mmol) was added with stirring to a cold (ice/methanol) solution of sodium ethoxide prepared from sodium (0.5 g, 22 mmol) in anhydrous ethanol (60 mL). The deep orange solution was stirred at room temperature for 1 h. A yellow orange substance precipitated and was separated by filtration to give 6.97 g (89%) of ylide **12c**. Purification by reprecipitation from CH_2Cl_2/heptane gave dark orange crystals: mp 178–179 °C; ^1H NMR δ 0.85 (s, 3 H, MeC=N), 2.99 (d, J_{PH} = 21.1, 1 H, CH=PPh_3), 6.19 (s, 1 H, PhCH=); ^{13}C NMR 13.4 (s, MeC=), 39.8 (d, J_{CP} = 124.0, CH=PPh_3) ppm; ^{31}P NMR 15.4 ppm; precise mass calcd for $C_{36}H_{31}N_2P$ 522.222, found 522.225.

General Procedures for Reactions with Ketenes. Method A. Triethylamine (16.8 mmol), in 10 mL dry toluene, was added dropwise with stirring, over a period of 0.5 h to a cooled (ice bath) solution of the acid chloride (16.5 mmol) in 10 mL of dry ether. The reaction mixture was further stirred at ambient temperature for 0.5 h. The phosphorane **12** (6.7 mmol) in 30 mL of dry toluene was added to the reaction mixture and the solution was immediately brought to a boil and heated under reflux for 24 h. After vacuum evaporation of the solvent the residue was chromatographed[10] on a 30 × 300 mm silica gel column, eluting with petroleum ether/ethyl acetate (95/5).

Method B. A solution of the acid chloride (6 mmol) in dry toluene [10 mL] was added dropwise over a period of 0.5 h at room temperature with stirring to a solution of the phosphorane **12** or **1b** (4 mmol) and triethylamine (12 mmol) in 50 mL of dry toluene. After all of the acid chloride had been introduced the solution was refluxed for 12 h. The mixture was cooled to room temperature and concentrated in vacuo. The residue was separated as above.

Method C. Ketene was generated by the pyrolysis of acetone according to the method of Williams and Hurd.[8] The ketene stream was bubbled through a solution of the phosphorane **12** (4 mmol) in 40 mL of dry toluene. After addition of ketene for 2 min the solution was warmed to 40–45 °C with stirring. The ketene stream was allowed to pass through the solution for 2 more min. The color of the solution had turned from orange to clear red. The solution was heated under reflux for 15 h. The mixture was cooled to room temperature and concentrated in vacuo. The residue was separated as above.

Tables I and II indicate the yields, melting points, and method of preparation for the pyrazoles **18**, **19**, and **24**.

Crystallographic Structural Determination of 18i. A colorless crystal of $C_{26}H_{22}N_2O$, **18i**, measuring (0.18 × 0.18 × 0.33 mm), grown by slow evaporation of an ethanolic solution, belonged to the monoclinic space group $P2_1/n$: a = 13.583 (4), b = 6.174 (2), and c = 24.730 (6) Å, β = 102.30 (2)°, V = 2026.4 (10) Å^3, Z = 4, and ρ (calc) = 1.194 g cm^{-3}. Of 2974 reflections collected at 23 °C (Nicolet P3 diffractometer, Mo K_α (4° ≤ 2θ ≤ 45°), 2634 were unique and 1755 with $F_o \geq 3\sigma[F_o]$ were used in the solution and refinement of the structure. All atoms including hydrogen atoms were located by direct methods (SHELXTL, SOLV) and subsequent difference Fourier syntheses. Refinement of all non-hydrogen atoms with an isotropic temperature factors (hydrogen atoms isotropic) led to convergence at R_f = 0.0533, R_{wf} = 0.0518, GOF = 1.159, with the highest peak on the final difference map of 0.16 e Å^{-3}.

2,5-Diphenyl-4-methylpyrazolo[1,5-*a*]pyridine (19c). A solution of **18i** (100 mg, 265 mmol) in absolute ethanol (25 mL) with a catalytic amount (1 mg) of *p*-toluenesulfonic acid was heated under reflux for 1 h. Chromatographic elution with petroleum ether/EtOAc (95/5) afforded, after evaporation of the solvent, **19c** (70 mg, 93%) as a white solid. Recrystallization from ethanol yielded an analyical sample: mp 133–134 °C; precise mass calculated for $C_{20}H_{16}N_2$ 284.131, found 284.130. The ^1H NMR and ^{13}C NMR are found in Tables IV and VII, respectively (supplementary material).

Acknowledgment. The generous support of the National Institute of General Medical Science (Grant No. GM 27620) is gratefully acknowledged. We thank the mass spectroscopy lab of the University of Delaware for the mass spectral data. Purchase of the Bruker WM 250 was supported, in part, by a grant (GM 27616) from the National Institutes of Health.

Supplementary Material Available: Tables of spectral characteristics for pyrazoles **18**, **19**, and **24** (11 pages). Ordering information is given on any current masthead page. X-ray data for **18i** is available from A. L. Rheingold upon request.

Reactions of Azines. 10. Synthesis of 4*H*,6*H*-Pyrazolo[1,5-*c*]oxazol-4-ylidines, 4*H*-Pyrrolo[1,2-*b*]pyrazol-4-ones, and/or 4*H*,8*H*-Pyrazolo[1,5-*c*][1,3]oxazepin-4-ones[1]

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Received June 23, 1986

The phosphoranes **1** underwent the Wittig reaction with the furandione **11**, exclusively at the lactone carbonyl, to produce the azine vinylogous lactones **21** in high yields. The structure of the azine vinylogous lactone **21d** was confirmed by X-ray analysis. Thermolysis of the azine vinylogous lactones **21** gave high yields of 4*H*,6*H*-pyrazolo[1,5-*c*]oxazol-4-ylidines **22**, 4*H*-pyrrolo[1,2-*b*]pyrazol-4-ones **23**, and/or 4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-ones **20**. The formation of the pyrazoles via the zwitterionic intermediates where R = Ph, R^1 = H, CH_3, C_2H_5, and COPh were shown to follow Baldwin's rules of ring closure, giving only **20**. Where R = R^1 = Ar, in **21**, mixtures of **20** and/or **22** plus **23** were obtained. Similar results were found for the reaction of phosphoranes **1** with furandione **14** and subsequent thermolysis of the azine vinylogous lactones **26**. Although no azine vinylogous lactones were observed in the reactions of phosphoranes **1b,d** with furandione **10** the pyrazoles **25b,d** were obtained by heating the reaction mixtures. The structural assignments of the pyrazoles **26e** and **27e** were made on the basis of X-ray analysis. A proposed mechanism for formation of the pyrazoles is discussed.

Introduction

In our preceding paper[2] we demonstrated the synthetic utility of azines **3** (X = CRR^1) for the preparation of 6,7-dihydropyrazolo[1,5-*a*]pyridines **5** (X = CRR^1). The azines were prepared by the Wittig reaction between phosphorane **1** and vinylketenes **2** (X = CRR^1) (eq 1). We desired to

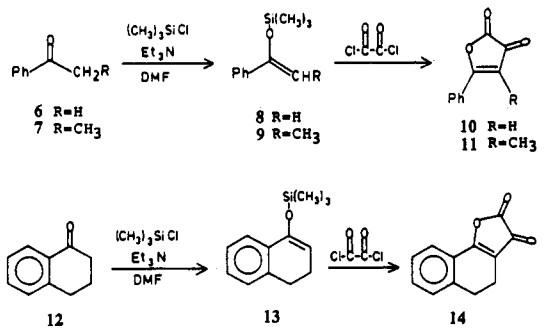
[†]For X-ray analysis.

(1) Presented at Middle Atlantic Regional Meeting of the American Chemical Society; May 23, 1985.

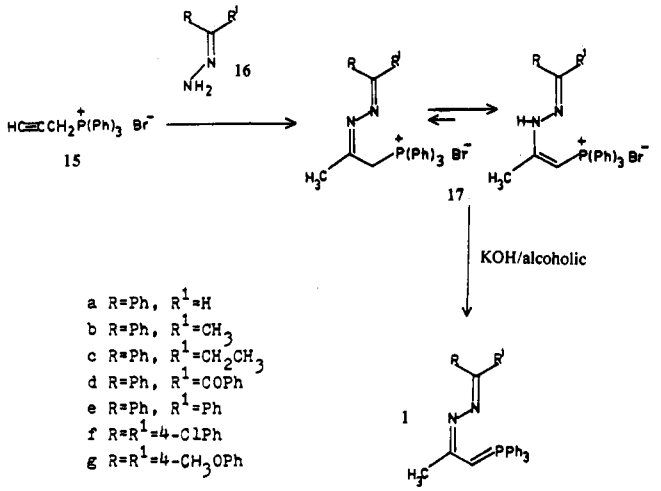
(2) Schweizer, E. E.; Hayes, J. E.; Hirwe, S. N.; Rheingold, A. L. *J. Org. Chem.*, previous paper in this issue.

0022-3263/87/1952-1324$01.50/0

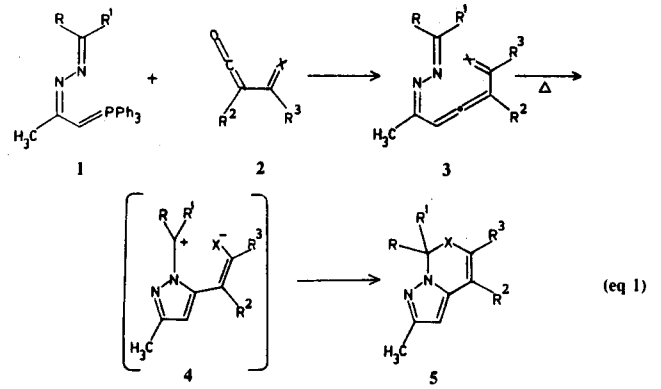
Scheme I



Scheme II



extend this method to the preparation of 7*H*-pyrazolo-[1,5-*c*][1,3]oxazines **5** (X = O) by reacting phosphorane **1** with keto ketenes **2** (X = O).

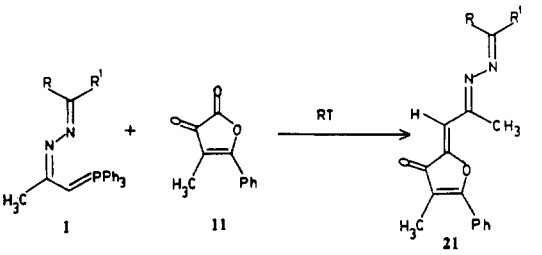


The usual[3] method for ketene preparation is the dehydrochlorination of acid chlorides. Because of the unavailability of β-keto acid chlorides[4] the required keto ketenes **2** [X = O] could not be prepared in this manner. Sonada has shown[5] that oxoketenes are intermediates in the thermal decomposition of 2,3-furandiones. At 80 °C the 2,3-furandiones lose CO to form oxoketenes. We envisioned that we could generate and trap the oxoketenes produced by Sonada's method with phosphoranes.

Results and Discussion

The furandiones **10**, **11**, and **14** were prepared as shown in Scheme I by a two-step reaction sequence from acetophenone **6**, propiophenone **7**, and tetralone **12**, respectively.[5] The phosphoranes **1a–g** were prepared by previously reported[6] procedures as shown in Scheme II.

Table I. Reactions of Phosphoranes 1 with Furandione 11. Isolated Yields and Melting Points for Preparation of Azine Vinylogous Lactones 21



product	R	R^1	yield (%)[a]	mp (°C)[b]
21a	Ph	H	78	137–138
21b	Ph	CH_3	88	115–116
21c	Ph	CH_2CH_3	83	140–141
21d	Ph	COPh	85	185–186
21e	Ph	Ph	89	143–144
21f	4-ClPh	4-ClPh	87	165–166
21g	4-MeOPh	4-MeOPh	86	109–110

[a] Isolated by column chromatography. [b] Recrystallized from diethyl ether.

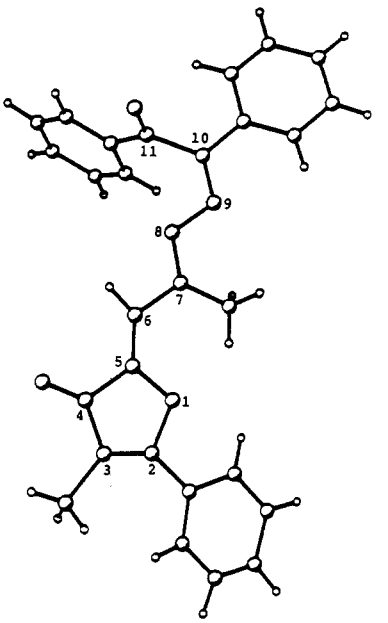


Figure 1. Bond-line drawing of azine vinylogous lactone **21d**.

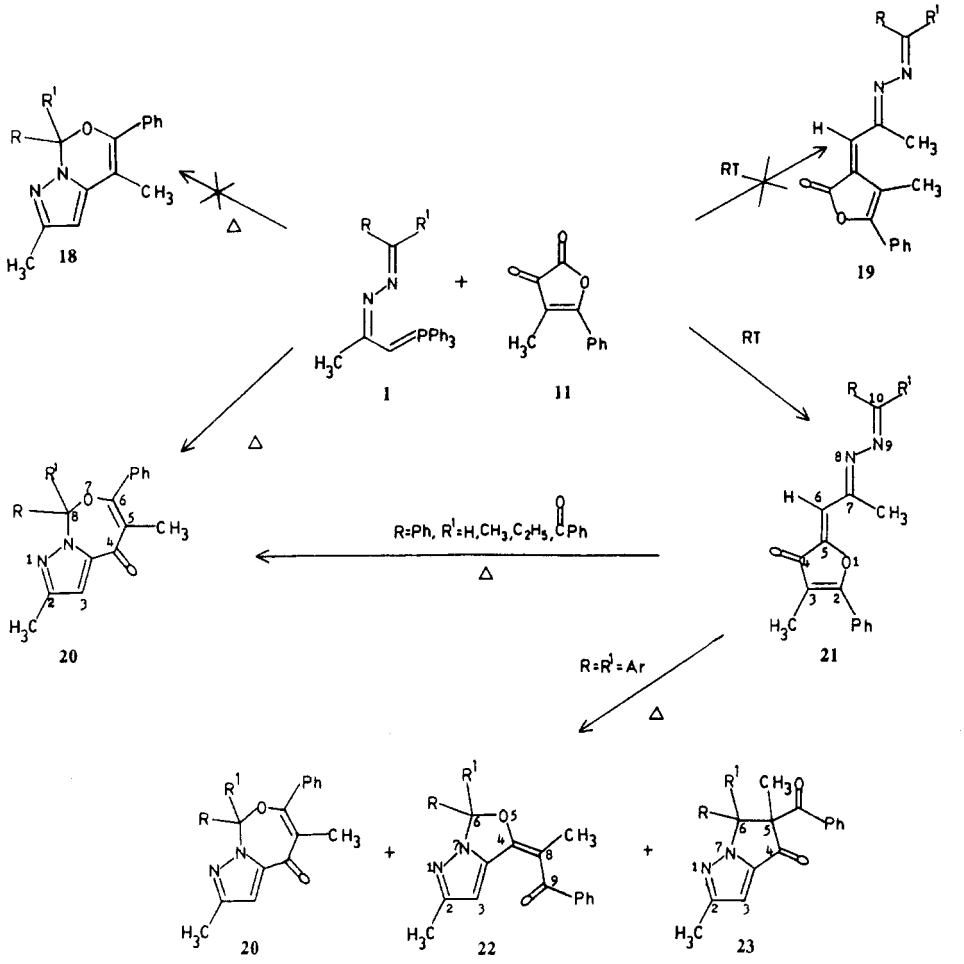
Reactions of Phosphorane 1 with Furandione 11. The products isolated from the reactions of phosphoranes **1a** and **1b** with furandione **11** in benzene solutions heated under reflux were the 4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-ones **20** and not the expected 7*H*-pyrazolo[1,5-*c*]-[1,3]oxazines **18** (**5**, X = O) (Scheme III).

These reactions were monitored by TLC and the formation and disappearance of a bright orange spot was observed. When the reactions were carried out at room temperature the azine vinylogous lactones **21** were isolated by column chromatography as yellow-orange crystals in high yield (Table I, Scheme III). The azine vinylogous

(3) For a review of the preparation of ketenes, see: *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Wiley: 1980; p 213.
(4) This is because β-keto acids easily decarboxylate.
(5) Sonoda, N.; Maurai, S.; Hasegawa K., *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 636.

(6) **1a** and **1c**: Boring, J. Masters Thesis, University of Delaware, Newark, DE, June 1984. **1b** and **1e**: Schweizer, E. E.; Hsueh, W.; Rheingold, A. L.; Durney, R. L. *J. Org. Chem.* **1983**, *48*, 3889. **1d**: Schweizer, E. E.; Albright, T. A.; Evans, S.; Kim, C. S.; Labaw, C. S.; Russiello, A. B. *J. Org. Chem.* **1977**, *42*, 3691. **1f** and **1g**: Hayes, J. E. Ph.D. Thesis, University of Delaware, Newark, DE, June 1986.

Scheme III



lactones **21** were shown to be a mixture of *Z*–*E* isomers by NMR (see Experimental Section).

The formation of the azine vinylogous lactones **21** was the result of the phosphoranes **1** undergoing a Wittig reaction with the lactone carbonyl of the furandione **11** rather than with the oxoketene. The other possible products from these reactions are the azine unsaturated lactones **19** which would result from a Wittig reaction with the carbonyl at the 3-position on the furandione (Scheme III). We have found no reports of the reaction of phosphoranes with furandiones. It has been reported that phosphoranes undergo the Wittig reaction with dihydrofurandiones at both the lactone and ketone carbonyls[6] and with benzofurandiones (coumarandiones) at the ketone carbonyl.[7] Both structures **19** and **21** were consistent with the ^{13}C NMR (carbonyl at 188.3–189.0 ppm) and IR spectral data (1790–1805 cm^{-1}) but compounds **19** were ruled out because it seemed unlikely that upon thermolysis they would produce pyrazoles **20**.

We have confirmed the structural assignment of **21d** by X-ray crystallography. A bond-line drawing of **21d** based on the X-ray analysis is shown in Figure 1.

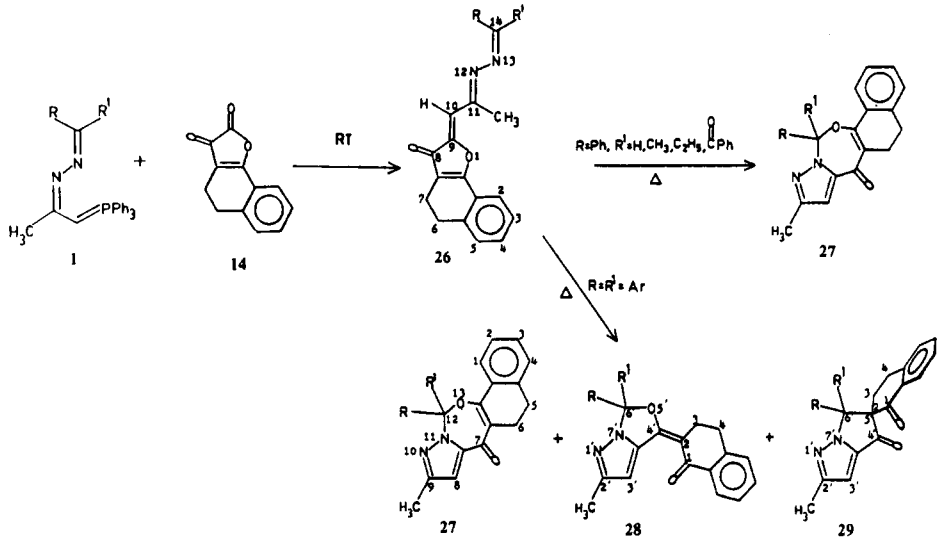
Thermolysis of Azine Vinylogous Lactones 21. Preparation of Pyrazoles 20, 22e, and 23e. Thermolysis of **21e** (R = R^1 = Ph) in toluene heated under reflux produced a mixture of three pyrazole isomers **20e**, **22e**, and **23e** in a ratio of 1:1.6:1.4 by quantitative ^{13}C NMR (Scheme III). The mixture was partially separated by column chromatography. Pyrazole **20e** was isolated pure (TLC, ^{13}C NMR). However pyrazoles **22e** and **23e** ran together by TLC and were isolated together by column chromatography. Both the ^1H NMR and ^{13}C NMR spectra of pyrazole **20e** were nearly identical with those for pyrazole **22e** except for the carbonyl signals in the ^{13}C NMR spectrum. Pyrazole **20e** had a signal at 179.5 ppm, and pyrazole **22e** had a signal at 188.1 ppm. On the basis of this information and an X-ray analysis of the pyrazoles from the reaction of phosphorane **1e** with furandione **14** (see later section) compound **20e** was assigned as the 4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-one (seven-membered vinylogous lactone) and compound **22e** as the 4*H*,6*H*-pyrazolo[1,5-*c*]oxazol-4-ylidene (five-membered vinylogous ester). Product **23e** had two carbonyl signals in its ^{13}C NMR spectrum at 198.2 and 195.7 ppm and signals for two quaternary carbons at 78.8 and 78.4 ppm. This information is consistent with the 4*H*-pyrrolo[1,2-*b*]pyrazole-4-one [five-membered diketone] structure for **23e**.

In contrast to the thermolysis of **21e**, the thermolysis of **21a–d** (R = Ph; R^1 = H, Me, Et, COPh) each produced only a single pyrazole product in nearly quantitative yields (Table II). The pyrazoles had carbonyl signals at 178.1–179.8 ppm in their ^{13}C NMR spectra and were assigned as the 4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-ones **20a–d**.

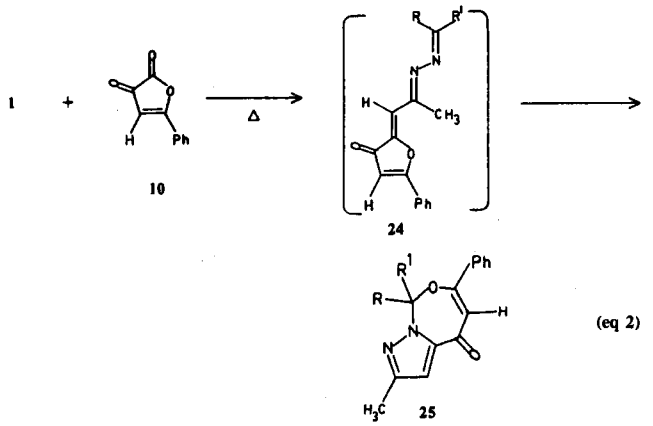
The reactions of phosphoranes **1b** and **1d** with furandione **10** were also investigated. The reactions appeared to occur at room temperature but unlike the reactions of **1** with furandiones **11** and **14** no lactones **24** were observed by TLC. When the reaction mixtures were heated under reflux the 4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-ones **25b** and **25d** were isolated by column chromatography in 45%

(7) Suda, M.; Fukushima, A. *Chem. Lett.* **1981**, 103.

Scheme IV



and 40% yields, respectively (eq 2). Although no azine vinylogous lactones **24** were observed, they are the presumed intermediates.



(eq 2)

Reactions of Phosphorane 1 with Furandione 14. Phosphoranes 1 reacted smoothly with furandione **14** at room temperature in a manner analogous to the reactions with furandione 11. The azine vinylogous lactones **26** were isolated as yellow-orange solids in high yield (Table III, Scheme IV) from these reactions. Azines **26** were produced as a mixture of *Z–E* isomers as determined by ^{13}C NMR (see Experimental Section).

Thermolysis of Azine Vinylogous Lactones 26. Preparation of Pyrazoles 27, 28, and 29. Thermolysis of **26** in toluene heated under reflux produced results analogous to those obtained from the thermolysis of **21** (Scheme IV). When R = R^1 = Ph a mixture of three pyrazoles **27e**, **28e**, and **29e** was formed in a ratio of 1.0:0.95:0.25 [by quantitative ^{13}C NMR] in 92% yield. The mixture was partially separated by column chromatography. Pyrazole **27e** was isolated pure (TLC, ^{13}C NMR). However pyrazoles **28e** and **29e** were indistinguishable by TLC and were isolated together by column chromatography. Fractional crystallization of this mixture from ethanol afforded pure crystals of pyrazole **28e**. Both the ^1H NMR and ^{13}C NMR spectra of pyrazole **27e** were nearly identical with those for pyrazole **28e** except for the carbonyl signals in the ^{13}C NMR spectra. Product **27e** had a signal at 177.9 ppm, and pyrazole **28e** had a signal at 186.3 ppm. We also were unable to identify the pyrazole isomers by their IR spectra. Pyrazole **27e** had an IR absorption at 1605 cm^{-1} while pyrazole **28e** had a band at 1675 cm^{-1} in its IR spectrum.

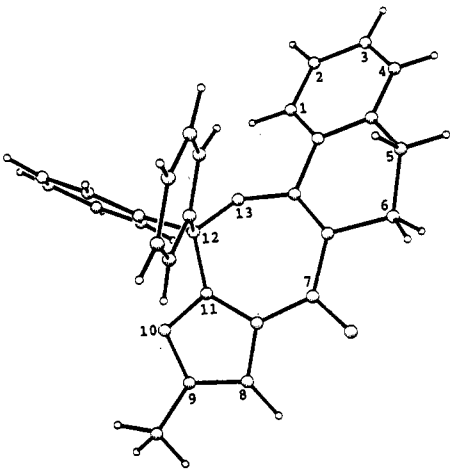


Figure 2. Bond-line drawing of 12,12-diphenyl-9-methyl-5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*]pyrazolo[1,5-*c*][1,3]oxazepin-7-one (**27e**).

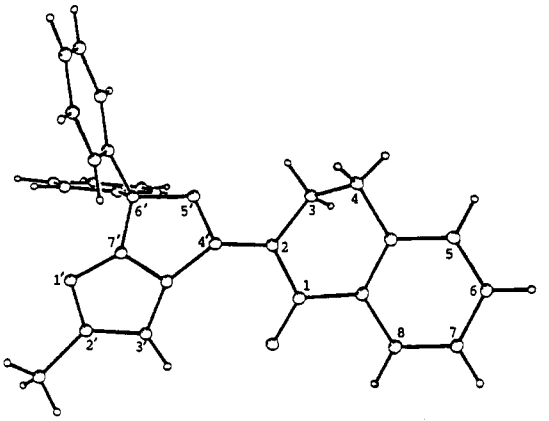
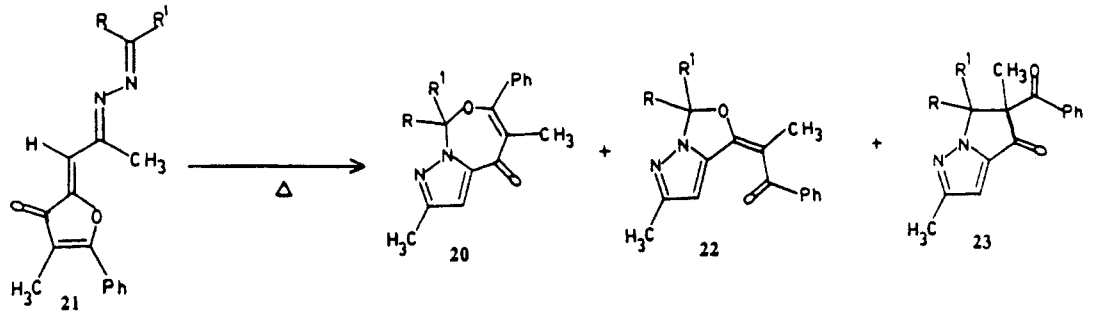


Figure 3. Bond-line drawing of (*E*)-3,4-dihydro-2-[6′,6′-diphenyl-2′-methyl-4*H*,6*H*-pyrazolo[1-,5′-*c*]oxazolidene]-1(2*H*)-naphthalenone (**28e**).

The structural assignments of **27e** and **28e** were based on X-ray crystallographic analysis. A bond-line drawing of **27e** based on the X-ray analysis is shown in Figure 2. The 4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-one and dihydronaphthalene rings are shown. Figure 3 is a bond-line drawing of **28e** based on the X-ray analysis and shows the 4′*H*,6′*H*-pyrazolo[1′,5′-*c*]oxazol-4′-ylidene and dihydronaphthalene rings.

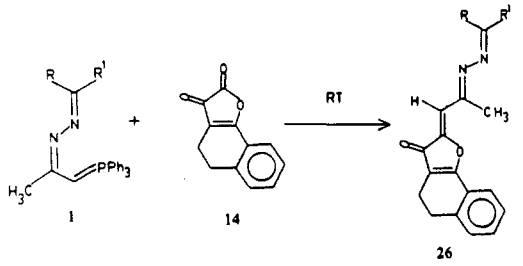
Table II. Thermolysis of Azine Vinylogous Lactones 21. Isolated Yields and Melting Points for Preparation of Pyrazoles 20, 22, and 23



entry	R	R^1	product ratio (%)[a] 20	20	23	total yield (%)[b]	mp (°C)[c]
a	Ph	H	100			90	130–131
b	Ph	CH_3	100			96	115–116
c	Ph	CH_2CH_3	100			93	110–112
d	Ph	COPh	100			91	88–89
e	Ph	Ph	25	40	35	94	159–160[d]
f	4-ClPh	4-ClPh	40	40	20	89	*e*
g	4-MeOPh	4-MeOPh		50	50	91	150–151[f]

[a] Determined by quantitative ^{13}C NMR of residue after removal of solvent. [b] Isolated by column chromatography. [c] Recrystallized from diethyl ether. [d] mp for **20e**. [e] See Experimental Section. [f] mp for **23g** recrystallized from ethanol.

Table III. Reactions of Phosphoranes 1 with Furandione 14. Isolated Yields and Melting Points for Preparation of Azine Vinylogous Lactones 26



product	R	R^1	yield (%)[a]	mp (°C)[b]
26a	Ph	H	82	143–144
26b	Ph	CH_3	86	124–125
26c	Ph	CH_2CH_3	85	140–141
26d	Ph	COPh	87	168–169
26e	Ph	Ph	90	156–157
26f	4-ClPh	4-ClPh	85	139–140
26g	4-MeOPh	4-MeOPh	86	75–76

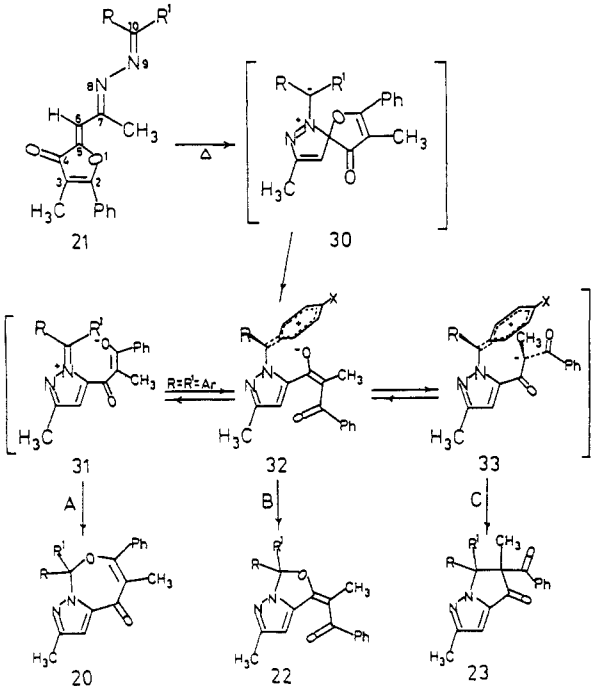
[a] Isolated by column chromatography. [b] Recrystallized from diethyl ether.

Product **29e** had two carbonyl signals in its ^{13}C NMR spectra at 193.1 and 189.3 ppm and signals for two quaternary carbons at 78.9 and 73.9 ppm. This information is consistent with the 3,4-dihydrospiro[naphthalene-2-(1*H*),5′(6′*H*)-(4′*H*)-pyrrolo[1′,2′-*b*]pyrazole-1,4′-dione (spiro diketone) structure for **29e**.

Thermolyses of **26a–d** (R = Ph; R^1 = H, Me, Et, COPh) each produced a single pyrazole product in nearly quantitative yields (Table IV, Scheme IV). The pyrazoles had carbonyl signals at 177.9–177.3 ppm in the ^{13}C NMR spectra and were assigned as the 5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*]pyrazolo[1,5-*c*][1,3]oxazepin-7-ones **27a–d**.

Proposed Mechanism for Formation of the Pyrazoles. A proposed mechanism for the formation of pyrazoles **20**, **22**, and **23** is shown in Scheme V. Nucleophilic attack by the imine nitrogen (N9→C5) on the exocyclic double bond in **21** would yield the azomethine imine intermediate **30** which could open to zwitterionic intermediates **31–33**. Since enolate anions exhibit ambident behavior as nucleophiles, ring closure can occur at carbon as well as at either of the two oxygens. Ring closure from **31** (path A) would yield the seven-membered vinylogous lactone **20**. Ring closure from **32** (path B) would yield the five-membered vinylogous ester **22**. Ring closure from **33** (path C) would yield the five-membered diketone **23**.

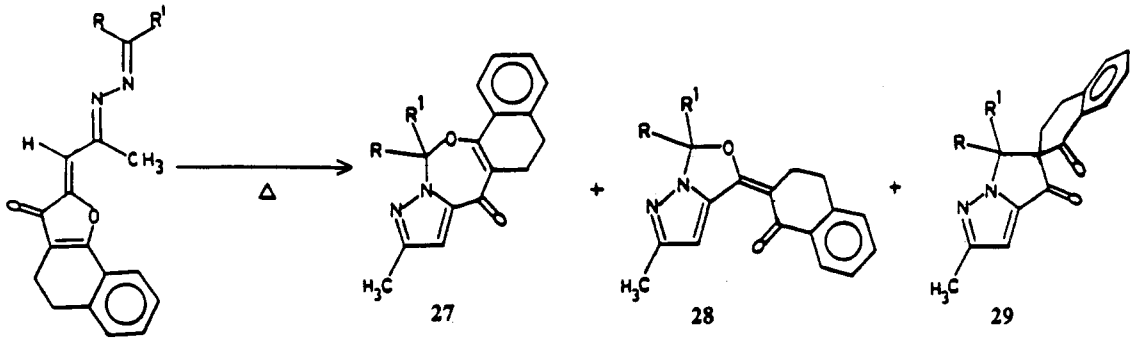
Scheme V



In the zwitterionic intermediates **31** in which the stabilization of the positive charge by the lone pair of electrons on the nitrogen is predominant, the CRR^1 group would be coplanar to the pyrazole ring. Baldwin's rules[9]

(8) (a) Sidky, M. M.; Boulos, L. S. *Phosphorous Sulfur* **1978**, 299. (b) For a review of the reactions of coumarandiones, see: Elderfield, R. C. *Heterocyclic Compounds*; Vol. 2. Palmer, M. H. *The Structure and Reactions of Heterocyclic Compounds*; Arnold: London, New York, 1951; 1967; p 330.

Table IV. Thermolysis of Azine Vinylogous Lactones 26. Isolated Yields and Melting Points for Preparation of Pyrazoles 27, 28, and 29



entry	R	R^1	product ratio (%)[a] 27	28	29	total yield (%)[b]	mp (°C)[c]
a	Ph	H	100			88	171–172
b	Ph	CH_3	100			94	156–157
c	Ph	CH_2CH_3	100			91	175–176
d	Ph	COPh	100			87	191–192
e	Ph	Ph	45	43	12	92	219–220[d]
							180–181[e]
f	4-ClPh	4-ClPh	52	40	8	85	205–206[f]
g	4-MeOPh	4-MeOPh		50	50	88	59–60[g]

[a] Determined by quantitative ^{13}C NMR of residue after removal of solvent. [b] Isolated by column chromatography. [c] Recrystallized from diethyl ether. [d] mp for **27e**. [e] mp for **28e**, recrystallized from ethanol. [f] mp for **27f**. [g] mp for **28g**.

attempt to provide a set of guidelines for ring-forming or ring-breaking reactions. They emphasize that there are substantial differences in the ease of ring formation which are dependent on ring size, geometry of reacting terminus, and the exo or endo nature of the reaction. Accordingly, both five-membered ring closures to give **22** and **23** would be a 5-*Endo-Trig* process and would be disfavored. The seven-membered ring closure (path A) is a 7-*Endo-Trig* process and is favored.

Thermolysis of **21a–d** (R = Ph, $R^1 \neq$ Ph) produces exclusively the pyrazolo[1,5-*c*][1,3]oxazepin-4-ones **20** which result from the seven-membered ring closure. This is in agreement with Baldwin's rules for ring closure.

When both R and R^1 were equal to 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 aromatic moieties would allow for rotation around the C–N bond (Scheme V). This would permit the pyrazoles **22e** and **23e** to be formed by 5-*Exo-Trig* ring closures which are also favorable according to Baldwins rules. Thermolysis of **21e**, R = R^1 = Ph, produced a mixture of three pyrazoles resulting from ring closures by paths B and C in addition to path A.

The formation of the pyrazoles **27**, **28** and **29**, from the thermolysis of **26**, may be rationalized in a similar manner.

Para Substituent Effects on the Thermolysis of Azine Vinylogous Lactones. Since the pyrazoles **22e** and **23e**, or **28e** and **29e**, which result from five-membered ring closure pathways, were only formed when both R and R^1 were phenyl the thermolysis of the azine vinylogous lactones with R and R^1 equal to substituted phenyl groups was examined.

Thermolysis of azine vinylogous lactone **21f** and of **26f** where R = R^1 = 4-ClPh each produced a mixture of the three pyrazole isomers **20f** + **22f** + **23f** and **27f** + **28f** + **29f**, respectively. However, thermolysis of azine vinylogous lactones **21g** and **26g** where R = R^1 = 4-MeOPh each produced a mixture of only two pyrazole isomers **22g** + **23g** and **28g** + **29g**, respectively. These pyrazoles result from the five-membered ring-closure pathways. The pyrazoles **20g** and **27g** which would have come from the seven-membered ring-closure pathways were not formed when R = R^1 = 4-MeOPh. The ratios are summarized in Tables II and IV.

A 4-MeOPh would allow for enhanced delocalization of the positive charge on the aromatic moieties compared to the unsubstituted phenyl ring. A 4-ClPh would be less able to stabilize the positive charge than an unsubstituted phenyl could. As the ability of the aromatic group to stabilize a carbocation increases, the ratio of the pyrazoles **22** + **23** or **28** + **29** formed from the five-membered ring-closure pathways to the pyrazoles **20** or **27** formed from the seven-membered ring-closure pathway increases (see Tables II and IV). This supports our rationale, described previously, that as the ability of the R groups to stabilize an adjacent carbocation increases, the stabilization of the carbocation by the lone pair of electrons on nitrogen becomes less significant. This shifts the ring closure from the *Endo-Trig* to the *Exo-Trig* form that favors the five-membered ring closures over the seven-membered ring closure.

The data also show that the relative percentages of **22** and **28** which result from five-membered ring closures on oxygen remain almost constant. As the relative percentages of **20** and **27** decrease the relative percentages of **23** and **29** increase but they never become the major products.

Several experiments were undertaken to determine if the products were isomerizing under the reaction conditions. Several isolated pyrazoles (**20b,e**; **22g**; **23g**; **27a,e**; **28e**; and **29g**) were heated under reflux in toluene for 24 h and the ^{13}C NMR spectrum of the residue after evaporation of the solvent was recorded. In all cases the starting pyrazoles were unchanged. Several azine vinylogous lactones (**21b,e,f**; **21e,g**) were heated for 6, 24, and 48 h. In all cases the ratios of pyrazoles obtained (determined by

(9) Baldwin, J. E.; Thomas, R. C.; Kruse, L. I.; Silberman L. *J. Org. Chem.* **1977**, *42*, 3846 and references cited therein.

quantitative ^{13}C NMR) did not vary. These results indicate that no isomerizations were occurring under the reaction conditions.

Conclusion

Thus it has been demonstrated that the Wittig reaction between phosphoranes 1 and 2,3-furandiones and subsequent thermolysis of the azine vinylogous lactones provides an excellent synthesis of pyrazolo[1,5-*c*][1,3]oxazepin-4-ones as long as R and R^1 are not both aromatic. This method, besides being experimentally simple and efficient, is useful because we have found no previous reports of the preparation of this ring system.

Studies into the reaction of phosphoranes 1 with preformed oxoketenes are underway.

Experimental Section

Spectral Procedures. The ^1H, ^{13}C, and ^{31}P NMR of approximately 10% (w/v) solutions in $CDCl_3$ were obtained on a Bruker Spectrospin Model WM250 or AM250. Chemical shifts are reported in parts per million (δ scale) by employing tetramethylsilane (phosphoric acid for ^{31}P NMR) as an internal standard. In reporting NMR data the following abbreviations have been employed: coupling constant in hertz (J), singlet (s), broad singlet (br s), doublet (d), doublet of doublet (dd), triplet (t), broad triplet (br t), quartet (q), multiplet (m). The quantitative analyses with ^{13}C NMR were performed by a combination of long pulse intervals to assure complete relaxation of all ^{13}C nuclei and a gated decoupling, which eliminated the nuclear Overhauser enhancement. Infrared spectra were recorded on a Unicap SP 1100 infrared spectrophotometer and calibrated by comparison with a standard polystyrene film sample.

The numbering schemes for the azine vinylogous lactones and pyrazoles are as shown in Schemes III and IV.

Several of the azine vinylogous lactones **21** were isolated as mixtures of *E*–*Z* isomers (**21** is shown as the *Z* isomer). In these cases the ^1H and ^{13}C NMR spectra showed two sets of absorptions. The major difference was in the chemical shifts for C6-H and C7-CH_3. In one case (*Z*-**21**) the C6-H is cis to the carbonyl moiety (C4) and the C7-CH_3 is trans to the carbonyl moiety (C4). In the other isomer ((*E*)-**21**) the C7-CH_3 is cis to the carbonyl moiety and the C6-H is trans to the carbonyl moiety. The ^1H NMR spectrum showed two singlets for the C7-CH_3 (2.23–2.61) and two singlets for the C6 methine (6.42–6.83 and 7.07–7.12). Table V (supplementary material) lists the ^1H NMR parameters for azines **21**. The ^{13}C NMR spectra was very similar for both isomers except for the chemical shifts of the C-3 methyl and the C-6 methine. One isomer had the C-7 methyl at 16.3–17.2 ppm and the C-6 methine at 111.3–112.1 ppm. The other isomer had the C-3 methyl at 22.7–23.1 ppm and the C-6 methine at 100.4–101.4 ppm. Table VI (supplementary material) lists the ^{13}C NMR parameters for azines **21**.

A few of the azine vinylogous lactones **26** were also isolated as mixtures of *E*–*Z* isomers. Table VII (supplementary material) lists the ^1H NMR parameters for azines **26**. The ^{13}C NMR spectra showed two sets of signals. Again the major difference was in the chemical shifts of the C-10 methine and C11-CH_3. One isomer had the C-10 methine at 101.1–101.8 and the C11-CH_3 at 21.8–23.2 ppm. The other isomer had the methine at 111.8–112.7 and methyl at 16.2–17.1 ppm. Table VIII (supplementary material) lists the ^{13}C NMR parameters for azines **26**.

Table IX (supplementary material) lists the ^1H NMR parameters for pyrazoles **20**. The ranges of the ^1H NMR parameters were δ 1.55–1.78 (C5-CH_3), 2.01–2.23 (C2-CH_3), and 6.65–6.94 (C3-H). Table X (supplementary material) lists the ^{13}C NMR parameters for pyrazoles **20**. The ranges of the ^{13}C NMR parameters were δ 147.5–148.6 (C2), 110.1–111.9 (C3), 143.3–144.8 (C3a), 178.4–179.5 (C4), 116.7–118.8 (C5), 160.1–163.2 (C6), 90.5–99.1 (C8), 13.0–13.5 (C2-CH_3), and 15.8–16.2 (C5-CH_3). Table XI (supplementary material) lists the ^1H NMR parameters for pyrazoles **27**. The ranges of the ^1H NMR parameters were δ 2.21–2.40 (C2-CH_3), 2.36–3.06 (CH_2-CH_2), 6.87–6.99 (C3-H). Table XII (supplementary material) lists the ^{13}C NMR parameters for pyrazoles **27**. The ranges of the ^{13}C NMR parameters were δ 117.5–118.7 (C6a), 176.9–177.9 (C7), 143.8–145.1 (C7a), 111.1–112.6 (C8), 147.3–148.8 (C9), 90.8–99.9 (C12), 156.6–158.2 (C13a), 13.2–13.6 (C9-CH_3), 21.6–22.1, 27.0–27.5 (CH_2CH_2).

Precise mass spectra were recorded on a Du Pont 21-492 B instrument with a resolution of 3300 or 5000. Tables XIII and XIV (supplementary material) list the mass spectral data for azine vinylogous lactones **21**, **26**, and pyrazoles **20**, **27**, respectively. All precise masses found were within 0.003 mass unit of the calculated values.

General Procedures. Dry nitrogen was routinely used as the reaction atmosphere in all reactions. All glassware was baked at 100–120 °C for a minimum of 2 h before being used. Melting points were obtained with a Thomas-Hoover apparatus and are uncorrected.

Toluene and benzene were dried and distilled from sodium metal. Dimethylformamide was dried and distilled under reduced pressure from calcium hydride. Eastman Chromatogram (silica gel with a fluorescent indicator on polyethylene) precoated sheets were employed in thin-layer chromatography (TLC). Baker silica gel (60–200 mesh) and EM7747 silica gel for column chromatography were used throughout for product separation.[10]

The phosphoranes 1 were prepared by known methods.[6] The procedure of House et al.[11] was used to prepare the silyl enol ethers **8**, **9**, and **13**. The furandiones **10**, **11**, and **14** were prepared from the reaction of the silyl enol ethers with oxalyl chloride according to the procedure of Sonada et al.[5]

General Procedure for the Reactions of Phosphoranes 1 with Furandione 11. Preparation of Azine Vinylogous Lactones 21. The furandione **11** (0.77 g, 4.1 mmol) was added with stirring at room temperature to a slurry of the phosphorane 1 (4.0 mmol) in 40 mL of dry benzene. The mixture, which immediately became a clear orange-red solution, was stirred at room temperature for 15 h after which time an orange precipitate had formed. The solvent was removed in vacuo, keeping the temperature below 50 °C. The residue was chromatographed, eluting with petroleum ether/ethyl acetate (85/15). The azine vinylogous lactones were isolated as orange-yellow solids that were recrystallized from diethyl ether. The yields and melting points for preparation of **21** are collected in Table I. The ^1H, ^{13}C NMR, and mass spectral data for **21** are found in Tables V, VI, and XIII, respectively.

Crystallographic Structural Determination of 21d. An orange crystal of $C_{28}H_{22}N_2O_2$, **21d**, grown by slow evaporation of an ethereal solution, belonged to the monoclinic space group, $P2_1/c$: a = 12.575 (4), b = 8.884 (2), and c = 20.815 (7) Å, β = 103.81 (2)°, V = 2258 (1) Å^3, Z = 4, and ρ(calc) = 1.28 g cm^{-3}. Of 2376 reflections collected at 24 °C (Nicolet R3 diffractometer, Mo Kα 4° ≤ 2θ ≤ 42°), 2185 were unique and 1345 with $F_o \leq 2.5\sigma(F_o)$ were used in the solution and refinement of the structure. All atoms including hydrogen atoms were located by direct methods (SOLV) and subsequent difference Fourier syntheses. Refinement of all non-hydrogen atoms with anisotropic temperature factors (hydrogen atoms isotropic) led to convergence at R_f = 0.0578, R_{wf} = 0.0609, GOF = 1.116, with the highest peak on the final difference map of 0.23 e Å^{-3}. Tables of the experimental data for the crystallographic structural determination are available as supplementary material.

General Procedure for Thermolysis of Azine Vinylogous Lactones 21a–d. Preparation of 4*H*,8*H*-Pyrazolo[1,5-*c*]-[1,3]oxazepin-4-ones 20a–d. A solution of the azine vinylogous lactones **21a–d** (3.0 mmol) in toluene (40 mL) was heated under reflux. The reaction was monitored by TLC and the heating was stopped 1 h after the disappearance of all the azine vinylogous lactone was observed. After cooling to room temperature, the solvent was removed in vacuo. Analysis by TLC and ^{13}C NMR indicated the presence of only one compound. The residue was chromatographed, eluting with petroleum ether/ethyl acetate (95/5). The pyrazoles **20a–d** were isolated as white solids which were recrystallized from diethyl ether. The yields and melting points are collected in Table II. The ^1H, ^{13}C NMR, and mass

(10) Chromatographic technique was that of Taber D. F. *J. Org. Chem.* **1982**, *47*, 1351.

(11) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. P. *J. Org. Chem.* **1969**, *34*, 2342.

spectral data for **20** are found in Tables IX, X, and XIV, respectively.

Thermolysis of Azine Vinylogous Lactone 21e. Preparation of Pyrazoles 20e, 22e, and 23e. A solution of the azine vinylogous lactone **20e** (1.22 g, 3.0 mmol) in 40 mL of toluene was heated under reflux for 10 h. After cooling to room temperature, the solvent was removed in vacuo. Analysis by TLC and quantitative ^{13}C NMR indicated a mixture of three compounds in a ratio of 25:40:35 (**20e:22e:23e**). The residue was chromatographed, eluting with petroleum ether/ethyl acetate (95/5). This yielded, in order of elution, the following.

(a) Mixture of 2,8-dimethyl-6,6-diphenyl-4-(1-benzoylethylidene)-4*H*,6*H*-pyrazolo[1,5-*c*]oxazole (22e) and 5-benzoyl-2,5-dimethyl-6,6-diphenyl-4*H*-pyrrolo[1,2-*b*]-pyrazol-4-one (23e) as a colorless oil (0.85 g, 70%) [Further attempts at separation were unsuccessful.): ^1H NMR of mixture δ 1.67 s, 1.82 s, 2.26 s, 2.34 s, 6.8–7.9 m; ^{13}C NMR of mixture δ 198.2 (s), 195.5 (s), 187.9 (s), 156.1 (s), 154.8 (s), 150.8 (s), 108.5 (s), 102.6 (d), 101.2 (d), 98.6 (s), 78.7 (s), 78.3 (s), 19.8 (q), 14.0 (q), 13.8 (q), 13.6 (q); precise mass of mixture calcd for $C_{27}H_{22}N_2O_2$ 406.168, found 406.167.

(b) 2,5-Dimethyl-6,8,8-triphenyl-4*H*,8*H*-pyrazolo[1,5-*c*]-[1,3]oxazepin-4-one (20e) (0.30 g, 24%) as a white solid. Recrystallization from ethanol yielded an analytical sample: mp 159–160 °C; IR (KBr) 1610 cm^{-1}. The ^1H NMR, ^{13}C NMR, and mass spectral data for **20e** are found in Tables IX, X, and XIV, respectively.

Thermolysis of Azine Vinylogous Lactone 21f. Preparation of Pyrazoles 20f, 22f, and 23f. Thermolysis of **21f** (1.43 g, 3.0 mmol) was carried out as above. Analysis by quantitative ^{13}C NMR indicated a mixture of three pyrazoles in a ratio of 40:40:20 (**20f:22f:23f**). The residue was chromatographed, eluting with petroleum ether/ethyl acetate (95/5). This yielded, in order of elution, the following.

(a) 5-Benzoyl-2,5-dimethyl-6,6-bis(*p*-chlorophenyl)-4*H*-pyrrolo[1,2-*b*]pyrazol-4-one (23f) (0.23 g, 16%) as a colorless oil: ^1H NMR δ 1.45 (s, 3 H, C5-CH_3), 2.33 (s, 3 H, C2-CH_3), 6.45 (d, J = 7.7, 2 H), 6.56 (s, 1 H, C3-H), 7.05–40 (m, 9 H, Ar), 7.57 (d, J = 8.2, 2 H); ^{13}C NMR δ 143.3 (C2), 102.1 (C3), 198.2 (C4), 78.1, 78.4 (C5,6), 14.4 (C2-CH_3), 20.5 (C5-CH_3), 187.6 (C5-COPh); IR ($CHCl_3$) 1736, 1697 cm^{-1}; precise mass calcd for $C_{27}H_{20}Cl_2N_2O_2$ 474.090, found 474.091.

(b) Mixture of 2,5-dimethyl-8,8-bis(*p*-chlorophenyl)-6-phenyl-4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-one (20f) and 2,8-dimethyl-6,6-bis(*p*-chlorophenyl)-4-(1-benzoylethylidene)-4*H*,6*H*-pyrazolo[1,5-*c*]oxazole (22f) was obtained as a white solid (1.04 g 73%) [Further attempts at separation were unsuccessful.]: ^1H NMR of mixture δ 1.71 (s, 3 H), 2.08 (s, 3 H), 2.10 (s, 3 H), 2.38 (s, 3 H), 6.25 (s, 1 H), 6.90–7.70 (m, Ar); ^{13}C NMR of mixture δ 196.0 (s), 179.3 (s), 159.6 (s), 156.4 (s), 155.6 (s), 108.5 (s), 103.0 (d), 101.0 (d), 98.9 (s), 98.1 (s), 15.7 (q), 14.2 (q), 14.0 (q), 13.4 (q); precise mass of mixture calcd for $C_{27}H_{20}Cl_2N_2O_2$ 474.090, found 474.089.

Thermolysis of Azine Vinylogous Lactone 21g. Preparation of Pyrazoles 22g and 23g. Thermolysis of **21g** (1.40 g, 3.0 mmol) was carried out as above. Analysis by quantitative ^{13}C NMR indicated a mixture of two pyrazoles in a ratio of 50:50 (**22g:23g**). TLC analysis in a variety of solvents showed one spot. Separation was achieved by fractional crystallization with ethanol. This afforded **5-benzoyl-2,5-dimethyl-6,6-bis(*p*-methoxyphenyl)-4*H*-pyrrolo[1,2-*b*]pyrazol-4-one (23g)** (0.60 g, 43%) as a tan solid which was recrystallized to a constant mp of 150–151 °C: ^1H NMR for **23g** δ 1.52 (s, 3 H, C5-CH_3), 2.43 (s, 3 H, C2-CH_3), 3.68 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 6.50–7.69 (m, 14 H, Ar and C3-H); ^{13}C NMR δ 14.4 (C2-CH_3), 20.1 (C5-CH_3), 55.1 (OCH_3), 78.5, 78.8 (C5, C6), 101.3 (C3), 188.9 (C5-COPh), 198.9 (C4); IR (KBr) 1733, 1701 cm^{-1}; precise mass calcd for $C_{29}H_{26}N_2O_4$ 466.189, found 466.188.

Evaporation of the ethanolic filtrate from the above fractional crystallization afforded **2,8-dimethyl-6,6-bis(*p*-methoxyphenyl)-4-(1-benzoylethylidene)-4*H*,6*H*-pyrazolo[1,5-*c*]oxazole (22g)** (0.67 g, 48%) as an orange oil which was contaminated with about 5% **23g** (by NMR) [Attempts at crystallization failed.]: ^1H NMR for **22g** δ 2.08 (s, 3 H), 2.13 (s, 3 H), 3.63 (br s, 6 H), 5.76 (s, 1 H, C3-H), 6.74–7.60 (m, 13 H, Ar); ^{13}C NMR δ 14.0, 14.2 (C2-CH_3, C8-CH_3), 55.1 (OCH_3), 99.1 (C6), 102.7 (C3), 108.5 (C8), 196.1 (C9); precise mass calcd for the mixture $C_{29}H_{26}N_2O_4$ 466.189, found 466.188.

Reaction of Phosphorane 1b with Furandione 10. Preparation of 2,8-Dimethyl-6,8-diphenyl-4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-one (25b). The furandione **10** (0.54 g, 3.1 mmol) was added with stirring at room temperature to a slurry of the phosphorane **1b** (1.30 g, 3.0 mmol) in 40 mL of dry benzene. The mixture immediately turned dark red and was stirred at room temperature for 1.5 h. TLC analysis showed only a broad band at the origin. There was no separate mobile orange spot for the azine vinylogous lactone as in the reactions of phosphoranes **1** with furandiones **11** and **14**. The reaction mixture was heated under reflux for 8 h. After cooling and concentrating in vacuo, the residue was chromatographed, eluting with petroleum ether/ethyl acetate (93/7). The pyrazole **25b** was collected as a white solid 0.45 g (45%). Recrystallization from ethanol produced an analytical sample: mp 187–188 °C; ^1H NMR δ 2.40 (s, 3 H), 2.48 (s, 3 H), 6.14 (s, 1 H, C5H), 6.72 (d, J = 7, 2 H, Ar), 6.87 (s, 1 H, C3H), 7.11–7.92 (m, 8 H, Ar); ^{13}C NMR δ 147.9 (C2), 111.1 (C3), 144.7 (C3a), 178.1 (C4), 108.5 (C5), 161.0 (C6), 97.3 (C8), 13.4 (C2-CH_3), 30.7 (C8-CH_3); precise mass calcd for $C_{21}H_{18}N_2O_2$ 330.137, found 330.138.

Reaction of Phosphorane 1d with Furandione 10. Preparation of 8-Benzoyl-6,8-diphenyl-2-methyl-4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-one (25d). The pyrazole **25d** was prepared by reacting phosphorane **1d** (1.57 g, 3.0 mmol) with furandione **10** (0.54 g, 3.1 mmol) as described in the preparation of **25b**. The pyrazole **25d** was collected as white solid, 0.50 g (40%). Recrystallization from ethanol produced an analytical sample: mp 187–188 °C; ^1H NMR δ 2.22 (s, 3 H, C2-CH_3), 6.27 (s, 1 H, C5H), 6.94 (s, 1 H, C3H), 7.23–7.85 (m, 15 H, Ar); ^{13}C NMR δ 149.0 (C2), 111.4 (C3), 144.8 (C3a), 177.1 (C4), 109.1 (C5), 160.7 (C6), 99.1 (C8), 13.4 (C2-CH_3), 190.2 (C8-*C*O); precise mass calcd for $C_{27}H_{20}N_2O_3$ 420.147, found 420.148.

General Procedure for the Reactions of Phosphoranes 1 with Furandione 14. Preparation of 26. The furandione **14** (0.83 g, 4.1 mmol) was added with stirring at room temperature to a slurry of the phosphorane **1** (4.0 mmol) in 40 mL of dry benzene. The mixture, which immediately became a clear orange-red solution, was stirred at room temperature for 15 h at which time a orange precipitate had formed. The solvent was removed in vacuo, keeping the temperature below 50 °C. The residue was chromatographed, eluting with petroleum ether/ethyl acetate (85/15). The azine vinylogous lactones **26** were isolated as orange-yellow solids which were recrystallized from diethyl ether. The yields and melting points for preparation of **26** are collected in Table III. The ^1H NMR, ^{13}C NMR, and mass spectral data are found in Tables VII, VIII, and XIII, respectively.

General Procedure for Thermolysis of Azine Vinylogous Lactones 26a–d. Preparation of 5,6-Dihydro-7*H*,12*H*-naphtho[2,1-*f*]pyrazolo[1,5-*c*][1,3]oxazepin-7-ones 27a–d. A solution of the azine vinylogous lactones **26a–d** (3.0 mmol) in toluene (40 mL) was heated under reflux. The reaction was monitored by TLC and the heating was stopped 1 h after the disappearance of all the azine vinylogous lactone was observed. After cooling to room temperature, the solvent was removed in vacuo. Analysis by TLC and ^{13}C NMR indicated the presence of only one compound. The residue was chromatographed, eluting with petroleum ether/ethyl acetate (95/5). The pyrazoles **27a–d** were isolated as white solids which were recrystallized from diethyl ether. The yields and melting points are collected in Table IV. The ^1H NMR, ^{13}C NMR, and mass spectral data are found in Tables XI, XII, and XIV, respectively.

Thermolysis of Azine Vinylogous Lactone 26e. Preparation of Pyrazoles 27e, 28e, and 29e. A solution of the azine vinylogous lactone **26e** (1.25 g, 3.0 mmol) in 40 mL of toluene was heated under reflux for 10 h. After cooling to room temperature, the solvent was removed in vacuo. Analysis by TLC and quantitative ^{13}C NMR indicated a mixture of three compounds in a ratio of 45/43/12 (**27e/28e/29e**). The residue was chromatographed, eluting with petroleum ether/ethyl acetate (95/5). This yielded, in order of elution, the following.

(a) Mixture of 6′,6′-diphenyl-2′-methyl-(*E*)-3,4-dihydro-2-(4′*H*,6′*H*-pyrazolo[1′,5′-*c*]oxazol-4′-ylidene)-1(2*H*)-naphthalenone (28e) and 6′,6′-diphenyl-2′-methyl-3,4-dihydrospiro(naphthalene-2(1*H*),5′(6′*H*)-(4′*H*)pyrrolo[1′,2′-

***b*]pyrazole)-1,4′-dione (29e)** as a colorless oil (0.63 g, 50%). Fractional crystallization of this mixture with ethanol yielded pure crystals of pyrazole **28e**. Recrystallization from ethanol yielded an analytical sample, mp: 180–181 °C; IR (KBr) 1675 cm^{-1}; ^1H NMR δ 2.41 (s, 3 H, C2′-CH_3), 2.96 (br t, 2 H, CH_2), 3.08 (br t, 2 H, CH_2), 7.21–8.12 (m, 15 H, Ar and C3′H); ^{13}C NMR δ 151.2 (C2′), 105.5 (C3′), 142.8 (C3′a), 155.2 (C4′), 99.3 (C6′), 109.3 (C2), 186.3 (C1), 14.4 (C2′-CH_3), 28.2, 24.0 (CH_2CH_2); precise mass calcd for $C_{28}H_{22}N_2O_2$ 418.168, found 418.168.

Although **29e** could not be obtained pure the ^1H and ^{13}C NMR assignments of pyrazole **29e** were made by subtraction of the NMR of **28e** from the NMR spectra of the mixture of pyrazoles: ^1H NMR for **29e** δ 2.32 (s, 3 H, C2′-CH_3), 2.25–2.81 (m, 4 H, CH_2CH_2); ^{13}C NMR for **29e** δ 98.8 (C3′), 193.1, 189.3 (C1, C4′), 78.9, 73.9 (C5′, C6′), 14.2 (C2′-CH_3), 29.3, 25.5 (CH_2CH_2); precise mass found for mixture 418.168.

(b) 12,12-Diphenyl-9-methyl-5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*]pyrazolo[1,5-*c*][1,3]oxazepin-7-one (27e) (0.52 g, 42%) as a white solid. Recrystallization from diethyl ether yielded an analytical sample, mp: 219–220 °C; IR (KBr) 1605 cm^{-1}. The ^1H NMR, ^{13}C NMR, and mass spectral data are found in Tables XI, XII, and XIV, respectively.

Crystallographic Structural Determination of 27e. A colorless crystal of $C_{28}H_{22}N_2O_2$; **27e**, grown by slow evaporation of an ethanolic solution, belonged to the triclinic space group $P\bar{1}$: a = 9.515 (3), b = 11.029 (4), and c = 11.687 (4) Å, α = 67.13 (3)°, β = 73.32 (3)°, δ = 88.58 (3)°, V = 1077.2 (8) Å^3, Z = 2, and ρ(calc) = 1.29 g cm^{-3}. Of 2979 reflections collected at 24 °C (Nicolet R3 diffractometer, Mo Kα 4° ≤ 2θ ≤ 45°), 2815 were unique and 2167 with $F_o \leq 2.5\sigma(F_o)$ were used in the solution and refinement of the structure. All atoms including hydrogen atoms were located by direct methods (SOLV) and subsequent difference Fourier syntheses. Refinement of all non-hydrogen atoms with anisotropic temperature factors (hydrogen atoms isotropic) led to convergence at R_f = 0.0612, R_{wf} = 0.0617, GOF = 1.929, with the highest peak on the final difference map of 0.38 e Å^{-3}. Tables of the experimental data for the crystallographic structural determination are available as supplementary material.

Crystallographic Structural Determination of 28e. A colorless crystal of $C_{28}H_{22}N_2O_2$; **28e**, grown by slow evaporation of an ethanolic solution, belonged to the triclinic space group $P\bar{1}$: a = 8.502 (2), b = 14.211 (5), and c = 18.714 (8) Å, α = 107.15 (3)°, β = 90.86 (3)°, δ = 89.91 (3)°, V = 2160 (1) Å^3, Z = 4, and ρ(calc) = 1.29 g cm^{-3}. Of 4838 reflections collected at 24 °C (Nicolet R3 diffractometer, Mo K_α 4° ≤ 2θ ≤ 42°), 4655 were unique and 2768 with $F_o \leq 5\sigma(F_o)$ were used in the solution and refinement of the structure. All atoms including hydrogen atoms were located by direct methods (SOLV) and subsequent difference Fourier syntheses. Refinement of all non-hydrogen atoms with anisotropic temperature factors (hydrogen atoms isotropic) led to convergence at R_f = 0.0494, R_{wf} = 0.0482, GOF = 1.587, with the highest peak on the final difference map of 0.21 e Å^3. Tables of the experimental data for the crystallographic structural determination are available as supplementary material.

Thermolysis of Azine Vinylogous Lactone 26f. Preparation of Pyrazoles 27f, 28f, and 29f. Thermolysis of **26f** (1.46 g, 3.0 mmol) was carried out as above. Analysis by quantitative ^{13}C NMR indicated a mixture of three pyrazoles in a ratio of 52:40:8 (**27f**:**28f**:**29f**). The residue was chromatographed, eluting with petroleum ether/ethyl acetate (95/5). This yielded, in order of elution, the following.

(a) Mixture of 6′,6′-bis(*p*-chlorophenyl)-2′-methyl-(*E*)-3,4-dihydro-2-(4′*H*,6′*H*-pyrazolo[1′,5′-*c*]oxazol-4′-ylidene)-1(2*H*)-naphthalenone (28f) and 6′,6′-bis(*p*-chlorophenyl)-2′-methyl-3,4-dihydrospiro(naphthalene-2(1*H*),5′(6′*H*)-(4′*H*)pyrrolo[1′,2′-*b*]pyrazole)-1,4′-dione (29f) as a colorless oil (0.59 g, 40%). No further attempts at separation were made. The ^1H NMR of the mixture was too complex to interpret. The ^{13}C NMR assignments of pyrazoles **28f** and **29f** were made by analogy to the NMR spectra of pyrazoles **28e** and **29e**: ^{13}C NMR for **28f** δ 105.8 (C3′), 155.9 (C4′), 97.9 (C6′), 109.9 (C2), 186.1 (C1), 14.4 (C2′-CH_3), 28.2, 24.1 (CH_2CH_2); ^{13}C NMR for **29f** δ 101.9 (C3′), 192.8, 188.6 (C1, C4′), 78.0, 73.9 (C5′, C6′); 14.4 (C2′-CH_3); 29.6, 25.6 (CH_2CH_2); precise mass of mixture calcd for $C_{28}H_{20}Cl_2N_2O_2$ 486.090, found 486.090.

(b) 12,12-Bis(*p*-chlorophenyl)-9-methyl-5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*]pyrazolo[1,5-*c*][1,3]oxazepin-7-one (27f) (0.65 g 45%) was obtained as a white solid. Recrystallization from diethyl ether yielded an analytical sample, mp: 205–206 °C; IR (KBr) 1608 cm^{-1}. The ^1H NMR, ^{13}C NMR, and mass spectral data are found in Tables XI, XII, and XIV, respectively.

Thermolysis of Azine Vinylogous Lactone 26g. Thermolysis of **26g** (1.43 g, 3.0 mmol) was carried out as above. Analysis by quantitative ^{13}C NMR indicated a mixture of two pyrazoles in a 50/50 ratio. The residue was chromatographed, eluting with petroleum ether/ethyl acetate (95/5). This yielded, in order of elution, the following.

(a) 6′,6′-Bis(*p*-methoxyphenyl)-2′-methyl-(*E*)-3,4-dihydro-2-(4′*H*,6′*H*-pyrazolo[1′,5′-*c*]oxazol-4′-ylidene)-1-(2*H*)-naphthalenone (28g) was obtained (0.64 g, 45%) as a colorless oil. Crystallization from diethyl ether afforded a white solid: mp 59–60 °C; ^1H NMR δ 2.40 (s, 3 H, C2′-CH_3), 2.91 (br t, 2 H, CH_2), 3.06 (br t, 2 H, CH_2), 3.70 (s, 6 H, OCH_3), 6.83–8.12 (m, 13 H, Ar and C3′H); ^{13}C NMR δ 151.0 (C2′), 105.1 (C3′), 142.4 (C3′a), 154.8 (C4′), 99.1 (C6′), 108.7 (C2), 185.6 (C1), 13.9 (C2′-CH_3), 28.1, 23.7 (CH_2CH_2), 54.6 (CH_3O); precise mass calcd for $C_{30}H_{26}N_2O$ 478.189, found 478.190.

(b) 6′,6′-Bis(*p*-methoxyphenyl)-2′-methyl-3,4-dihydrospiro(naphthalene-2(1*H*),5′(6′*H*)-(4′*H*)pyrrolo[1′,2′-*b*]pyrazole)-1,4′-dione (29g) was obtained (0.61 g, 43%) as a colorless oil: IR ($CHCl_3$) 1738, 1691 cm^{-1}; ^1H NMR δ 2.32 (s, 3 H, C2′-CH_3), 2.28–2.72 (m, 4 H, CH_2CH_2), 3.68 (br s, 6 H, OCH_3), 6.75–8.23 (m, 13 H, Ar and C3′H); ^{13}C NMR δ 155.5 (C2′); 100.8 (C3′); 142.7 (C3′a); 193.2, 189.5 (C1,C4′); 78.4, 73.9 (C5′, C6′); 14.0 (C2′-CH_3); 29.0, 25.4 (CH_2CH_2); 54.6 (CH_3O); precise mass calcd for $C_{30}H_{26}N_2O$ 478.189, found 478.190.

Acknowledgment. The generous support of the National Institute of General Medical Science (Grant No. GM 27620) is gratefully acknowledged. We thank the mass spectroscopy lab of the Univerisity of Delaware for the mass spectral data. Purchase of the Bruker WM 250 was supported, in part, by a grant (GM 27616) from the National Institutes of Health.

Supplementary Material Available: Tables of ^1H and ^{13}C NMR data for azines **21** (Tables V and VI), azines **26** (Tables VII and VIII), pyrazoles **20** (Tables IX and X), and pyrazoles **27** (Tables XI and XII); mass spectral data for azines **21** and **26** (Table XIII) and pyrazoles **20** and **27** (Table XIV); tables for the atomic coordinates, bond distances, bond angles, anisotropic temperature coefficients, and hydrogen atom coordinates for compounds **21d**, **27e**, and **28e** (25 pages). Ordering information is given on any current masthead page. The structure factor tables for **21d**, **27e**, and **28e** may be obtained directly from the authors and are not included in the microfilm edition.