Reactions of Azines. 16. Preparation of 6-(Phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepines, 5*H*,7*H*-Pyrazolo[1,5-*d*][2]benzazepin-6-one, and Indeno[2,3-*c*]pyridine-3,9-diones

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The reactions of azine phosphoranes **1a–f** (R = aromatic or methyl, R^1 = alkyl) with benzalphthalide (**2a**) in xylene under reflux gave the 6-(phenylmethylene)-5*H*-pyrazolo[1,5-d][2,4]benzoxazepines **9a–f**. The phosphoranes **1g** (R = R^1 = phenyl) and **2a** similarly treated gave 5*H*,7*H*-pyrazolo[1,5-*d*][2]benzazepin-6-one **10g**. Similar treatment of phosphorane **1h** or **1i** (R = R^1 = *p*-chlorophenyl or *p*-methoxyphenyl) gave the azine ylidene **6h** or **6i**. Only compound **6h** was converted into the corresponding **9h** in a sealed tube at 240 °C. A mechanism for the formation of products **9** and **10** was proposed. The configuration of the exocyclic double bond of ring-closed compounds **9** was determined both by NOE experiments and by X-ray crystallographic analysis. The reactions of a number of azine phosphoranes **1** with lactones **2b** and **2c** were also discussed. Ethyl (*E*)-(3′-oxo-1,3-dihydrobenzofuran-1-ylidene)acetate (**2c**) gave the unusual 2*H*-indeno[2,3-*e*]pyridine-3,9-diones **18** rather than the expected pyrazolo-fused heterocyclic compounds commonly encountered in azine rearrangements. The structures of **18c** and **18d** were confirmed by X-ray crystallographic analyses. 3-(Cyanomethylene)phthalide (**2b**) gave an azine compound **16h**. Mechanisms for the reactions were proposed. ^1H, ^{13}C, and mass spectral data of all of the products were reported.

Previously, we have shown that pyrazolo-fused heterocyclic compounds have been obtained exclusively (apart from $Ph_3P{=}O$) from the reactions of azine phosphoranes with various electrophilic compounds such as ketenes, isocyanates, and anhydrides.[1-10] On the basis of previous work we thought that the reactions of azine phosphoranes **1** with benzalphthalide (**2a**), 3-(cyanomethylene)phthalide (**2b**), and ethyl (*E*)-(3′-oxo-1,3-dihydrobenzofuran-1-ylidene)acetate (**2c**) would similarly give only pyrazolo-fused products. Indeed, the corresponding pyrazolo-fused heterocyclic compounds **9** or **10** were obtained from benzalphthalide (**2a**). However, when the enol lactone **2c** was employed, instead of finding the expected pyrazolo-fused heterocyclic compounds, the unusual fused heterocyclic compounds, 2*H*-indeno[2,3-*e*]pyridine-3,9-diones **18**, were isolated.

Results and Discussion

On heating the mixture of phosphorane **1h** (R = R^1 = *p*-ClC_6H_4) or **1i** (R = R^1 = *p*-$MeOC_6H_4$) and benzalphthalide (**2a**) under reflux in xylene for 48 h, only azine ylidenes **6h** or **6i** were obtained in the yields of 79% or 71%, respectively. The pure azine ylidene **6h** was sealed in a pipet tube and was heated at 240 ± 10 °C for 15 h; after column chromatography, a 40% yield of the pyrazolobenzoxazepine **9h** was isolated. When pure **6i** was heated at 240 °C in a sealed tube even for 1 day, the corresponding rearrangement reaction did not occur, and 100% recovery of the starting material was observed. When heated at 260 °C or higher, azine ylidene **6i** was carbonized.

When the azine phosphoranes **1** (R = Me, Ph, *p*-MeC_6H_4, *o*-$MeOC_6H_4$, and R^1 = Me, Et, i-Pr) were treated with benzalphthalide (**2a**) in xylene under reflux the corresponding pyrazolobenzoxazepines **9a–f** were isolated in yields of 70%–78% (Scheme I).

All of the products **9** were isolated as one isomer. To determine the configuration about the exocyclic double bond of the indenone moiety of products **9**, nuclear Overhauser effect (NOE) difference experiments were performed on product **9b**. When the C-11 proton (at 5.7 ppm) was irradiated, positive enhancements of approximately 17% to two different aromatic protons (at 7.8 and 7.3 ppm, respectively) were observed. Two-dimensional COSY experiments identified these protons as C7-H and C13-H (see numbering in Scheme II). This implies that C11-H is spatially very close to both of these aromatic rings. Furthermore, a positive enhancement of 8% was observed to the C17-H when the C4-methyl group was irradiated. Therefore, the double bond between C6 and C11 has a *Z* configuration, which is energetically favorable due to the trans orientation of two bulky benzene rings. This result is confirmed by X-ray crystallographic analysis (Figure 1).

When the azine phosphorane **1g** (R = R^1 = Ph) was allowed to react with **2a** in xylene under reflux, only the corresponding 5*H*,7*H*-pyrazolo[1,5-*d*][2]benzazepin-6-one **10g** was obtained with triphenylphosphine oxide. None of the corresponding compounds **6g** or **9g** were found.

Azine ylidene **6** is proposed as the intermediate in the pathway of **2a** to all of the products **9** and the product **10**. The proposed mechanism for the formation of ylidene **6** is shown in Scheme II. The nucleophilic attack of

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‡ Address questions regarding NOE and COSY data to this author.

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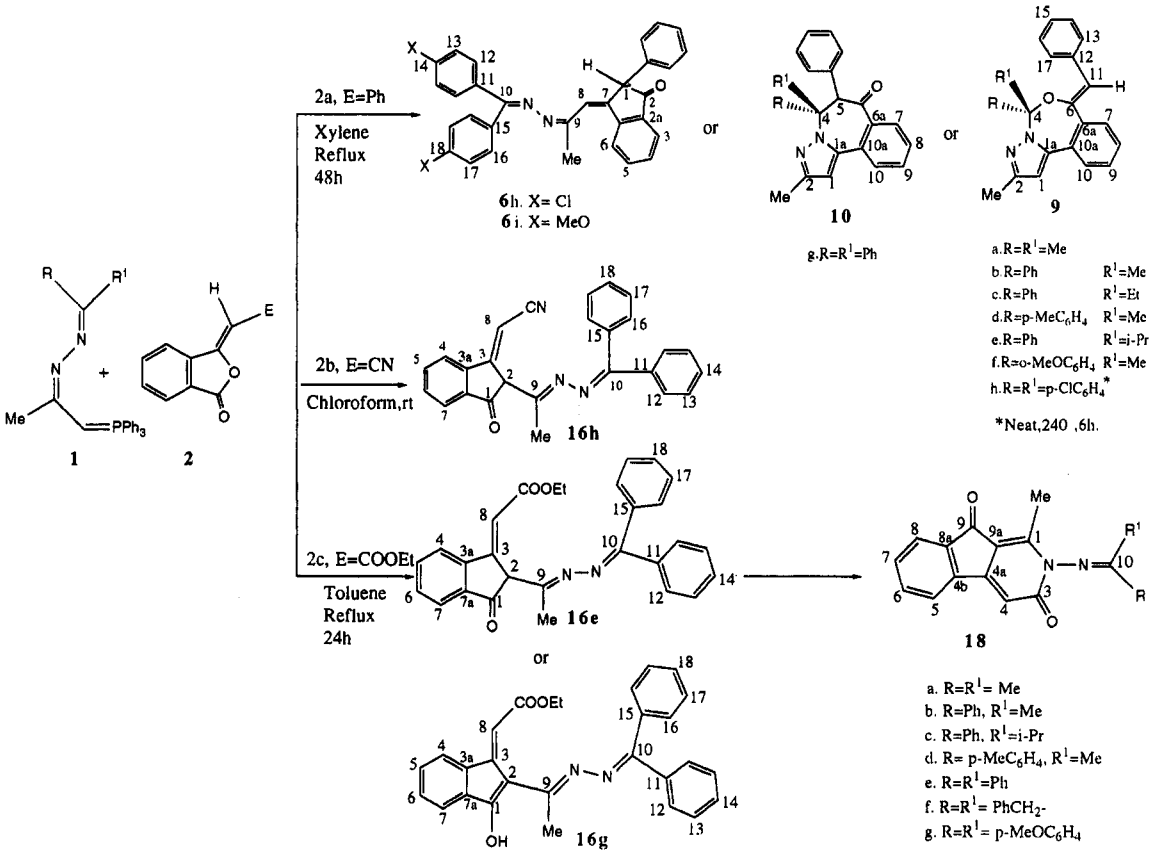
(10) Schweizer, E. E.; Cao, Z. S.; Rheingold, A. L.; Bruch, M.; *J. Org. Chem.* **1990**, *55*, 6363.

0022-3263/93/1958-4339$04.00/0

Scheme I



phosphorane **1** on the carbonyl carbon of benzalphthalide (**2a**) would give the alkoxybetain **3** which could undergo a rearrangement to form an acylated phosphonium ion **4**; the intramolecular nucleophilic attack of the enolate carboanion in **4** on the carbonyl carbon would give the betain **5** which could lose one molecule of triphenylphosphine oxide in a classical Wittig olefination reaction to form azine ylidene **6**. The final pyrazolo-ring-closed compounds **9** and **10** would arise from the thermal rearrangement of azine ylidene **6**. Initial intramolecular attack by the imine nitrogen attached to C10 on the alkenyl terminus C7 would yield the azomethine imine intermediate **7** which could open to intermediates **8a–c**. Since enolate anions exhibit ambident behavior as nucleophiles, ring closure can occur at carbon as well as at oxygen. Ring closure from **8a** (path A) would yield the seven-membered enol ethers **9**; ring closure from **8c** (path C) would yield the seven-membered ketone **10**.

In fact, the first step (**6** to **7**) of the pyrazolo rearrangement is the initial step of a "criss–cross"[11] cycloaddition reaction which works best with electron-deficient dienophiles.[12] When a strong electron-donating group such as a methoxyl group is introduced in the aromatic R and R^1 groups at the para position, the electron density on the C7 increases due to electron delocalization. In other words, the double bond between C7 and C8 becomes an electron-rich dienophile which inhibits the above-mentioned first step of the intramolecular "criss–cross" cycloaddition reaction. Thus, the thermal rearrangement of **6i** to **9i** (or **10i**) is repressed.

In the intermediate **8a** in which the stabilization of the positive charge by the lone pair of electrons on nitrogen is predominant, the CRR^1 group would be coplanar to the pyrazole ring. The bond between the CRR^1 carbon atom and N atom would have more π property which could restrict the rotation of the CRR^1 group around the C–N bond. Thus, the overlap between the p orbital on the CRR^1 carbon atom with an sp^3 orbital on the enolate carboanion atom would be energetically unfavorable, while the overlap between the p orbital on the CRR^1 carbon atom with sp^3 orbitals on the enolate oxygen atom would be favorable. When R = methyl, phenyl, *p*-methylphenyl, or *o*-methoxyphenyl and R^1 = alkyl group (Me, Et, or i-Pr) in azine phosphoranes **1**, the 6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepines **9** were thus exclusively obtained. When R = R^1 = *p*-chlorophenyl, the thermal rearrangement of ylidene **6h** also produced the seven-membered enol ether **9h** exclusively due to the electron-withdrawing nature of chlorine atom which destabilizes the incipient CRR^1 carbocation. When R = R^1 = phenyl, one would expect stabilization of the carbocation by the lone pair of electrons on nitrogen to be less significant. Greater delocalization of the charge on the diphenyl carbocation and the phenyl rings would allow for the rotation around the C–N bond (**8c**, Scheme II); this would permit the bond formation between the empty p orbital on the CRR^1 carbocation and sp^3 orbital on the enolate carboanion in a head-to-head manner (path C).

When the mixture of azine phosphorane **1e** and 3-(cyanomethylene)phthalide (**2b**) was stirred in chloroform solvent under room temperature for 24 h, azine compound **16h** was isolated in a yield of 74% (Scheme I).

On heating the mixture of azine phosphorane **1e** and ethyl (*E*)-(3′-oxo-1,3-dihydrobenzofuran-1-ylidene)acetate (**2c**) in toluene under reflux for 24 h, the azine **16e** and 2*H*-indeno[2,3-*c*]pyridine-3,9-dione **18e** were isolated in yields of 10% and 65%, respectively (Scheme I). When the mixture of azine phosphorane **1g** and **2c** was stirred

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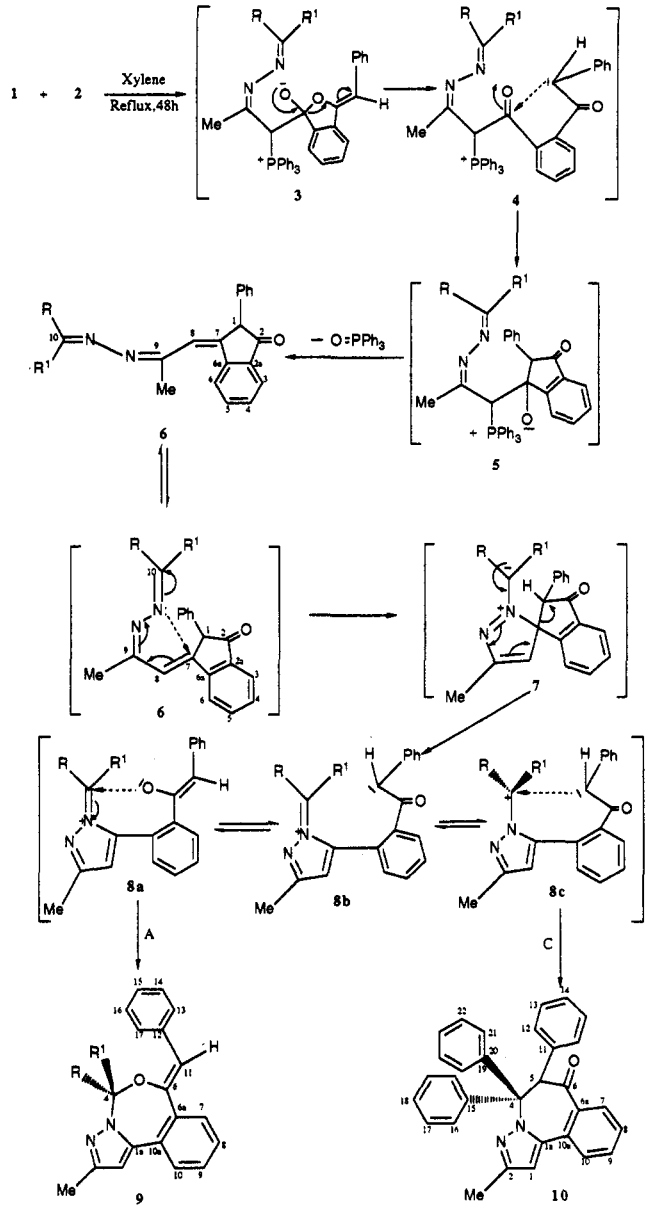
(12) Steven, E. Ph.D. Thesis, University of Delaware, Newark, DE, June, 1977.

Scheme II. Mechanism for the Formation of Azine Ylidene 6 and Pyrazolo Ring Compounds 9 and 10



in toluene under reflux for 24 h, azine compound **16g** and 2*H*-indeno[2,3-*c*]pyridine-3,9-dione **18g** were obtained in yields of 35% and 40%, respectively (Scheme I).

Heating the mixture of phosphoranes **1** (R = methyl, *p*-methylphenyl, or benzyl; R^1 = methyl, isopropyl, or benzyl) with **2c** in toluene under reflux for 24 h gave only 2*H*-indeno[2,3-*c*]pyridine-3,9-diones **18** (and triphenylphosphine oxide) after column chromatography in yields of 62%–85%; none of the corresponding azine compounds **16** were found.

The thermal cyclization reactions of azine **16e** and **16g** (obtained above by refluxing in toluene) occurred to give the corresponding 2*H*-indeno[2,3-*c*]pyridine-3,9-diones **18e** and **18g**, respectively, when the corresponding **16e** or **16g** was heated in xylene under reflux. On heating **16h** in toluene under reflux, 100% recovery of starting **16h** was observed; when heated in xylene under reflux, azine compound **16h** was decomposed.

^{13}C NMR spectral editing experiments were performed on **16h** to determine the numbers of primary, secondary, tertiary, and quaternary carbons present, and these results agree with what was expected from the proposed structure

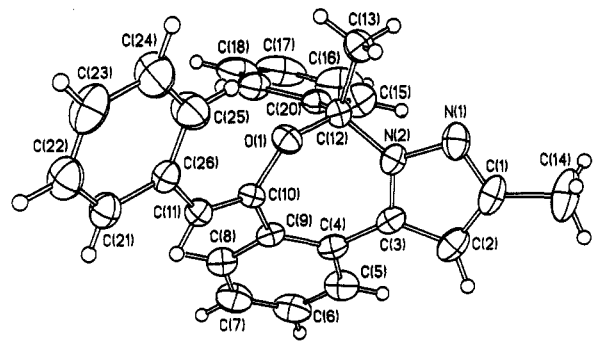


Figure 1. ORTEP diagram for **9b**. Ellipsoids are drawn at 35% probability.

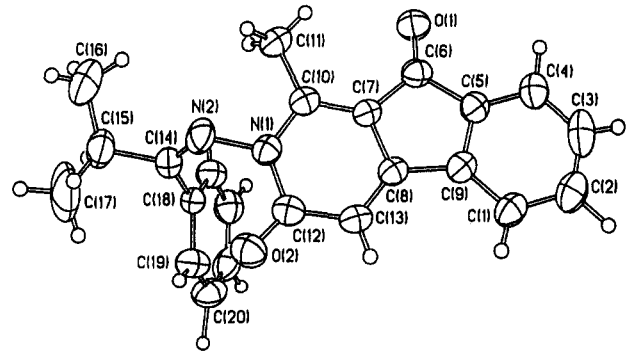


Figure 2. ORTEP diagram for **18c**. Ellipsoids are drawn at 35% probability.

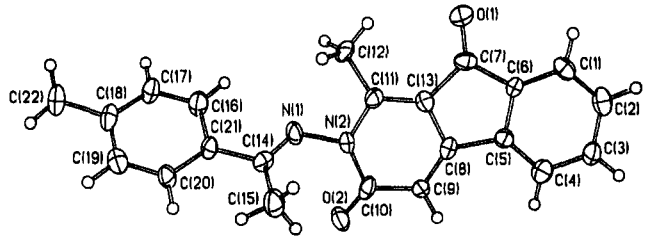


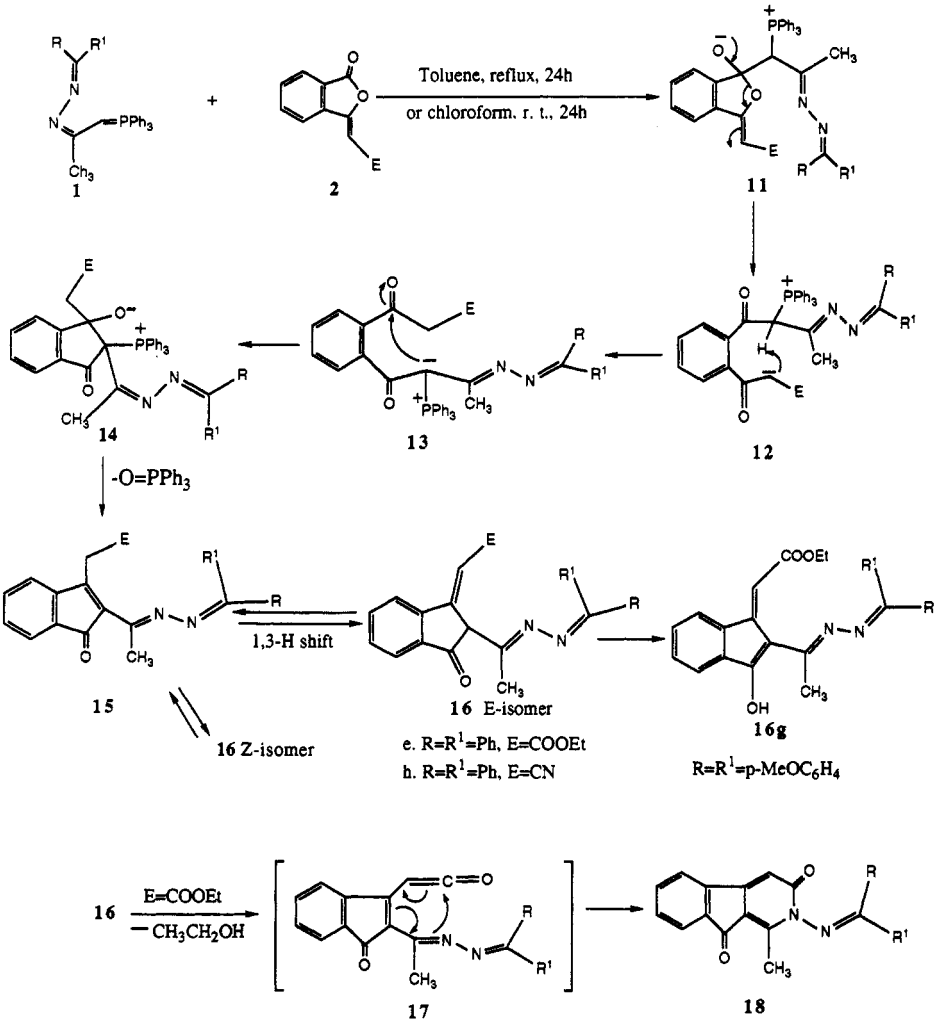
Figure 3. ORTEP diagram for **18d**. Ellipsoids are drawn at 35% probability.

of azine compound **16h**. None of the methylene carbon signals were observed for this structure. Proton NOE difference experiments showed a positive enhancement of 30% for the C2-proton when C9-methyl protons were irradiated. No NOE interaction between C8-H and C9-Me was observed. This result implies that C8-H is not spatially close to C9-Me, which means that the double bond between C3 and C8 has the *E*-configuration. It should be noted that, in the *E*-configuration, the C8-H should be spatially close to the C4-H and a positive NOE should be observed between these two protons; however, this anticipated NOE could not be observed since the chemical shifts of these two protons are very similar.

^1H and ^{13}C NMR data of azine compounds **16e** and **16g** are very comparable to azine compound **16h** (see Experimental Section). Therefore, the compounds **16e** and **16g** are assumed to have the *E*-configuration as well.

The proposed mechanism for the formation of the azine compounds **16** and the final products **18** is depicted in Scheme III. The nucleophilic attack of the azine phosphorane **1** on the carbonyl group of the enol lactone **2b** (or **2c**) would give alkoxybetain **11** which could rearrange to form the acylated azine phosphonium ion **12**. Azine phosphorane **13** would be formed by an intramolecular proton transfer from the carbon atom attached to the

Scheme III



phosphonium group to the enolate anion. The intramolecular nucleophilic attack of azine ylide **13** on the acyl carbonyl group followed by loss of triphenylphosphine oxide would lead to the formation of intermediate **15**. A 1,3-H shift in **15** would give the corresponding azine **16**. The loss of one molecule of ethanol from **16** would give the corresponding ketene **17**. The thermal cycloaddition reaction of the ketene **17** would yield the final 2*H*-indeno-[2,3-*e*]pyridine-3,9-dione **18**. The inability of **16h** to lose ethanol to give a ketene intermediate inhibited its further cyclization to an indenopyridine compound.

The last two steps proposed above are similar to those found in mechanisms suggested earlier for similar conversions.[13]

The structure of this unusual indenopyridine ring system from azine rearrangement was determined by X-ray analyses on products **18c** and **18d**.

The isomerization of the *E*-form to *Z*-form for azine **16e** was observed when the pure sample of *E*-isomer was dissolved in $CDCl_3$. Freshly prepared solution of the *E*-isomer for **16e** in $CDCl_3$ showed 100% of *E*-form on taking the proton NMR spectra immediately. However, ^1H NMR data showed a mixture of *E*/*Z*-isomers with a 1.75:1 ratio of *E* to *Z* on retaking the proton NMR spectra after 1 week. After 1 month, the ratio of *E* to *Z* was still 1.75:1. This would be rationalized by the equilibrium between the *E*-isomer, intermediate **15**, and *Z*-isomer (Scheme III). This isomerization reaction was also observed for the azine compound **16g**. The final equilibrium ratio of the *E*-form to *Z*-form for **16g** was 1.80:1.

We have shown in this new work that the benzalphthalide (**2a**) reaction with the azine phosphoranes **1a** gave (or are presumed to give when not isolated) azines. These azines undergo thermal rearrangement yielding multiring fused pyrazolo heterocycles as expected from our experience in previously published work.[1-10] However, this is the first time we have observed a thermal rearrangement of an azine which does not give compounds with fused pyrazolo moieties. Instead, high yields of 2*H*-indeno[2,3-*e*]pyridine-3,9-diones, **18**, were obtained.

Spectral Data

The proton NMR of 6-(phenylmethylene)-5*H*-pyrazolo-[1,5-*d*][2,4]benzoxazepines **9** showed characteristic peaks at 2.35 ± 0.05 ppm for C2-methyl protons, the C1-proton on the pyrazolo ring absorbed in the region of 6.33–6.75 ppm, and the C11-proton had absorption at 5.95 ● 0.28 ppm. The aromatic multiplets fell in the region from 6.70 to 7.80 ppm. The ^{13}C NMR of pyrazolo compounds **9** had characteristic peaks in the 13.50–14.59 ppm region for the C2-methyl group, 91.96–97.90 ppm region for C4, 105.27–105.98 ppm region for C11, and 111.29–113.05 ppm region for C1. The proton NMR of compound **10g** showed characteristic peaks at 2.29 ppm for C2-methyl protons, 5.26 ppm for the C5-proton, 6.72 ppm for the C1-proton. All of aromatic multiplets fell in the region of 6.75–8.04 ppm. The ^{13}C NMR showed characteristic absorption at

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13.81 ppm for the C2-methyl carbon, 69.21 ppm for C5, 72.25 ppm for C4, and 108.83 ppm for C1. The other aromatic carbons and quaternary carbons appeared in the region of 126.47–146.52 ppm. The carbonyl C6 absorbed at 197.08 ppm.

The corresponding ^1H and ^{13}C NMR data for the products 18 are reported in the Experimental Section. The numbering system is shown in Schemes I and II. ^1H NMR data of 2*H*-indeno[2,3-*e*]pyridine-3,9-diones 18 showed characteristic absorptions at 2.52 ± 0.29 ppm for C1-methyl protons and 6.61 ± 0.18 ppm for C4-H. All of the aromatic multiplets fell in the region of 6.82–8.05 ppm. ^{13}C NMR data of the compounds 18 showed characteristic peaks at 14.36 ± 0.32 ppm for the C1-methyl carbon, 107.50 ± 0.10 ppm for C4, 149.06 ± 0.39 ppm for C4a, 139.50 ± 0.20 ppm for C4b, 131.48 ± 0.46 ppm for C5, 121.94 ± 0.08 ppm for C6, 123.74 ± 0.13 ppm for C7, 133.92 ± 0.14 ppm for C8, 158.30 ± 0.37 ppm for C1, and 149.80 ± 0.34 ppm for C10. C8a absorbed in the region of 132.78–138.13 ppm, and C9a absorbed in the region of 110.72–118.69 ppm. Carbonyl C3 absorbed in the region of 176.30–187.55 ppm, and the other carbonyl C9 had the characteristic peak at 189.43 ± 0.22 ppm.

Experimental Section

Melting points were obtained with a Mel-Temp capillary apparatus and were uncorrected. The ^1H and ^{13}C NMR spectra of approximately 5% (w/v) solution in $CDCl_3$ were obtained on a Bruker Spectrospin Model AM 250 or WM 250. Chemical shifts are reported in parts per million (ppm) employing tetramethylsilane as internal standard. Precise mass spectra were recorded by using a Du Pont 21-492B instrument with a resolution of 3300 or 5000. All of the precise masses observed were within 0.003 mass units of the calculated values.

All of the solvents were dried and distilled before use. Baker silica gel 60–200 mesh and 230–400 mesh for column chromatography were used throughout for product separation. Eastman chromagram (silica gel with a fluorescent indicator on polyethylene) precoated sheets were employed in TLC operation.

The numbering system employed in reporting the NMR data is the same as in Schemes I and II.

All of the phosphoranes 1 were freshly prepared before use according to the known procedure.[1-10] Benzalphthalide (**2a**) is commercially available (Aldrich, cat. no. B180-6). Ethyl (*E*)-(3′-oxo-1,3-dihydrobenzofuran-1-ylidene)acetate (**2c**) and 3-(cyanomethylene)phthalide (**2b**) were prepared by using a reported method.[14]

Preparation of Azine Ylidene 6. To 50 mL of dry xylene in a 100-mL round-bottom flask were added 1.0 g of azine phosphorane **1g** or **1h** and 0.30 g of sublimated benzalphthalide (**2a**) all at once. The mixture was stirred under reflux in xylene for 48 h. After the mixture was cooled to room temperature, xylene was removed by rotary evaporator. The residue was dissolved in 15 mL of dry methylene chloride, and then 5.0 g of silica gel (60–200 mesh) was added. After the methylene chloride was removed by rotary evaporator, the remains were added to the top of a prepared-ready column (45 × 3 cm with 100 g of Baker silica gel, 60–200 mesh) and chromatographically separated with diethyl ether–petroleum ether (1:1) as eluent. The product **6h** or **6i** isolated from the column was purified by recrystallization from diethyl ether. TLC showed one spot.

2-Phenyl-3-(((bis(4′-chlorophenyl)methylidene)hydrazono)propylidene)indanone (Azine Ylidene) (6h). Yellow crystals, mp 115–115.5 °C. Yield: 79%. ^1H NMR: 2.37 (3H, s, C9-Me), 6.13 (1H, s, C8-H), 6.70–6.90 (7H, m, C1-H, Ar-H), 7.08–7.37 (10H, m, Ar-H), 7.80 (1H, d, C3-H, J = 7.3 Hz). ^{13}C NMR: 12.97 (C9-*Me*), 105.76 (C1), 127.02, 127.84, 128.29, 128.37, 128.52, 129.57, 130.12, 130.21, 130.99, 131.35, 132.20 (C2a, C3–6, C8, C12–13, C16–17, C20–22), 134.34 (C14), 134.51 (C18), 138.91 (C7), 139.61 (C11, C15), 139.32 (C19), 139.77 (C6a), 142.21 (C10), 147.13 (C9), 202.07 (C2). Precise mass: found 508.112, calcd 508.111. The ^1H and ^{13}C NMR data were comparable to the NMR data of the almost identical azine found in previous work.[10]

2-Phenyl-3-(((bis-(4′-methoxyphenyl)methylidene)hydrazono)propylidene)indanone (Azine Ylidene) (6i). Yellow crystals, mp 203–204°C. Yield: 71%. ^1H NMR: 2.37 (3H, s, C9-Me), 3.67 (3H, s, *p*-*Me*OC_6H_4 for R), 3.74 (3H, s, *p*-*Me*OC_6H_4 for R^1), 6.13 (1H, s, C8-H), 6.33 (2H, d, ortho protons for R, J = 8.6 Hz), 6.65 (2H, d, ortho protons for R^1, J = 8.9 Hz), 6.72 (2H, d, meta protons for R, J = 8.6 Hz), 6.93 (2H, d, meta protons for R^1, J = 8.7 Hz), 7.16–7.30 (8H, m, C1-H, C4-5-H, C20-22-H), 7.38 (1H, dd, C6-H, J = 1.4, 7.7 Hz), 7.86 (1H, d, C3-H, J = 7.6 Hz). ^{13}C NMR: 13.33 (C9-Me), 54.97 (*p*-*Me*OC_6H_4, R), 55.12 (*p*-*Me*OC_6H_4, R^1), 105.69 (C1), 113.24C13), 113.49 (C17), 126.83, 127.14, 128.40, 129.31, 130.21, 139.90, 131.58, 132.77 (C3–6, C8, C12–13, C16–17, C20–22), 133.25 (C2a), 134.84 (C7), 139.49 (C19), 140.14 (C11, C15), 140.79 (C6a, C10), 150.91 (C9), 203.56 (C2). Precise mass: found 500.211, calcd 500.210. The ^1H and ^{13}C NMR data were comparable to the NMR data of the almost identical azine found in previous work.[10]

Preparation of Azine Compound 16h. Freshly prepared phosphorane **1e** (1.0 g) and freshly prepared **2b** (0.3 g) were added, all at once, to 50 mL of dry $CHCl_3$ in a 100-mL round-bottomed flask. The mixture was stirred at room temperature for 24 h. After 5.0 g of Baker silica gel (60–200 mesh) was added, the chloroform was removed by rotary evaporator. The residual mixture was added to the top of a prepared column (45 × 3 cm with 100 g of Baker silica gel, 60–200 mesh) and was chromatographically separated with methylene chloride–petroleum ether (3:2) as eluent. The product **16h** isolated from the column was purified by recrystallization from diethyl ether. The pure product was obtained as yellow crystals, mp 214–215°C. Yield: 74%. TLC showed one spot. ^1H NMR: 2.84 (3H, s, C9-Me), 5.58 (1H, s, C2-H), 7.34–7.44 (7H, m, C8-H, and Ar-H), 7.51–7.70 (8H, m, Ar-H), 8.56 (1H, d, C7-H, J = 7.9 Hz). ^{13}C NMR: 15.53 (C9-Me), 81.88 (C2), 104.89 (C8-*C*N), 119.27 (C7a), 122.34 (C8), 123.81, 127.99, 128.37, 128.44, 129.90, 130.25, 130.36, 130.69, 132.89 (C4–7, C12–14, C16–18), 132.49 (C3), 136.98 (C11), 140.55 (C15), 152.76 (C3a), 156.11 (C9), 159.36 (C10), 190.27 (C1). IR: 1660 (s, C=O), 2200 (s, CN) cm^{-1}. Precise mass: found 389.160, calcd 389.158.

Preparation of Azine Compound 16e and 2*H*-Indeno-[2,3-*e*]pyridine-3,9-dione 18e. Freshly prepared phosphorane **1e** (1.0 g) and freshly prepared **2c** (0.3 g) were added, all at once, to 50 mL of dry toluene in a 100-mL round-bottomed flask. The mixture was stirred under reflux for 24 h. After the mixture was cooled to room temperature, toluene was removed by rotary evaporator. The residue was dissolved in 5 mL of dry methylene chloride, and then 5.0 g of Baker silica gel (60–200 mesh) was added. After the solution was strongly shaken for about 1 min, the methylene chloride was removed by rotary evaporator. The residual mixture was added to the top of a prepared column (45 × 3 cm with 100 g of Baker silica gel, 230–400 mesh) and was chromatographically separated with diethyl ether–petroleum ether as eluent (1:3 at beginning and 1:0 at end). The product **16e** eluted first, **18e** was second, O=PPh_3 came off last. The **16e** and **18e** isolated from column chromatography showed only one spot by TLC and were each purified by recrystallization from diethyl ether.

Azine Compound 16e. Yellow crystals, mp 185–186°C. Yield: 10%. ^1H NMR: 1.35 (3H, t, C8-$COOCH_2CH_3$, J = 7.0 Hz), 2.87 (3H, s, C9-Me), 4.27 (2H, q, C8-$COOCH_2CH_3$, J = 7.1 Hz), 6.24 (1H, s, C8-H), 7.24–7.46 (9H, m, C2-H, Ar-H), 7.55–7.68 (5H, m, Ar-H), 8.79 (1H, d, C7-H, J = 7.9 Hz). ^{13}C NMR: 14.34 (C8-$COOCH_2CH_3$), 15.78 (C9-Me), 60.15 (C8-$COOCH_2CH_3$), 109.30 (C2), 121.83 (C8), 127.29, 127.74, 128.29, 128.40, 129.76, 130.08, 132.35 (C4–7, C12–14, C16–18), 132.73 (C7a), 137.29 (C3), 137.84 (C11), 140.67 (C15), 148.60 (C3a), 154.45 (C9), 158.07 (C10), 166.85 (C8-*C*OOEt), 190.60 (C1). Precise mass: found 436.180, calcd 436.179.

1-Methyl-2-(diphenylimino)-2*H*-indeno[2,3-*e*]pyridine-3,9-dione (18e). Yellowish crystals, mp 201–202°C. Yield: 65%. ^1H NMR: 2.81 (C1-Me), 6.49 (C4-H), 7.24–7.57 (11, m, Ar-H), 7.73–7.80 (3H, m, Ar-H). ^{13}C NMR: 14.67 (C1-Me), 158.18 (C1), 178.56 (C3), 107.48 (C4), 131.09 (C5), 121.90 (C6), 123.68 (C7), 133.83 (C8), 189.49 (C9), 149.46 (C10), 149.21 (C4a), 139.83 (C4b), 134.02 (C8a), 111.03 (C9a), 124.95, 127.50, 128.15, 128.41, 129.95,

(14) Ingham, C. F.; Massy-Westropp, R. A.; Reynolds, G. D.; Thorpe, W. D. *Aust. J. Chem.* **1975**, *28*, 2499.

132.30, 135.79, 138.12 (C10-R and C10-R¹, R = R = Ph). Precise mass: found 390.134, calcd 390.136.

Preparation of Azine Compound 16g and 2*H*-Indeno[2,3-*e*]pyridine-3,9-dione 18g. The procedure used for the preparation of **16g** and **18g** is the same as the preparation of **16e** and **18e**.

Azine Compound 16g. Yellow crystals, mp 168–169°C. Yield: 35%. ^{1}H NMR: 1.35 (3H, t, C8-COOCH$_2$C*H*$_3$, J = 7.1 Hz), 2.85 (3H, s, C9-Me), 3.08 (3H, s, p-*Me*OC$_6$H$_4$, R), 3.92 (3H, s, p-*Me*OC$_6$H$_4$, R¹), 4.24 (2H, q, C8-COOC*H*$_2$CH$_3$, J = 7.1 Hz), 6.23 (1H, s, C8-H), 6.86 (2H, d, C13-protons for R, J = 9.0 Hz), 7.14 (2H, d, C17-protons for R¹, J = 8.8 Hz), 7.30 (2H, d, C12-protons for R, J = 8.7 Hz), 7.34 (1H, m, C5-H), 7.45 (1H, s, C6-H), 7.53 (2H, d, C16-protons for R¹, J = 9.0 Hz), 7.56 (1H, d, C4-H, J = 10.1 Hz), 8.82 (1H, d, C7-H, J = 7.8 Hz), 13.85 (1H, s, C1-O*H*). ^{13}C NMR: 14.36 (C8-COOCH$_2$*C*H$_3$), 15.85 (C9-Me), 55.27 (*p*-*Me*OC$_6$H$_4$ for both R and R¹), 60.08 (C8-COO*C*H$_2$CH$_3$), 108.80 (C2), 113.71 (C13), 115.07 (C15), 121.63 (C8), 124.75 (C7a), 127.31 (C5), 129.50 (C6, C12), 129.79 (C4), 130.14 (C16), 130.48 (C3), 132.17 (C7), 137.99 (C11), 140.56 (C15), 148.93 (C3a), 154.68 (C9), 158.24 (C10), 160.71 (C14), 161.13 (C18), 166.89 (C8-*C*OOEt), 190.27 (C1). Precise mass: found 496.195, calcd 496.198.

1-Methyl-2-(bis(2′-*p*-methoxyphenyl)imino)-2*H*-indeno[2,3-*e*]pyridine-3,9-dione (18g). Yellow crystals, mp 120–121°C. Yield: 62%. ^{1}H NMR: 2.75 (C1-Me), 6.45 (C4-H), 6.82 (2H, d, *p*-MeOC$_6$*H*$_4$, J = 8.8 Hz, C10-R), 6.93 (2H, d, *p*-MeOC$_6$*H*$_4$, J = 7.8 Hz, C10-R¹), 7.20 (2H, d, *p*-MeOC$_6$*H*$_4$, J = 8.8 Hz, C10-R), 7.78 (2H, d, *p*-MeOC$_6$*H*$_4$, J = 8.9 Hz), 7.40 (3H, m, C4-H, C5-H, C6-H), 7.76 (1H, d, C8-H, J = 8.8 Hz). ^{13}C NMR: 14.64 (C1-Me), 158.67 (C1), 177.46 (C3), 107.50 (C4), 131.02 (C5), 121.87 (C6), 123.63 (C7), 133.79 (C8), 189.60 (C9), 149.48 (C10), 149.44 (C4a), 139.88 (C4b), 138.11 (C8a), 110.72 (C9a), 55.14 (*p*-*Me*OC$_6$H$_4$, C10-R), 55.43 (*p*-*Me*OC$_6$H$_4$, C10-R¹), 113.56, 113.74, 128.24, 128.66, 129.40, 131.62, 160.64, 162.99 (*p*-MeO*C*$_6$H$_4$ for C10-R and C10-R¹). Precise mass: the M$^+$ peak could not be detected, but the M$^+$ – CH$_2$C$_6$H$_5$ (m/z 327) peak was obtained with 100% relative intensity.

Preparation of 6-(Phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepines 9. General Procedure. Benzalphthalide (0.0015 mol) was added, all at once, to 0.0020 mol of azine ylide in 50 mL of dry xylene. The mixture was stirred under reflux for 48 h. After the mixture was cooled to room temperature, xylene was removed by simple distillation under vacuum. The residue was dissolved in 15 mL of methylene chloride, and then 5 g of silica gel (60–200 mesh) was added. After methylene chloride was removed by rotary evaporator, the remains were added to the top of a prepared-ready column (45 × 3 cm with 100 g of Baker silica gel, 230–400 mesh), and was chromatographically separated with diethyl ether–petroleum ether (1:8) as eluent. The products **9** isolated from column were purified by recrystallization from diethyl ether–petroleum ether (1:3). The calculation of percentage yield was based on benzalphthalide.

2,4,4-Trimethyl-6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepine (9a). White sticky liquid. Yield: 70%. ^{1}H NMR: 1.92 (6H, s, C4-*Me*(*Me*)), 2.30 (3H, s, C2-*Me*), 5.97 (1H, s, C11-H), 6.38 (1H, s, C1-H), 7.17–7.20 (1H, m, Ar-H), 7.28–7.40 (4H, m, Ar-H), 7.53–7.57 (1H, m, Ar-H), 7.67–7.70 (3H, m, Ar-H). ^{13}C NMR: 13.50 (C2-Me), 27.97 (C4-Me), 113.05 (C1), 146.83 (C2), 91.96 (C4), 151.43 (C6), 105.98 (C11), 142.50 (C1a), 128.77 (C6a), 135.44 (C10a), 126.45, 128.19, 128.38, 128.90, 128.94, 136.17 (Ar-C). Precise mass: found 316.154, calcd 316.157.

2,4-Dimethyl-4-phenyl-6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepine (9b). White crystals, mp 158–159°C. Yield: 78%. ^{1}H NMR: 2.40 (3H, s, C2-Me), 2.41 (3H, s, C4-Me), 5.70 (1H, s, C11-H), 6.40 (1H, s, C1-H), 6.84–6.88 (2H, m, Ar-H), 6.98–7.11 (5H, m, Ar-H), 7.18–7.39 (5H, m, Ar-H), 7.80 (2H, dd, C13-H, C17-H, J = 7.9, 8.6 Hz). ^{13}C NMR: 13.74 (C2-Me), 31.92 (C4-Me), 111.36 (C1), 147.53 (C2), 93.50 (C4), 152.46 (C6), 105.77 (C11), 143.43 (C1a), 142.80 (C10a), 125.03, 126.27, 127.23, 127.64, 127.89, 128.20, 128.30, 128.44, 128.55, 128.79, 135.53, 136.27 (Ar-C). The C6a is hidden. Precise mass: found 378.171, calcd 378.173.

2-Methyl-4-ethyl-4-phenyl-6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepine (9c). White crystals, mp 148–149°C. Yield: 73%. ^{1}H NMR: 1.12 (3H, t, C4-CH$_2$C*H*$_3$, J = 7.3 Hz), 2.40 (3H, s, C2-Me), 2.70 (1H, dq, C4-C*H*HCH$_3$, J = 14.5, 7.4 Hz), 2.93 (1H, dq, C4-CH*H*CH$_3$, J = 14.5, 7.4 Hz), 5.69 (1H, s, C11-H), 6.36 (1H, s, C1-H), 6.78–6.83 (2H, m, Ar-H), 6.98–7.39 (10H, m, Ar-H), 7.80 (2H, d, C13-H and C17-H, J = 8.5, 8.1 Hz). ^{13}C NMR: 13.77 (C2-Me), 8.82 (C4-CH$_2$*C*H$_3$), 36.12 (C4-*C*H$_2$CH$_3$), 111.63 (C1), 147.45 (C2), 95.72 (C4), 152.63 (C6), 105.61 (C11), 143.80 (C1a), 128.52 (C6a), 140.91 (C10a), 126.08, 126.27, 127.15, 127.40, 127.58, 128.21, 128.29, 128.42, 128.73, 128.84, 136.04, 136.34 (Ar-C). Precise mass: found 392.189, calcd 392.189.

2,4-Dimethyl-4-(*p*-methylphenyl)-6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepine (9d). Sticky liquid. Yield: 75%. ^{1}H NMR: 2.11 (3H, s, *p*-*Me*C$_6$H$_4$), 2.39 (3H, s, C2-Me), 2.39 (3H, s, C4-Me), 5.70 (1H, s, C11-H), 6.39 (1H, s, C1-H), 6.70–6.82 (4H, m, Ar-H), 6.98–7.38 (7H, m, Ar-H), 7.80 (2H, dd, C13-H and C17-H, J = 8.5, 8.1 Hz). ^{13}C NMR: 13.71 (C2-Me), 20.86 (C4-*p*-*Me*C$_6$H$_4$), 32.06 (C4-Me), 111.29 (C1), 147.40 (C2), 93.65 (C4), 152.58 (C6), 105.71 (C11), 143.45 (C1a), 127.97 (C6a), 139.89 (C10a), 124.89, 126.20, 127.29, 128.14, 128.28, 128.38, 128.44, 128.56, 128.80, 135.57, 136.38, 137.25 (Ar-C). Precise mass: found 392.190, calcd 392.189.

2-Methyl-4-isopropyl-4-phenyl-6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepine (9e). Sticky liquid. Yield: 73%. ^{1}H NMR: 1.03 (3H, d, C4-CH(C*H*$_3$)CH$_3$, J = 6.0 Hz), 1.38 (3H, d, C4-CH(CH$_3$)C*H*$_3$, J = 6.7 Hz), 2.37 (3H, s, C2-Me), 3.29 (1H, sept, C4-C*H*(CH$_3$)CH$_3$, J = 6.6 Hz), 5.67 (1H, s, C11-H), 6.30 (1H, s, C1-H), 6.77–7.10 (7H, m, Ar-H), 7.15–7.37 (5H, m, Ar-H), 7.77–7.80 (2H, m, C13-H and C17-H). ^{13}C NMR: 13.79 (C2-Me), 18.43 (C4-CH(*Me*)Me), 19.03 (C4-CH(Me)*Me*), 38.24 (C4-*C*H(Me)Me), 111.70 (C1), 146.96 (C2), 97.90 (C4), 152.64 (C6), 105.33 (C11), 144.19 (C1a), 127.80 (C6a), 136.21 (C10a), 126.17, 126.88, 126.94, 127.43, 127.99, 128.11, 128.24, 128.71, 128.90, 136.21, 139.80 (Ar-C). Precise mass: found 406.199, calcd 406.202.

2,4-Dimethyl-4-(*o*-methoxyphenyl)-6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepine (9f). White crystals, mp 182–183°C. Yield: 70%. ^{1}H NMR: 2.39 (3H, s, C2-Me), 2.48 (3H, s, C4-Me), 3.51 (3H, s, *o*-*Me*OC$_6$H$_4$), 5.68 (1H, s, C11-H), 6.37 (1H, s, C1-H), 6.47–6.64 (3H, m, Ar-H), 6.96–7.37 (8H, m, Ar-H), 7.82–7.83 (2H, m, Ar-H). ^{13}C NMR: 13.71 (C2-Me), 27.93 (C4-Me), 55.64 (*o*-*Me*OC$_6$H$_4$), 111.38 (C1), 145.85 (C2), 93.18 (C4), 152.85 (C6), 105.27 (C11), 143.26 (C1a), 129.08 (C6a), 136.61 (C10a), 110.61, 119.82, 125.97, 127.41, 127.69, 127.95, 128.10, 128.25, 128.81, 129.43, 135.73, 136.61, 156.16 (Ar-C). Precise mass: found 408.184, calcd 408.184.

Preparation of 2-Methyl-4,4-bis(*p*-chlorophenyl)-6-(phenylmethylene)-5*H*-pyrazolo[1,5-*d*][2,4]benzoxazepine (9h). The corresponding azine ylidene **6h** (100 mg) was sealed in a pipet tube and was heated at 240 ± 10°C for 15 h. After column chromatography (diethyl ether–petroleum ether (1:3) as eluent), a 40% yield of the product **9h** was isolated. The pure product was obtained as white crystals after recrystallization from diethyl ether–petroleum ether solvent system (1:3), mp 163–164°C. ^{1}H NMR: 2.36 (3H, s, C2-Me), 6.22 (1H, s, C11-H), 6.75 (1H, s, C1-H), 6.47–6.51 (3H, m, Ar-H), 6.89–7.03 (5H, m, Ar-H), 7.14–7.34 (7H, m, Ar-H), 7.50–7.54 (2H, m, Ar-H). ^{13}C NMR: 14.59 (C2-Me), 111.85 (C1), 147.50 (C2), 97.07 (C4), 154.47 (C6), 105.50 (C11), 144.03 (C1a), 129.98 (C6a), 142.00 (C10a), 121.98, 122.345, 123.37, 127.64, 127.74, 127.93, 128.75, 128.83, 128.90, 129.16, 130.77, 133.15, 134.04, 144.03 (Ar-C). Precise mass: found 508.108, calcd 508.111.

Preparation of 5*H*,6*H*-Pyrazolo[1,5-*d*][2]benzazepin-6-ones 10. The general procedure employed in preparing product **10** is the same as the preparation of compounds **9**.

2-Methyl-4,4,5-triphenyl-5*H*,6*H*-pyrazolo[1,5-*d*][4]-benzazepin-6-one (10g). Yellowish crystals, mp 179–180°C. Yield: 74%. TLC showed one spot. ^{1}H NMR: 2.29 (3H, s, C2-Me), 5.26 (1H, s, C5-H), 6.72 (1H, s, C1-H), 6.75–7.23 (16H, m, Ar-H), 7.37–7.43 (1H, m, C8-H), 7.61 (1H, d, C10-H, J = 8.0 Hz), 8.04 (1H, dd, C7-H, J = 1.5, 8.1 Hz); ^{13}C NMR: 13.81 (C2-Me), 69.21 (C5), 72.25 (C4), 108.83 (C1), 126.47, 127.57, 127.65, 127.80, 127.88, 128.37, 128.66, 129.24, 130.45, 131.13, 133.45 (C7–10, C12–14, C16–18, C20–22), 130.06 (C6a), 131.32 (C10a), 135.27 (C19), 140.62 (C15), 143.37 (C11), 143.67 (C1a), 146.52 (C2), 197.08 (C6). Precise mass: found 440.188, calcd 440.188.

Preparation of 2*H*-Indeno[2,3-*e*]pyridine-3,9-diones 18a–d and 18f. The procedure for the preparation of **18a–18d** and **18f** is the same as the preparation of **18e** and **18g**.

Product 18a. Yellow crystals, mp 155–156 °C. Yield: 75%. ^{1}H NMR: 1.86 (3H, s, C10-Me), 2.36 (3H, s, C10-Me), 2.36 (3H,

s, C1-Me), 6.37 (1H, s, C4-H), 7.47–7.53 (1H, m, C6-H), 7.57–7.63 (1H, m, C7-H), 7.69 (1H, d, C5-H, J = 8.6 Hz), 7.78 (1H, d, C8-H, J = 7.6 Hz). ^{13}C NMR: 14.04 (C1-Me), 20.14 (C10-Me), 25.07 (C10-Me), 158.49 (C1), 180.64 (C3), 107.59 (C4), 131.03 (C5), 122.01 (C6), 123.86 (C7), 134.06 (C8), 189.64 (C9), 150.06 (C10), 148.83 (C4a), 139.90 (C4b), 138.13 (C8a), 111.07 (C9a). Precise mass: found 266.101, calcd 266.103.

Product 18b. Yellow crystals, mp 175–176°C. Yield: 65%. ^{1}H NMR: 2.26 (3H, s, C1-Me), 2.69 (3H, s, C10-Me), 6.78 (1H, s, C1-H), 7.46–7.56 (3H, m, Ar-H), 7.58–7.64 (2H, m, C6-H and C7-H), 7.70 (1H, d, C5-H, J = 7.4 Hz), 7.80 (1H, m, C8-H), 8.00–8.05 (2H, m, Ar-H). ^{13}C NMR: 14.17 (C1-Me), 17.06 (C10-Me), 158.28 (C1), 176.61 (C3), 107.49 (C4), 131.94 (C5), 121.89 (C6), 123.83 (C7), 134.01 (C8), 189.53 (C9), 150.03 (C10), 149.24 (C4a), 139.89 (C4b), 135.66 (C8a), 111.17 (C9a), 127.66, 128.65, 131.27, 138.14 (C10-Ph). Precise mass: found 328.121, calcd 328.121.

Product 18c. Yellow crystals, mp 195–196°C. Yield: 71%. ^{1}H NMR: 1.28 (3H, d, C10-CH(Me)*Me*, J = 6.8 Hz), 1.38 (3H, d, C10-CH(*Me*)Me, J = 6.6 Hz), 2.74 (3H, s, C1-Me), 3.18 (1H, sept., C10-C*H*(Me)Me, J = 6.9 Hz), 6.43 (C4-H), 7.13–7.18 (2H, m, Ar-H), 7.26–7.31 (3H, m, Ar-H), 7.40–7.56 (3H, m, Ar-H), 7.70–7.74 (1H, m, Ar-H). ^{13}C NMR: 14.40 (C1-Me), 19.94 (C10-CH(*Me*)Me), 20.28 (C10-CH(Me)*Me*), 37.87 (C10-*C*H(Me)Me), 158.22 (C1), 187.56 (C3), 107.48 (C4), 131.03 (C5), 121.86 (C6), 123.61 (C7), 133.78 (C8), 189.52 (C9), 149.46 (C10), 148.67 (C4a), 139.86 (C4b), 135.11 (C8a), 116.40 (C9a), 125.55, 128.16, 129.40, 138.12 (C10-Ph). Precise mass: found 356.153, calcd 356.153.

Product 18d. Yellow crystals, mp 233–234°C. Yield: 85%. ^{1}H NMR: 2.23 (3H, s, C1-me), 2.43 (3H, s, C10-*p*-*Me*C$_6$H$_4$), 2.68 (3H, s, C10-Me), 6.77 (1H, s, C4-H), 7.29 (2H, m, C10-*p*-MeC$_6$H$_4$), 7.51 (1H, m, C6-H), 7.61 (1H, m, C7-H), 7.69 (1H, d, C5-H, J = 7.5 Hz), 7.79 (1H, d, C8-H, J = 7.2 Hz), 7.92 (2H, d, C10-*p*-MeC$_6$H$_4$, J = 8.2 Hz). ^{13}C NMR: 14.14 (C1-Me), 16.82 (C10-Me), 21.50 (C10-*p*-*Me*C$_6$H$_4$), 158.34 (C1), 176.30 (C3), 107.40 (C4), 131.18 (C5), 121.91 (C6), 123.72 (C7), 133.94 (C8), 189.48 (C9), 149.91 (C10), 149.24 (C4a), 139.82 (C4b), 132.78 (C8a), 111.05 (C9a), 124.28, 127.85, 138.05, 142.48 (C10-p-Me*C*$_6$H$_4$). Precise mass: found 342.133, calcd 342.136.

Product 18f. Yellow crystals, mp 222–223°C. Yield: 40%. ^{1}H NMR: 2.51 (3H, s, C1-Me), 3.47 (2H, s, C10-C*H*$_2$Ph), 3.87 (2H, s, C10-C*H*$_2$), 6.74 (1H, s, C4-H), 6.87–6.91 (2H, m, Ar-H), 7.17–7.21 (3H, m, Ar-H), 7.29–7.37 (5H, m, Ar-H), 7.47–7.63 (2H, m, C6-H, C7-H), 7.68–7.71 (1H, m, C5-H), 7.77 (1H, dd, C8-H, J = 0.9, 7.3 Hz). ^{13}C NMR: 14.13 (C1-Me), 38.42 (C10-*C*H$_2$Ph), 43.28 (C10-*C*H$_2$Ph), 158.47 (C1), 182.31 (C3), 107.42 (C4), 131.28 (C5), 121.99 (C6), 123.79 (C7), 133.97 (C8), 189.21 (C9), 150.14 (C10), 149.20 (C4a), 139.50 (C4b), 134.16 (C8a), 118.69 (C9a), 127.28, 128.80, 129.52, 138.10 (C10-CH$_2$*Ph*), 127.28, 128.80, 129.33, 135.14 (C10-CH$_2$*Ph*). Precise mass: The M$^+$ peak could not be detected, but the M$^+$ – CH$_2$Ph (m/z 327) peak was obtained with 100% of relative intensity.

Conversion of 16e (16g) into 18e (18g). Conversion of **16e** (**13g**) into final product **18e** (**18g**) was accomplished by heating for 24 h in xylene solvent. The **18e** (**18g**) was isolated as described above. The recovered yield of **18e** was 68% (60% for **18g**). The mp, precise mass, and ^{1}H and ^{13}C NMR data were identical with the products obtained employing the general reaction, given above.

NOE Experiments. Nuclear overhauser effect (NOE) experiments were performed at ambient temperature in the difference mode. Either 128 or 256 transients were accumulated with the decoupler on-resonance for the irradiated peak, and a equal number of transients were accumulated with the decoupler placed off-resonance. The free induction decay (FID) off-resonance was subtracted from the FID on-resonance, and Fourier transformation of the result (after premultiplication by an exponential weighing function employing 0.5-Hz line broading) yielded the difference spectrum. The relaxation delay was 1–2 s, the irradiation time was 5 s, and the acquisition time was 2.3 s (16K complex data points, 3500 Hz spectral width). The decoupler power used was the minimum required to completely saturate the peak of interest. Integrated intensities of the difference spectrum were measured relative to the intensities in the off-resonance spectrum, and NOEs are reported as a percentage enhancement.

Two-dimensional correlated (2D COSY) spectra were obtained in the absolute value mode and were multiplied by a sine-bell apodization function prior to Founier transformation. The matrix consisted of 256 (or 512) increments containing 1k (or 2k) complex points each and were zero-filled to 512 (or 1204) real points in both dimensions. The spectral width was approximately 2300 Hz in both dimensions. The relaxation delay was 2 s, and transients were accumulated per $t1$ value.

Crystallographic Structural Determination for 9b. The structure of **9b** was obtained at ambient temperature (22–25 °C) with a Nicolet R3m diffractometer. All software is contained in the SHELXTL (5.1) software package (Sheldrick, G. Nicolet XRD, Madison, WI). Crystal data for **9b**: monoclinic, $P2_1/n$, a = 8.397(9) Å, b = 18.951(17) Å, c = 13.078(8) Å, β = 92.24(7)°, V = 2080(3) Å^3, Z = 4, μ(Mo Kα) = 0.60 cm^{-1}, D(calcd) = 1.209 g/cm^3. Data were collected (Nicolet, R3m, $2\theta_{max}$ = 45°) yielding 1485 independent observed reflections, $F_o \geq 5\sigma(F_o)$. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were found and were refined isotropically. $R(f)$ = 6.96%, $R(wf)$ = 7.43%, GOF = 1.434, $\Delta(\rho)$ = 0.218 e Å^{-3}, Δ/σ(max) = 0.034.[15]

Crystallographic Structural Determination for $C_{23}H_{20}N_2O_2$ (18c) and $C_{22}H_{18}N_2O_2$ (18d). The well-formed specimens of **18c** and **18d**, each recrystallized from diethyl ether, were mounted on fine glass fibers with epoxy cement. The unit cell parameters were obtained from a least-squares fit of 25 reflections ($20° \leq 2\theta \leq 25°$). The preliminary photographic characterization of **18c** and **18d** showed mmm and $\bar{1}$ laue symmetry, respectively. E-statistics suggested the centrosymmetric alternative for **18c**, and the chemically sensible results of refinement proved that $P\bar{1}$ is the correct space group. The systematic absences in the diffraction data of **18c** established the space group as either $Pca2_1$ or $Pcam$ (nonstandard $Pbcm$). E-statistics for **18d** were inconclusive. **18d** was solved in the centrosymmetric setting but then was worked up in the noncentrosymmetric setting due to the lack of a mirror plane in the molecule. The chemically sensible results of refinement showed that $Pca2_1$ was the correct choice for the space group of **18d**. The result of the refinement of a multiplicative term for $\Delta f''$ for **18d** were inconclusive, thus not allowing the correct hand to be determined unambiguously. No correction for absorption was required by any of the data set. Crystal data for **18c**: triclinic, $P\bar{1}$, a = 8.192(2) Å, b = 10.839(2) Å, c = 12.150(3) Å, α = 106.6(2)°, β = 107.7(2)°, γ = 100.3(2)°, V = 942.8(5) Å^3, Z = 2, μ(Mo Kα) = 0.75 cm^{-1}, D(calcd) = 1.255 g/cm^3. Crystal Data for **18d**: orthorhombic, $Pca2_1$, a = 34.007(10) Å, b = 6.5769(20) Å, c = 7.6337(22) Å, V = 1707.4(8) Å^3, Z = 4, μ(Mo Kα) = 0.80 cm^{-1}, D(calcd) = 1.332 g/cm^3. Data were collected (Nicolet, R3m, $2\theta_{max}$ = 50 for **18c**, 40 for **18d**) yielding 2046 independent observed reflections for **15c** and 617 independent observed reflections for **18d**.

Products **18c** and **18d** were each solved by direct methods. All non-hydrogen atoms were refined anisotropically. For **18c**, all hydrogen atoms except for those on carbons 16 and 17 (Figure 1) were found and refined isotropically. All hydrogen atoms of **18d** were included as idealized isotropic contributions (d_{CH} = 0.960 Å, U = 1.2 U for attached C). Refinement parameters for **18c**: $R(f)$ = 6.67%, $R(wf)$ = 7.49%, GOF = 1.608, $\Delta(\rho)$ = 0.388 e Å^{-3}, Δ/σ(max) = 0.046. Refinement parameters for **18d**: $R(f)$ = 4.54%, $R(wf)$ = 4.56%, GOF = 1.112, Δ/σ(max) = 0.045. All computer programs and sources of the scattering factors are contained in the SHELXTL program library (5.1) (Sheldrick, G. Nicolet (Siemens); Madison, Wi.).[15]

Supplementary Material Available: ^{1}H NMR spectra of all new compounds (19 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.

(15) The authors have deposited atomic coordinates for **9b**, **18c**, and **18d** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.