concomitant ring closure, affords fused diazetidines **4** (Scheme II). This mechanism is in accord with recent results obtained in our laboratory[4b,6b] that clearly show that an arylimino-phosphorane group is more reactive than a β-styryliminophosphorane group in aza Wittig-type reactions with isocyanates and isothiocyanates. Strong support for this mechanism was found from the reaction of bis(iminophosphorane) **2** with isocyanates or isothiocyanates substituted with an electron-withdrawing group. For example, the reaction of bis(iminophosphorane) **2** with 1 equiv of *p*-cyanophenyl or *p*-(ethoxycarbonyl)phenyl isocyanate or isothiocyanate in toluene at room temperature afforded

**Scheme III**[a]

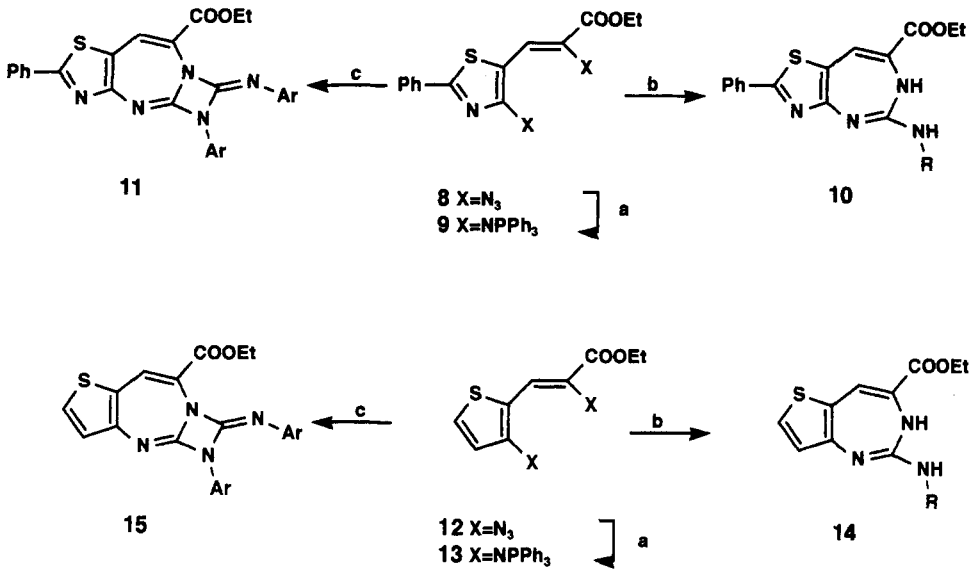



[a] Reagents: (a) $Ar^1NCX$ (X = O, S), toluene, rt; (b) HCl, aqueous EtOH, rt; (c) $Ar^2NCX$ (X = O, S), toluene, reflux.

the corresponding zwitterionic intermediates **6** as crystalline solids in excellent yields. These compounds undergo hydrolytic cleavage by the action of hydrochloric acid in ethanol at room temperature to give the fused 1,3-diazepines **3**. Conversion of intermediates **6** into tricyclic compounds **4** was achieved by the reactions of **6** with 1 equiv of the same or a different isocyanate or isothiocyanate

(11) Claramunt, R. M.; Foces-Foces, M. C.; Hernández Cano, F.; Fruchier, A.; Molina, P.; Alajarín, M.; López Leonardo, C.; Elguero, J. *J. Chem. Soc., Perkin Trans 2* **1990**, 1859.

**Scheme IV**[a]




[a] Reagents: (a) $PPh_3$, $CH_2Cl_2$, 0 °C; (b) RNCO, toluene, rt; (c) 2ArNCO, toluene, rt.

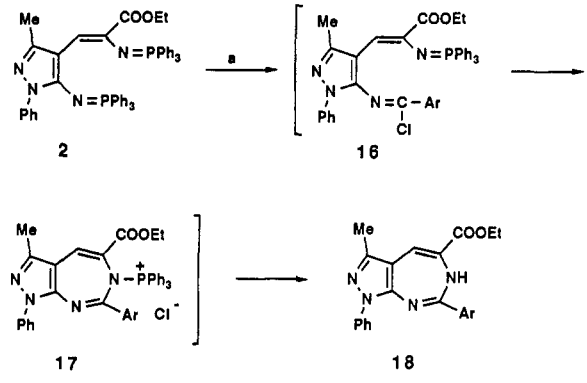
in toluene at reflux temperature (Scheme III). The electron-withdrawing substituents on the aromatic ring delocalize the negative charge on the exocyclic nitrogen atom and consequently increase the stability of compounds **6a** and **6b**.

In an analogous reaction sequence, related bis(azides) **8** and **12**, readily available from ethyl azidoacetate and 4-azido-5-formyl-2-phenylthiazole[7] or 3-azido-2-formylthiophene,[12] respectively, also resulted in the smooth formation of bis(iminophosphoranes) **9** and **13**, which were converted into fused 1,3-diazepines **10** and **14** in 50–72% yields by treatment with 1 equiv of aromatic isocyanate. Similarly, conversion of these bis(iminophosphoranes) into tricyclic compounds **11** and **15** was achieved in 50–61% yields by reaction with two equiv of aromatic isocyanate under the same conditions (Scheme IV). $^{13}C$ NMR chemical shifts for representative 1,3-diazetoazolo[1,3]diazepines are shown in Table I (values were assigned by decoupling methods and 2D H–C correlation techniques).

This experimentally convenient sequence provides direct access to fused 1,3-diazepines in a one-step process. In general, this annelation reaction proceeded without complications for a range of substrates. To the best of our knowledge, this transformation, based on a tandem aza Wittig/heterocumulene-mediated cyclization, is the first example reported of a double annelation involving the simultaneous formation of a four- and a seven-membered ring.

Having established the reactivity of compounds **2**, **9**, and **13** in aza Wittig-type reactions with isocyanates and isothiocyanates, we turned our attention to the behavior of this sort of bis(iminophosphorane) toward acyl chlorides. Bis(iminophosphorane) **2** reacts with aroyl chlorides in dry methylene chloride in the presence of triethylamine to give pyrazolo[3,4-*d*][1,3]diazepines **18** in 53–60% yields (Scheme V). Presumably, the formation of **18** involves initial formation of imidoyl chloride **16** as an intermediate,[13] which cleanly undergoes cyclization by nucleophilic attack of the nitrogen atom of the iminophosphorane

**Scheme V**[a]




[a] Reagents: (a) ArCOCl, $Et_3N$, $CH_2Cl_2$, reflux.

portion and subsequent hydrolytic P–N bond cleavage (Scheme V).

A final word of about the reactivity of tricyclic compounds **4** is relevant. It is well-known[14] that 2,4-bis(imino)-1,3-diazetidines undergo ring-opening by the action of primary amines to give biguanides. In this way, compounds **4** were converted into imidazo[1′,5′-*g*]pyrazolo-[3,4-*d*][1,3]diazepine derivatives **20** in excellent yields (87–90%) by reaction with methylamine in dry methylene chloride at room temperature. This conversion can be rationalized in terms of an initial nucleophilic attack of the amine on the C-8a carbon atom with concomitant ring opening of the four-membered ring to give biguanide-substituted intermediate **19** which undergoes regioselective cyclization across the ester functionality to give **20**. However, the reaction with sodium methoxide in methanol or chloroform at room temperature led to ring-opened products **21** in good yields (68–74%) (Scheme VI).

In conclusion, we have developed a simple and highly reliable bis(iminophosphorane)-mediated synthesis of a variety of fully unsaturated fused [1,3]diazepines with varied substituents at the [1,3]diazepine ring. These

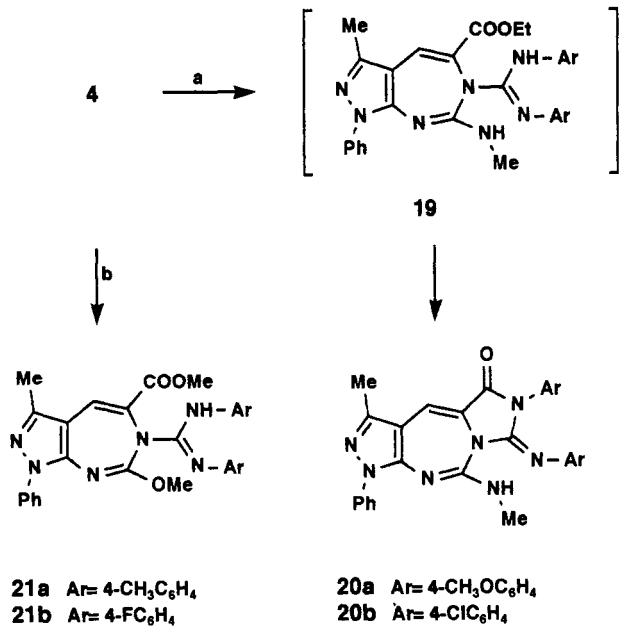
(12) Gronowitz, S.; Westerlund, C.; Hörnfeldt, A.-B. *Acta Chem. Scand. B* **1975**, *29*, 224.
(13) Zbiral, E.; Bauer, E. *Phosphorus* **1972**, *2*, 35.
(14) Molina, P.; Alajarín, M.; López Leonardo, C.; Foces-Focs, M. C.; Hernández Cano, F.; Claramunt, R. M.; Elguero, J. *J. Org. Chem.* **1989**, *54*, 1264.

Table I. $^{13}C$ Chemical Shifts (ppm) for Carbon Atoms in the Heteroaromatic Rings of Compounds 4, 11, and 15 ($J$, Hz)[a]

| compd | CO | C2 | C3 | C3a | C4 | C4a | C5 | C6 | C7 | C8 | C8a | C9 | C9a |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **4b** | 162.1 | | 148.9, qd, $^2J$ = 6.7, $^3J$ = 2.8 | 105.5, q, $^3J$ = 3.0 | 114.4, d, $^1J$ = 163.2 | | 123.1, d, $^2J$ = 1.9 | | 137.9, s | | 151.1, s | | 143.64, d, $^3J$ = 7.0 |
| **4c** | 162.1 | | 148.9, qd, $^2J$ = 6.7, $^3J$ = 2.8 | 105.5, q, $^3J$ = 3.0 | 114.6, d, $^1J$ = 163.1 | | 123.1, d, $^2J$ = 1.9 | | 137.6, s | | 151.1, s | | 143.7, d, $^3J$ = 7.9 |
| **11b** | 164.7 | 170.0 | | 144.8 | | 149.5 | | 137.3 | | 128.9 | | 116.5 | 111.3 |
| **11c** | 164.8 | 170.1 | | 145.0 | | 149.6 | | 137.3 | | 128.4 | | 116.5 | 111.5 |
| **15a** | 162.1 | 127.7 | 129.1 | 145.6 | | 149.2 | | 138.6 | | 123.0* | | 114.2 | 126.0* |
| **15b** | 161.8, d, $^3J$ = 3.9 | 128.2, dd, $^1J$ = 186.7, $^2J$ = 6.5 | 129.2, dd, $^1J$ = 169.2, $^2J$ = 9.9 | 145.4, dd, $^3J$ = 8.4, $^2J$ = 3.9 | | 148.5, s | | 139.2, s | | 123.2*# | | 114.7, dd, $^1J$ = 165.2, $^4J$ = 1.5 | 125.6*# |

[a] *, interchangeables; #, not observed.

**Scheme VI**[a]




[a] Reagents: (a) $MeNH_2$, $CH_2Cl_2$, rt; (b) NaMeO, MeOH, rt.

relatively complex structures are assembled in a simple one-pot procedure in good yields, under mild conditions, and from readily available starting materials. It should be noted that the [1,3]diazepine derivatives prepared represent variations in structural diversity not accessible by the classical synthetic route.[15] Although iminophosphorane-mediated syntheses of nitrogen heterocycles have been utilized for five- and six-membered rings, this work significantly expands the scope of the method for the synthesis of four- and seven-membered rings.

## Experimental Section

**General Methods.** All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions on a Nicolet FT-5DX spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker AC-200 and Varian Unity-300 spectrometers, and chemical shifts are expressed in parts per million ($\delta$) relative to tetramethylsilane. Electron-impact mass spectra were carried out on a Hewlett-Packard 5993C spectrometer at an ionization potential of 70 eV. Microanalyses were performed on a Carlo Erba EA1108 instrument.

**General Procedure for the Preparation of Bis(azides) 1, 8, and 12.** A solution of ethyl azidoacetate (5.16 g, 40 mmol) and the appropriate $\beta$-formylazidoazole (10 mmol) in 50 mL of dry ethanol was added dropwise to a well-stirred solution of sodium (0.92 g) in 50 mL of ethanol under nitrogen at −25 °C. The reaction mixture was stirred for 5 h, poured into aqueous 35% ammonium chloride (80 mL), and then extracted with ether (3 × 100 mL). The organic layers were washed with water (2 × 100 mL) and dried over $MgSO_4$. The $MgSO_4$ was filtered, and the filtrate was concentrated to dryness. The crude product was slurried in cold ethanol and chromatographed (silica gel; *n*-hexane/ethyl acetate (3:1)).

1: yield 63%; mp 73 °C; yellow prisms; IR (Nujol) 2139, 2107, 1704 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.40 (t, 3H, $J$ = 7.1 Hz), 2.29 (s, 3H), 4.38 (q, 2H, $J$ = 7.1 Hz), 6.81 (s, 1H), 7.30–7.48 (m, 3H), 7.59 (d, 2H, $J$ = 7.4 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.2 ($CH_3CH_2O$), 14.0 ($CH_3$-C-3), 62.3 ($CH_3CH_2O$), 105.9 (C-4), 114.6 ($C_\beta$), 123.6 ($C_o$),

(15) The only method previously reported for the preparation of fully unsaturated fused [1,3]diazepines is based on the photochemical ring expansion of quinoline *N*-imides: Tsuchiya, T.; Enkaku, M.; Kurita, J.; Sawanishi, H. *J. Chem. Soc., Chem. Commun.* **1979**, 534. Tsuchiya, T.; Enkaku, M.; Okajima, S. *Chem. Pharm. Bull.* **1980**, *28*, 2602.

126.5 ($C_o$), 127.6 ($C_p$), 128.9 ($C_m$) 133.7 (C-5), 137.6 ($C_i$), 149.0 (C-3), 162.5 (C=O); mass spectrum $m/z$ (relative intensity) 338 ($M^+$, 2), 282 (26), 209 (35), 132 (91), 77 (100). Anal. Calcd for $C_{15}H_{14}N_8O_2$: C, 53.25; H, 4.17; N, 33.12. Found: C, 54.09; H, 4.02; N, 33.05.

**8**: yield 20%; mp 104 °C; yellow prisms; IR (Nujol) 2191, 2107, 1716 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.38 (t, 3H, $^3J$ = 7.2 Hz), 4.33 (q, 2H, $^3J$ = 7.2 Hz), 6.96 (s, 1H), 7.39–7.45 (m, 3H), 7.92 (dd, 2H, $^3J$ = 7.4 Hz, $^4J$ = 3.9 Hz, $H_o$); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.1 ($CH_3$-$CH_2O$), 62.1 ($CH_3CH_2O$), 113.6 ($C_\beta$), 114.0 (C-5), 122.8 ($C_\alpha$), 126.2 ($C_o$), 128.9 ($C_m$), 130.9 ($C_p$), 132.5 ($C_i$), 150.0 (C-4), 162.5 (C=O), 168.5 (C-2); mass spectrum $m/z$ (relative intensity) 341 ($M^+$, 3), 138 (21), 103 (100). Anal. Calcd for $C_{14}H_{11}N_7O_2S$: C, 49.26; H, 3.24; N, 28.72. Found: C, 49.13; H, 3.33; N, 28.67.

**12**: yield 75%; mp 62 °C; yellow prisms; IR (Nujol) 2129, 2101, 1704 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.30 (t, 3H, $^3J$ = 7.2 Hz), 4.35 (q, 2H, $^3J$ = 7.2 Hz), 6.95 (d, 1H, $^3J$ = 5.5 Hz), 7.12 (s, 1H), 7.47 (d, 1H, $^3J$ = 5.3 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.1 ($CH_3CH_2O$), 62.0 ($CH_3CH_2O$), 114.6 ($C_\beta$), 118.7 (C-4), 121.9, 122.0, 130.1 (C-5), 138.3, 162.9 (C=O); mass spectrum $m/z$ (relative intensity) 207 (10), 139 (42), 132 (100). Anal. Calcd for $C_9H_8N_6O_2S$: C, 40.90; H, 3.05; N, 31.80. Found: C, 41.02; H, 3.08; N, 31.91.

**General Procedure for the Preparation of Bis(iminophosphoranes) 2, 9, and 13.** A solution of triphenylphosphine (5.24 g, 20 mmol) in 60 mL of dry methylene chloride was added dropwise to a stirred solution of the appropriate bis(azide) (1, 8, or 12, 10 mmol) in 60 mL of $CH_2Cl_2$ at 0 °C under nitrogen. The stirring was continued for 1 h at the same temperature, the solution was slowly warmed to rt and allowed to remain at rt for 12 h, and the solvent was removed under reduced pressure. The residual material was recrystallized from an appropriate solvent.

**2**: yield 86%; mp 181–182 °C; yellow prisms (methylene chloride/diethyl ether); IR (Nujol) 1680, 1179, 1041 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.86 (t, 3H, $^3J$ = 7.0 Hz), 2.25 (s, 3H), 3.62 (q, 2H, $^3J$ = 7.0 Hz), 6.17 (d, 1H, $^4J_P$ = 8.4 Hz), 7.14–7.46 (m, 21H), 7.52–7.71 (m, 14H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.8 ($CH_3$-C-3), 15.4 ($CH_3$-$CH_2O$), 59.9 ($CH_3CH_2O$), 106.9 (C-4, $^3J_P$ = 3.9 Hz), 113.0 ($C_\beta$, $^3J_P$ = 22.8 Hz), 124.9 ($C_o$), 127.7 ($C_m$), 127.8 ($^3J_P$ = 12.0 Hz), 128.1 ($^3J_P$ = 12.2 Hz), 130.4 ($^4J_P$ = 3.6 Hz), 131.3 ($^4J_P$ = 2.6 Hz), 132.3 ($^2J_P$ = 10.1 Hz), 132.5 ($^2J_P$ = 10.3), 134.0 ($^1J_P$ = 102.9 Hz), 134.1 ($C_\alpha$, $^2J_P$ = 5.1 Hz), 140.62 ($C_i$), 145.72 (C-5, $^2J_P$ = 3.9 Hz), 148.86 (C-3, $^4J_P$ = 2.2 Hz), 167.40 (C=O, $^3J_P$ = 6.5 Hz). Two carbon atoms are not observed; mass spectrum $m/z$ (relative intensity) 530 (10), 472 (93), 183 (100). Anal. Calcd for $C_{51}H_{44}N_4O_2P_2$: C, 75.92; H, 5.49; N, 6.94. Found: C, 74.78; H, 5.34; N, 6.89.

**9**: yield 80%; mp 225–226 °C; yellow prisms (methylene chloride/diethyl ether); IR (Nujol) 1676, 1212, 1042 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.03 (t, 3H, $^3J$ = 7.1 Hz), 3.88 (q, 2H, $^3J$ = 7.1 Hz), 7.14–7.23 (m, 3H), 7.30–7.50 (m, 21H), 7.74 (ddd, 6H, $^3J_P$ = 12.0 Hz, $^3J$ = 6.9 Hz, $^4J$ = 1.5 Hz), 7.88 (ddd, 6H, $^3J_P$ = 12.0 Hz, $^3J$ = 7.2 Hz, $^4J$ = 1.4 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.0 ($CH_3$-$CH_2O$), 59.9 ($CH_3$-$CH_2O$), 114.7 ($C_\beta$), 125.0 ($C_\alpha$), 127.8 ($^3J_P$ = 12.0 Hz), 128.0 ($^3J_P$ = 11.9 Hz), 130.6 ($^4J_P$ = 2.5 Hz), 131.1 ($^1J_P$ = 100.3 Hz), 131.2 ($^4J_P$ = 2.6 Hz), 132.5 ($^2J_P$ = 9.7 Hz), 132.87 ($^1J_P$ = 97.4 Hz), 133.0 ($^2J_P$ = 9.6 Hz), 159.9 (C=O, $^3J_P$ = 6.2 Hz); mass spectrum $m/z$ (relative intensity) 532 (5), 278 (45), 277 (100). Anal. Calcd for $C_{50}H_{41}N_3O_2SP_2$: C, 74.15; H, 5.10; N, 5.18. Found: C, 74.27; H, 5.00; N, 5.30.

**13**: yield 70%; mp 217–218 °C; IR (Nujol) 1680, 1224, 1045 cm$^{-1}$; yellow prisms (methylene chloride/*n*-hexane); $^1$H NMR ($CDCl_3$) $\delta$ 1.01 (t, 3H, $^3J$ = 6.8 Hz), 3.79 (q, 2H, $^3J$ = 6.8 Hz), 6.21 (d, 1H, $^3J$ = 5.4 Hz, 7.29–7.46 (m, 20H), 7.62–7.70 (m, 12H); mass spectrum $m/z$ (relative intensity) 732 ($M^+$, 6), 455 (15), 183 (100). Anal. Calcd for $C_{45}H_{38}N_2O_2P_2S$: C, 73.75; H, 5.22; N, 3.82. Found: C, 73.88; H, 5.30; N, 3.76.

**Pyrazolo[3,4-*d*][1,3]diazepines 3, Thiadiazolo[4,5-*d*][1,3]-diazepines 10, and Thieno[3,2-*d*][1,3]diazepines 14.** The appropriate isocyanate (1 mmol) was added to a suspension of bis(iminophosphorane) **2**, **9**, or **13** (1 mmol) in 40 mL of dry toluene. The reaction mixture was stirred at rt for 12 h. The solvent was removed under reduced pressure, and the resulting material was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (2:1) ($R_f$ = 0.5).

**3a (R = $C_2H_5$)**: yield 65%; mp 168–169 °C; red prisms; IR (Nujol) 3347, 3239, 1690, 1662 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 339 ($M^+$, 41), 265 (18), 264 (100). Anal. Calcd for $C_{18}H_{21}N_5O_2$: C, 63.70; H, 6.23; N, 20.63. Found: C, 63.58; H, 6.15; N, 20.70.

**3b (R = *n*-$C_3H_7$)**: yield 60%; mp 163–164 °C; red prisms; IR (Nujol) 3364, 1648, 1619, 1565 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 353 ($M^+$, 71), 279 (22), 278 (100). Anal. Calcd for $C_{19}H_{23}N_5O_2$: C, 64.57; H, 6.56; N, 19.81. Found: C, 64.43; H, 6.50; N, 19.90.

**3c (R = $C_6H_5CH$=CH)**: yield 70%; mp 112–113 °C; red prisms; IR (Nujol) 3251, 3166, 1693, 1670 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 413 ($M^+$, 42), 338 (38), 77 (100). Anal. Calcd for $C_{24}H_{23}N_5O_2$: C, 69.71; H, 5.60; N, 16.93. Found: C, 69.61; H, 5.72; N, 16.85.

**3d (R = $C_6H_5$)**: yield 65%; mp 199–200 °C; red prisms; IR (Nujol) 3285, 1693, 1668, 1620, 1596 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 387 ($M^+$, 100), 313 (19), 312 (60). Anal. Calcd for $C_{22}H_{21}N_5O_2$: C, 68.20; H, 5.46; N, 18.07. Found: C, 68.12; H, 5.35; N, 17.99.

**3e (R = 4-$CH_3C_6H_4$)**: yield 53%; mp 174–175 °C; red prisms; IR (Nujol) 1699, 1671, 1642 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 401 ($M^+$, 100), 327 (19), 326 (56). Anal. Calcd for $C_{23}H_{23}N_5O_2$: C, 68.81; H, 5.77; N, 17.44. Found, C, 68.92; H, 5.67; N, 17.56.

**3f (R = 4-$CH_3OC_6H_4$)**: yield 55%; mp 175–176 °C; red prisms; IR (Nujol) 3358, 3330, 1671, 1650 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 417 ($M^+$, 100), 343 (10), 342 (34). Anal. Calcd for $C_{23}H_{23}N_5O_3$: C, 66.17; H, 5.55; N, 16.77. Found: C, 66.02; H, 5.43; N, 16.62.

**3g: (R = 4-$FC_6H_4$)**: yield 67%; mp 220–221 °C; red prisms; IR (Nujol) 3341, 3239, 1689, 1664, 1620 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 405 ($M^+$, 27), 331 (17), 330 (57), 77 (100). Anal. Calcd for $C_{22}H_{20}FN_5O_2$: C, 65.17; H, 4.97; N, 17.27. Found: C, 65.03; H, 4.83; N, 17.20.

**3h (R = 4-$CNC_6H_4$)**: yield 62%; mp 238–239 °C; red prisms; IR (Nujol) 3341, 3239, 2221, 1669, 1618 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 412 ($M^+$, 80), 338 (31), 337 (100). Anal. Calcd for $C_{23}H_{20}N_6O_2$: C, 66.97; H, 4.88; N, 20.37. Found: C, 66.77; H, 4.92; N, 20.50.

**3i (R = 4-$EtOOCC_6H_4$)**: yield 59%; mp 131–132 °C; red prisms; IR (Nujol) 3222, 1669, 1624, 1585, 1567 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 459 ($M^+$, 59), 384 (47), 312 (35), 77 (100). Anal. Calcd for $C_{25}H_{25}N_5O_4$: C, 65.34; H, 5.48; N, 15.24. Found: C, 65.42; H, 5.51; N, 15.31.

**10a (R = $C_6H_5$)**: yield 65%; mp 213–214 °C; orange prisms; IR (Nujol) 3330, 3234, 1698, 1668, 1636 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 390 ($M^+$, 67), 316 (35), 215 (36), 104 (100). Anal. Calcd for $C_{21}H_{18}N_4O_2S$: C, 64.59; H, 4.64; N, 14.34. Found: C, 64.50; H, 4.75; N, 14.28.

**10b (R = 4-$CH_3C_6H_4$)**: yield 72%; mp 218–219 °C; orange prisms; IR (Nujol) 3421, 3307, 1709, 1661 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 404 ($M^+$, 100), 331 (29), 330 (42). Anal. Calcd for $C_{22}H_{20}N_4O_2S$: C, 65.32; H, 4.98; N, 13.85. Found: C, 65.18; H, 4.90; N, 13.78.

**10c (R = 4-$CH_3OC_6H_4$)**: yield 70%; mp 215–216 °C; orange prisms; IR (Nujol) 3426, 3302, 1704, 1642 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 420 ($M^+$, 100), 331 (25), 214 (20). Anal. Calcd for $C_{22}H_{20}N_4O_3S$: C, 62.84; H, 4.79; N, 13.32. Found: C, 62.96; H, 4.85; N, 13.40.

**14a (R = 4-$CH_3C_6H_4$)**: yield 50%; mp 189–190 °C; yellow prisms; IR (Nujol) 3415, 3381, 3279, 1723, 1674, 1631 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 327 ($M^+$, 46), 254 (37), 253 (96), 91 (100). Anal. Calcd for $C_{17}H_{17}N_3O_2S$: C, 62.36; H, 5.23; N, 12.83. Found: C, 62.20; H, 5.18; N, 12.75.

**14b (R = 4-$FC_6H_4$)**: yield 52%; mp 174–175 °C; yellow prisms; IR (Nujol) 3409, 3341, 1704, 1674, 1640 cm$^{-1}$; mass spectrum $m/z$ (relative intensity) 331 ($M^+$, 59), 258 (33), 257 (100). Anal. Calcd for $C_{16}H_{14}FN_3O_2S$: C, 57.99; H, 4.25; N, 12.68. Found: C, 58.10; H, 4.19; N, 12.60.

**1,3-Diazeto[1′,2′-*a*]pyrazolo[3,4-*d*][1,3]diazepines 4, 1,3-Diazeto[1′,2′-*a*]thiazolo[4,5-*d*][1,3]diazepines 11, and 1,3-Diazeto[1′,2′-*a*]thieno[3,2-*d*][1,3]diazepines 15.** The appropriate aromatic isocyanate (2 mmol) was added to a suspension of bis(iminophosphorane) **2**, **9**, or **13** (1 mmol) in 40 mL of dry toluene. The reaction mixture was stirred at rt for 12 h. The solvent was removed under reduced pressure, and the resulting material was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (2:1) ($R_f$ = 0.8).

**4a (R = $C_6H_5$)**: yield 60%; mp 150–151 °C; yellow prisms; IR (Nujol) 1783, 1722, 1671, 1626, 1594 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 488 ($M^+$, 100), 443 (4), 416 (30), 77 (13). Anal. Calcd for $C_{29}H_{24}N_6O_2$: C, 71.29; H, 4.95; N, 17.20. Found: C, 71.15; H, 4.87; N, 17.29.

**4b (R = 4-$CH_3C_6H_4$)**: yield 66%; mp 190–191 °C; yellow prisms; IR (Nujol) 1787, 1720, 1674, 1639, 1599 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 516 ($M^+$, 9), 444 (6), 443 (18), 222 (100). Anal. Calcd for $C_{31}H_{28}N_6O_2$: C, 72.07; H, 5.46; N, 16.26. Found: C, 71.90; H, 5.53; N, 16.20.

**4c (R = 4-$CH_3OC_6H_4$)**: yield 50%; mp 143–144 °C; yellow prisms; IR (Nujol) 1779, 1723, 1662, 1623, 1523 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 548 ($M^+$, 8), 476 (6), 475 (20), 239 (100). Anal. Calcd for $C_{31}H_{28}N_6O_4$: C, 67.87; H, 5.14; N, 15.31. Found: C, 67.98; H, 5.00; N, 15.25.

**4d (R = 4-$FC_6H_4$)**: yield 55%; mp 201–202 °C; yellow prisms; IR (Nujol) 1795, 1709, 1679, 1621, 1600 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 524 ($M^+$, 43), 452 (33), 451 (100). Anal. Calcd for $C_{29}H_{22}F_2N_6O_2$: C, 66.4; H, 4.22; N, 16.02. Found: C, 66.57; H, 4.15; N, 15.93.

**4e (R = 4-$ClC_6H_4$)**: yield 68%; mp 223–224 °C; yellow prisms; IR (Nujol) 1795, 1706, 1677, 1619, 1593 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 556 ($M^+$, 8), 485 (12), 262 (100). Anal. Calcd for $C_{29}H_{22}Cl_2N_6O_2$: C, 62.48; H, 3.97; N, 15.07. Found: C, 62.67; H, 3.87; N, 14.99.

**4f (R = 4-$CN_6H_4$)**: yield 55%; mp 242–243 °C; orange prisms; IR (Nujol) 2223, 1798, 1716, 1683, 1640 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 538 ($M^+$, 2), 245 (16), 244 (86), 102 (100). Anal. Calcd for $C_{31}H_{22}N_8O_2$: C, 69.13; H, 4.11; N, 20.80. Found: C, 68.98; H, 4.05; N, 20.87.

**11a (Ar = $C_6H_5$)**: yield 50%; mp 156–157 °C; orange prisms; IR (Nujol) 1805, 1707, 1690, 1639, 1620 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 491 ($M^+$, 33), 418 (15), 194 (100). Anal. Calcd for $C_{28}H_{21}N_5O_2S$: C, 68.41; H, 4.30; N, 14.24. Found: C, 68.60; H, 4.23; N, 14.20.

**11b (Ar = 4-$CH_3C_6H_4$)**: yield 58%; mp 198–199 °C; orange prisms; IR (Nujol) 1805, 1703, 1688, 1640, 1617 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 519 ($M^+$, 8), 446 (10), 222 (100). Anal. Calcd for $C_{30}H_{25}N_5O_2S$: C, 69.34; H, 4.84; N, 13.47. Found: C, 69.50; H, 4.72; N, 13.38.

**11c (Ar = 4-$CH_3OC_6H_4$)**: yield 50%; mp 182–183 °C; orange prisms; IR (Nujol) 1796, 1713, 1683 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 551 ($M^+$, 6), 255 (12), 239 (100). Anal. Calcd for $C_{30}H_{25}N_5O_4S$: C, 65.32; H, 4.56; N, 12.69. Found: C, 65.21; H, 4.67; N, 12.58.

**15a (Ar = 4-$CH_3OC_6H_4$)**: yield 51%; mp 114–115 °C; orange prisms; IR (Nujol) 1784, 1721, 1665, 1642, 1619 cm1$^{-1}$; mass spectrum *m/z* (relative intensity) 474 ($M^+$, 100), 473 (11), 402 (14). Anal. Calcd for $C_{25}H_{22}N_4O_4S$: C, 63.27; H, 4.67; N, 11.80. Found: C, 63.15; H, 4.59; N, 11.68.

**15b (Ar = 4-$FC_6H_4$)**: yield 61%; mp 155–156 °C; yellow prisms; IR (Nujol) 1793, 1733, 1683, 1642, 1618 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 450 ($M^+$, 42), 377 (26), 256 (26), 95 (100). Anal. Calcd for $C_{23}H_{16}F_2N_4O_2S$: C, 61.32; H, 3.58; N, 12.43. Found: C, 61.51; H, 3.65; N, 12.52.

**Isolation and Reactivity of Intermediates 6.** To a suspension of bis(iminophosphorane) **2** (0.8 g, 1 mmol) in 30 mL of dry toluene was added 4-cyanophenyl or 4-(ethoxycarbonyl)-phenyl isocyanate or isothiocyanate (1 mmol). The mixture was stirred at rt for 12 h. The precipitated solid was collected by filtration and washed with dry diethyl ether to give **6a** or **6b**, respectively.

**6a (R = 4-$CNC_6H_4$)**: yield 90%; mp 189–190 °C; yellow prisms; IR (Nujol) 3404, 3233, 3137, 2214, 1693 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 616 (3), 589 (3), 277 (100). Anal. Calcd for $C_{41}H_{33}N_6O_2P$: C, 73.20; H, 4.94; N, 12.49. Found: C, 72.98; H, 4.85; N, 12.59.

**6b (R = 4-$EtOOCC_6H_4$)**: yield 77%; mp 182–183 °C; yellow prisms; IR (Nujol) 3404, 1699, 1619 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 425 (16), 424 (11), 183 (100). Anal. Calcd for $C_{43}H_{38}N_5O_4P$: C, 71.75; H, 5.32; N, 9.72. Found: C, 71.60; H, 5.39; N, 9.64.

To a solution of intermediate **6a** or **6b** (1 mmol) in 20 mL of ethanol was added 1 mL of concentrated HCl. The mixture was stirred at rt for 5 min, and 20 mL of water was added. The resultant solution was neutralized with 1 N NaOH, and the precipitated solid was collected by filtration and purified by chromatography (silica gel, *n*-hexane/ethyl acetate (2:1)) to give **3h** or **3i**.

4-Methylphenyl isocyanate (0.067 g, 0.5 mmol) was added to a solution of intermediate **6a** (0.34 g, 0.5 mmol) in 20 mL of dry toluene. The reaction mixture was stirred at reflux temperature under nitrogen for 2 h. After cooling, the solvent was removed under reduced pressure, and the resulting product was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (2:1) to give **4g**: yield 56%; mp 227–228 °C; yellow prisms; IR (Nujol) 2226, 1791, 1726, 1675 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.05 (t, 3H, $^3J$ = 6.9 Hz, $CH_3CH_2O$), 2.28 (s, 3H), 2.33 (s, 3H), 3.68 (q, 2H, $^3J$ = 6.9 Hz, $CH_3CH_2O$), 6.35 (s, 1H, H-4), 7.12–7.18 (m, 4H), 7.38 (t, 1H, $^3J$ = 7.3 Hz, $H_p$), 7.46 (t, 2H, $^3J$ = 7.1 Hz, $H_m$), 7.60 (d, 2H, $^3J$ = 8.3 Hz), 7.70–7.78 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 11.9 ($CH_3$-C-3), 13.8 ($CH_3CH_2O$), 20.9 ($CH_3$), 61.7 ($CH_3CH_2O$), 105.6 (C-3a), 107.1, 115.2 (C-4), 118.2 (CH), 118.8 (CN), 122.4 (C-5), 123.8 (CH), 123.8 ($C_o$), 127.3 ($C_p$), 128.5 ($C_m$), 129.5 (CH), 132.5, 132.8 (CH), 135.1* ($C_i$), 138.0* (C-7), 140.3, 143.1 (C-9a), 148.4, 149.1 (C-3), 149.9 (C-8a), 161.7 (C=O); mass spectrum *m/z* (relative intensity) 527 ($M^+$, 13), 454 (28), 233 (100). Anal. Calcd for $C_{31}H_{25}N_7O_2$: C, 70.57; H, 4.77; N, 18.58. Found: C, 70.42; H, 4.70; N, 18.49.

Compound **4f** was obtained by the method described above from *p*-cyanophenyl isothiocyanate.

**General Procedure for the Preparation of Pyrazolo[3,4-*d*][1,3]diazepines 18.** The appropriate aroyl chloride (1 mmol) and triethylamine (1 mmol) were added to a solution of bis-(iminophosphorane) **2** (0.8 g, 2 mmol) in 50 mL of dry methylene chloride. The reaction mixture was stirred at reflux temperature for 7 h. After cooling, the solvent was removed under reduced pressure, and the residue was treated with 30 mL of dry benzene. The formed solid was separated by filtration, and the filtrate was concentrated to dryness. The resulting product was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (2:1) ($R_f$ = 0.7).

**18a (Ar = $C_6H_5$)**: yield 55%; mp 131–132 °C; brown prisms; IR (Nujol) 3409, 1694, 1674 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 372 ($M^+$, 51), 298 (28), 297 (83), 77 (100). Anal. Calcd for $C_{22}H_{20}N_4O_2$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.83; H, 5.67; N, 15.15.

**18b (Ar = 4-$CH_3C_6H_4$)**: yield 56%; mp 169–170 °C; brown prisms; IR (Nujol) 3404, 1691, 1666 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 386 ($M^+$, 28), 312 (18), 311 (58), 77 (100). Anal. Calcd for $C_{23}H_{22}N_4O_2$: C, 71.48; H, 5.73; N, 14.49. Found: C, 71.63; H, 5.65; N, 14.39.

**18c (Ar = 4-$CNC_6H_4$)**: yield 53%; mp 168–169 °C; brown prisms; IR (Nujol) 3364, 2231, 1733, 1699, 1665 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 397 ($M^+$, 5), 322 (9), 77 (100). Anal. Calcd for $C_{23}H_{19}N_5O_2$: C, 69.50; H, 4.81; N, 17.62. Found: C, 69.67; H, 4.78; N, 17.71.

**18d (Ar = 4-$FC_6H_4$)**: yield 60%; mp 183–184 °C; brown prisms; IR (Nujol) 3404, 1690, 1675 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 390 ($M^+$, 22), 316 (19), 315 (60), 77 (100). Anal. Calcd for $C_{22}H_{19}FN_4O_2$: C, 67.68; H, 4.90; N, 14.35. Found: C, 67.55; H, 4.83; N, 14.47.

**Imidazo[1′,5′-*g*]pyrazolo[3,4-*d*][1,3]diazepines 20.** Methylamine (0.06 g, 2 mmol) was added to a well-stirred solution of the appropriate 1,3-diazeto[1′,2′-*a*]pyrazolo[3,4-*d*][1,3]diazepine **4** (2 mmol) in 10 mL of dry methylene chloride. The resultant solution was stirred at rt for 6 h. The solvent was removed under reduced pressure, and the crude product was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (2:1) ($R_f$ = 0.4).

**20a (Ar = 4-$CH_3OC_6H_4$)**: yield 90%; mp 281–282 °C; red prisms; IR (Nujol) 3476, 1738, 1669, 1652 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 533 ($M^+$, 4), 267 (5), 250 (100). Anal. Calcd for $C_{30}H_{27}N_7O_3$: C, 67.52; H, 5.10; N, 23.47. Found: C, 67.42; H, 5.01; N, 23.36.

**20b (Ar = 4-$ClC_6H_4$)**: yield 87%; mp 285–286 °C; red prisms; IR (Nujol) 3409, 1743, 1732, 1668 cm$^{-1}$; mass spectrum *m/z* (relative intensity) 543 ($M^+$ + 2, 3), 541 ($M^+$, 4), 251 (25), 250 (100). Anal. Calcd for $C_{28}H_{21}Cl_2N_7O$: C, 61.99; H, 3.90; N, 18.07. Found: C, 62.12; H, 3.99; N, 18.15.

**Preparation of Pyrazolo[3,4-*d*][1,3]diazepines 21.** The appropriate [1,3]diazepine **4** (2 mmol) was added to a solution

of sodium methoxide (0.11 g, 2 mmol) in 10 mL of anhydrous methanol. The solution was stirred at rt for 7 h. The solvent was removed under reduced pressure, and the residue was washed with water (2 × 10 mL) and then chromatographed on a silica gel column with *n*-hexane/ethyl acetate (2:1) ($R_f$ = 0.4).

**21a (Ar = 4-$CH_3C_6H_4$)**: yield 68%; mp 182–183 °C; yellow prisms; IR (Nujol) 3364, 1720, 1674 $cm^{-1}$; mass spectrum *m/z* (relative intensity) 534 ($M^+$, 50), 501 (19), 267 (31), 91 (100), 77 (86). Anal. Calcd for $C_{31}H_{30}N_6O_3$: C, 69.64; H, 5.65; N, 15.71. Found: C, 69.52; H, 5.74; N, 15.65.

**21b (Ar = 4-$FC_6H_4$)**: yield 74%; mp 187–188 °C; yellow prisms; IR (Nujol) 3409, 1742, 1674 $cm^{-1}$; mass spectrum *m/z* (relative intensity) 542 ($M^+$, 26), 541 (75), 509 (13), 251 (100). Anal. Calcd for $C_{29}H_{24}F_2N_6O_3$: C, 64.20; H, 4.45; N, 15.48. Found: 64.03; H, 4.35; N, 15.40.

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**Supplementary Material Available:** NMR data for most compounds (9 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.