2950 (s), 2880 (s), 2230 (m), 1720 (s), 1575 (s), 1460 (m) cm^{-1}; MS, m/z 267 (EI), 268 (CI); MS, exact mass calcd for $C_{15}H_{25}NO_3$ 267.1834, found 267.1819.

1,1-Dimethylethyl 2-Cyano-3-[(1,1-dimethylethyl)oxy]-oct-2-enoate (18d). Into a refluxing solution of 100 mL of dry *tert*-butyl alcohol was added dropwise a solution of 0.20 g (0.57 mmol) of 2,5-diazido-3,6-di-1-hexynyl-2,5-cyclohexadien-1,4-dione (**2a**) in 40 mL of toluene under an atmosphere of argon for 30 min. After refluxing for 4 h, the dark red solution turned clear yellow. The reaction was then concentrated and the dark oily residue absorbed onto silica gel and subjected to flash chromatography (hexane/ethyl acetate) to give 0.11 g (31%) of a yellowish oil: ^1H NMR δ 2.54–2.60 (m, 2 H), 1.66–1.72 (m, 2 H), 1.55 (s, 18 H), 1.33–1.39 (m, 4 H), 0.88–0.93 (m, 3 H); IR ($CHCl_3$) 2999 (s), 2980 (s), 2950 (s), 2880 (s), 2230 (m), 1725 (s), 1580 (s), 1470 (m) cm^{-1}; MS, m/z 295 (EI), 296 (CI).

High-resolution mass spectrometry did not show the molecular ion. Fragmentation gave a peak at 224 which corresponds to M − 71 or loss of C_5H_{11}: exact mass calcd for this fragment ($C_{12}H_{18}O_3N$) 224.1286, found 224.1257.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health (CA-11890, AI-15651) for financial support of this work.

Reactions of Azines. 9. Preparation of 4,5-Dihydropyrazolo[1,5-*a*]pyridines, 6,7-Dihydropyrazolo[1,5-*a*]pyridines, and Pyrazolo[1,5-*a*]pyridines

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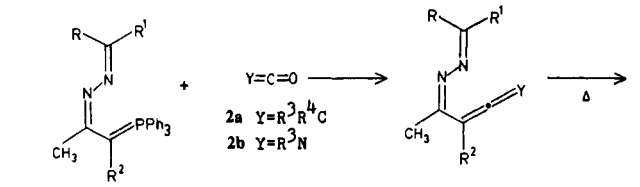
The reactions of (3,4-diaza-2,4,6-heptatrienylidene)triphenylphosphoranes **12** with ketenes **15** provide a general route to 4,5-dihydropyrazolo[1,5-*a*]pyridines **18** via the thermal rearrangements of the allenylazine **16** intermediates. When one of the substituents on the ketene is acetoxy, or phenoxy, elimination may occur to form the corresponding fully aromatized pyrazolo[1,5-*a*]pyridines **19**. When [2-[(diphenylmethylene)hydrazono]propylidene]triphenylphosphorane (**1b**) was allowed to react with vinylketenes **21** the 6,7-dihydropyrazolo[1,5-*a*]pyridines **24** were formed.

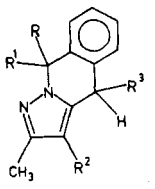
Introduction

We have previously reported[1-4] that cumulated azines **3** proved to be versatile synthons for a large variety of fused pyrazolo-substituted species. To date we have prepared all of the azines **3** by allowing the appropriate azine phosphoranes **1** to react with ketenes **2a** or isocyanates **2b**. Preparation of 4,5-dihydropyrazolo[1,5-*b*]isoquinolines **4**,[1-3] pyrazolo[5,1-*c*]-1,4-oxazines **5**,[1,2] 4,9-dihydropyrazolo[5,1-*b*]quinazolines **6**,[4] and 2,3-dihydro-1*H*-imidazo[1,2-*b*]-pyrazol-2-ones **7**[4] have been reported.



1a R=PhCO; R^1=Ph; R^2=H, alkyl
1b R=Ph; R^1=Ph; R^2=H
1c R=CH_3; R^1=Ph; R^2=H

3



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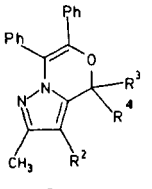

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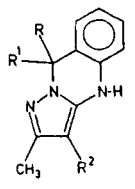

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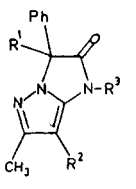
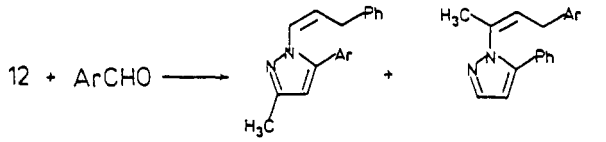


7

Continuing our interest in the reactions of conjugated azines to prepare fused pyrazolo ring systems, we chose to explore the reactions of allenylazine species that could be used to prepare 4,5- and 6,7-dihydropyrazolo[1,5-*a*]-pyridines.

It has been shown[5] that (2-methyl-7-phenyl-3,4-diaza-2,4,6-heptatrienylidene)triphenylphosphorane (**12a**) and (2,7-diphenyl-3,4-diaza-2,4,6-heptatrienylidene)triphenylphosphorane (**12b**) may be prepared readily by allowing (2-propynyl)triphenylphosphonium bromide (**8**) or (phenylethynyl)triphenylphosphonium bromide (**9**) to react initially with an equivalent amount of hydrazine followed by the addition of cinnamaldehyde (Scheme I). Treatment of salt **11** with ethanolic sodium ethoxide gave the corresponding ylides **12**. When the ylides **12a,b** were



13 **14**

allowed to react with aldehydes, pyrazoles **13** and **14** were formed.[5] The known[6] reactions of phosphonium ylides with ketenes to form allenes suggested a route to the 4,5-dihydropyrazolo[1,5-*a*]pyridines outlined in Scheme II.

We envisioned that the pathway to the pyrazolo[1,5-*a*]pyridines with the 6,7-dihydro orientation could arise from the reaction of vinylketenes **21** with ylide **1b** (Scheme III).

† For X-ray analysis.

(1) Schweizer, E. E.; Evans, S. *J. Org. Chem.* **1978**, *43*, 4328.
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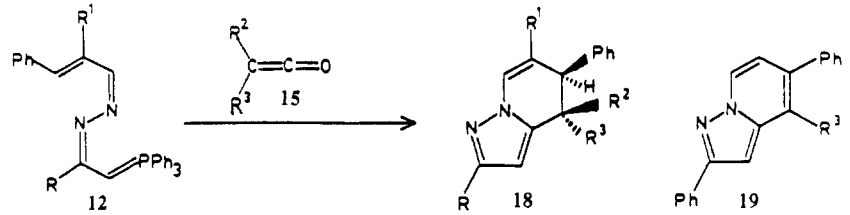
(6) Wittig, G.; Haag, A. *Chem. Ber.* **1963**, *96*, 1535. Harket, Z.; Barker, W. D. *Synthesis* **1970**, *1*, 543.

0022-3263/87/1952-1319$01.50/0

Table I. Reactions of Phosphoranes 12 with Ketenes 15. Isolated Yields and Melting Points for Preparation of 4,5-Dihydropyrazolo[1,5-*a*]pyridines 18 and Pyrazolo[1,5-*a*]pyridines 19



compd	R	R^1	R^2	R^3	yield (%)	mp (°C)	method[a]
18a	Ph	H	Ph	Ph	75	212–213[b]	A
18b	CH_3	H	Ph	Ph	51	165–166[c]	A
18c	Ph	CH_3	Ph	Ph	62	228–229[d]	B
18d	Ph	H	H	H	36	113–114[c]	C
18e	CH_3	H	H	H	32	*e*	C
18f	Ph	CH_3	H	H	45	127–128[d]	C
18g	CH_3	H	CH_3CH_2	H[f]	51	*e*	A
18h	CH_3	H	$PhCH_2$	H[f]	57	*e*	A
18i	Ph	H	OPh	CH_3	68	184–185[d]	B
19a	Ph	H		Ph	72	195–196[d]	B
19b	Ph	H		H	61	174–175[b]	B

[a] See Experimental Section. Compounds were recrystallized from [b] ethyl acetate, [c] methanol, and [d] ethanol. [e] Isolated as oils. [f] Compounds **18g** and **18h** were isolated as a mixture of diastereomers.

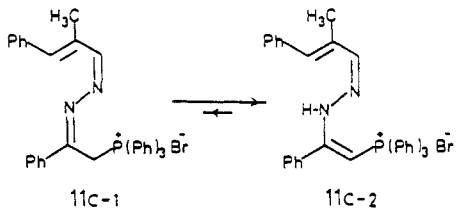


Figure 1.

Results and Discussion

A. Preparation of 4,5-Dihydropyrazolo[1,5-*a*]pyridines 18 and Pyrazolo[1,5-*a*]pyridines 19. The phosphonium salts **11a** and **11b** were prepared by a previously reported procedure.[5] The phosphonium salt **11c** was prepared in 86% yield by a similar method by substituting α-methylcinnamaldehyde (**10**, $R^1 = CH_3$) for cinnamaldehyde (Scheme I). Phosphonium salt **11c** existed in two tautomeric forms **11c-1** and **11c-2** (Figure 1) in contrast to the phosphonium salts **11a** and **11b**, which only exist in the vinylamine form. The ^{31}P NMR clearly showed[7] that the predominant form of **11c** is the N-substituted vinylamine phosphonium species **11c-2** (85%). Treatment of the phosphonium salts with ethanolic sodium ethoxide yielded the phosphoranes **12a–c**.

The ketenes **15** used were generated in situ either by allowing the appropriate acid chlorides to react with triethylamine or by the pyrolysis of acetone ($R^2 = R^3 = H$).[8] The intermediate allenylazines **16** were too unstable to isolate so the thermolyses were carried out directly by briefly heating the crude reaction mixtures. Products were isolated by column chromatography.

The products from the reactions of phosphoranes **12a–c** with simple ketenes **15** (in CR^2R^3, the R = alkyl, aryl) were identified (on the basis of spectral data) as 4,5-dihydropyrazolo[1,5-*a*]pyridines **18** (Scheme II, Table I). In the reactions with monoethylketene and monobenzylketene the products **18g** and **18h** were a mixture of diastereomers and were separated by gas chromatography.

(7) It has been shown previously that N-substituted vinylphosphonium salts absorb in the ^{31}P range 12.9–18.8 ppm and imine methyl phosphonium salts appear in the ^{31}P range 19.1–22.5 ppm. Schweizer, E. E.; Devoe-Goff, S.; Murray, W. P. *J. Org. Chem.* **1977**, *42*, 200.
(8) Williams, J. W.; Hurd, C. D. *J. Org. Chem.* **1940**, *5*, 122.

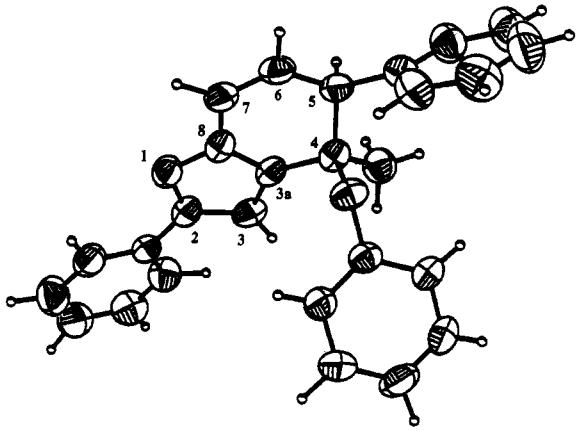


Figure 2. ORTEP perspective drawing of *cis*-2,5-diphenyl-4-methyl-4-phenoxy-4,5-dihydropyrazolo[1,5-*a*]pyridine (**18i**).

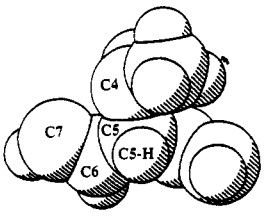
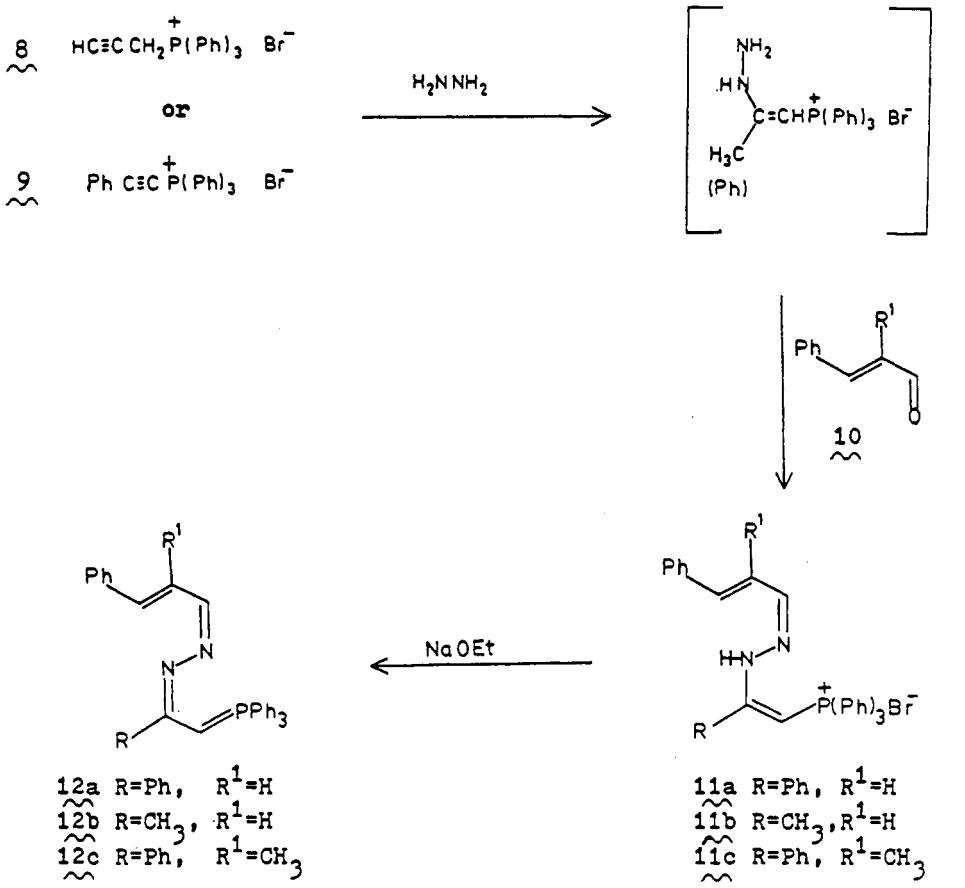


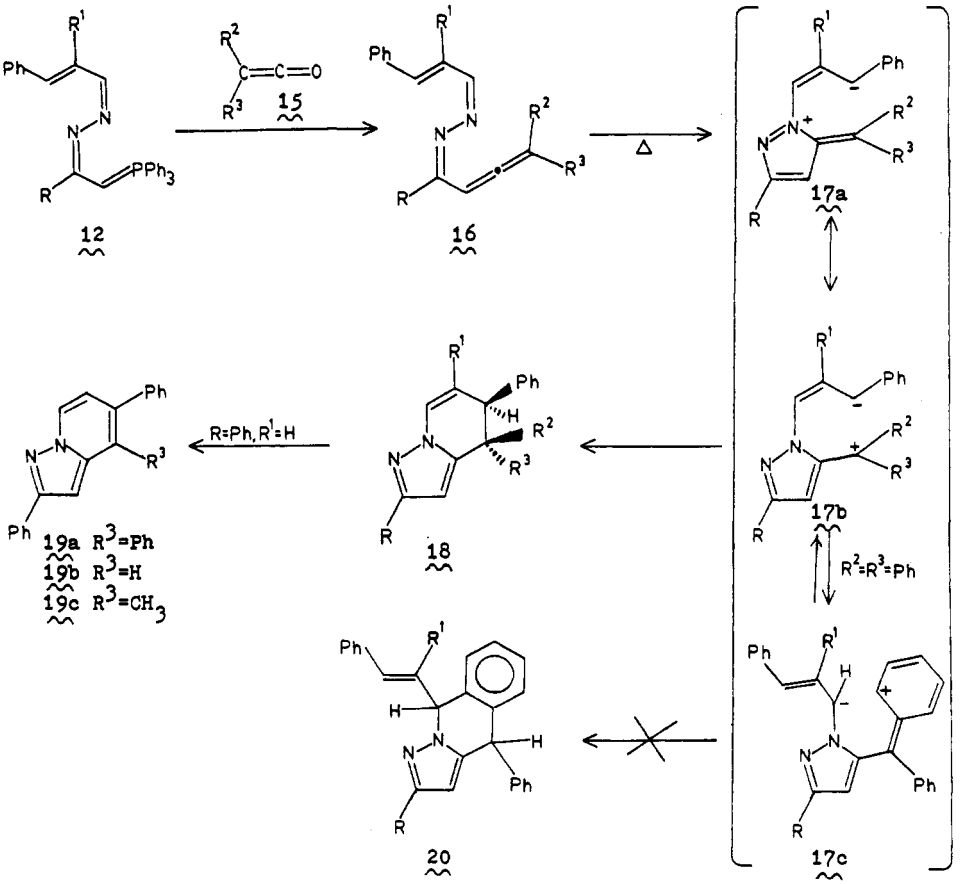
Figure 3. Space-filling diagram of C-5 region of *cis*-2,5-diphenyl-4-methyl-4-phenoxy-4,5-dihydropyrazolo[1,5-*a*]pyridine (**18i**).

In the reaction of phosphorane **12a** with phenylacetoxyketene (**15**, R^2 = OAc, R^3 = Ph) or monophenoxyketene (**15**, R^2 = OPh, R^3 = H), the presumed 4,5-dihydropyrazolo[1,5-*a*]pyridine **18** intermediates spontaneously eliminated acetic acid or phenol producing pyrazolo[1,5-*a*]pyridines **19a** and **19b** in 72% and 61% yields, respectively. However, in the reaction of phosphorane **12a** with methylphenoxyketene (**15**, R^2 = OPh, $R^3 = CH_3$) elimination of phenol did not occur and the 4,5-dihydropyrazolo[1,5-*a*]pyridine (**18i**) was isolated in 68% yield. Treatment of isolated **18i** with triethylamine did not cause elimination of phenol. This suggested that the phenoxy and the C-5 hydrogen were not transperiplanar and thus would not readily allign for elimination. An X-ray analysis of the crystal showed the phenoxy and the C-5 hydrogen

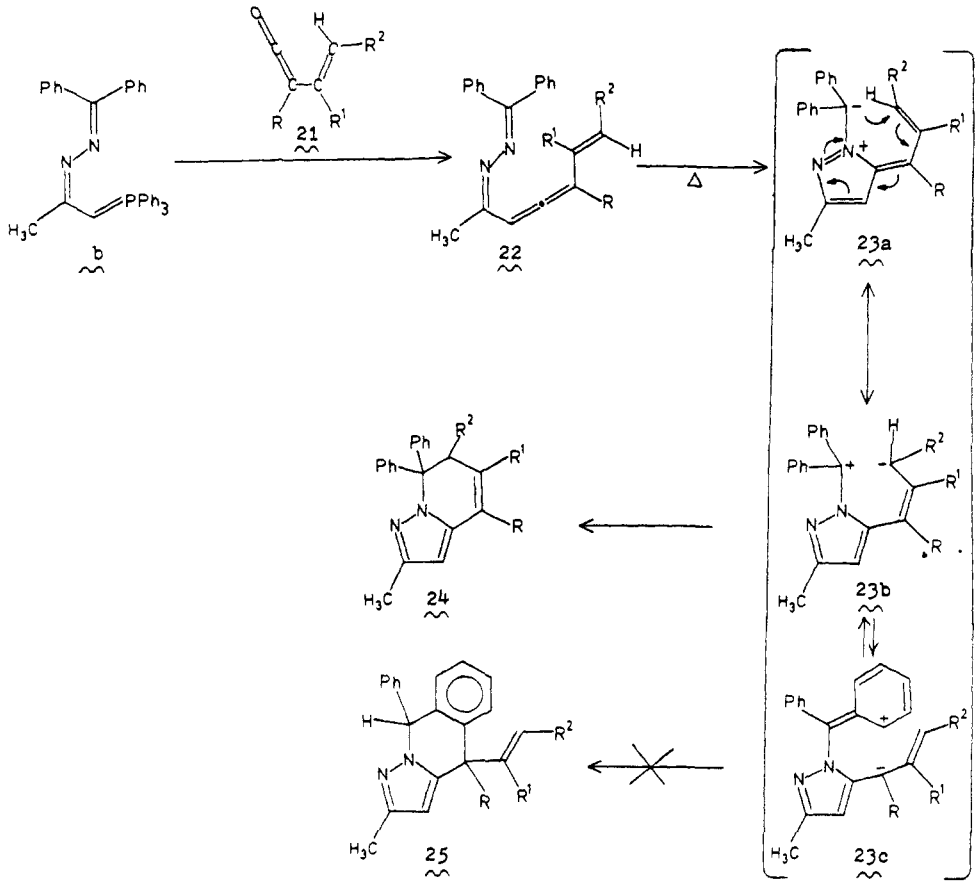
Scheme I



Scheme II



Scheme III



almost perfectly alligned for transperiplanar elimination (dihedral angle of 168.2°, see Figure 2). The X-ray data also showed steric crowding around the C-5 hydrogen by the C-4 methyl hydrogens and one of the ortho hydrogens on the C-5 phenyl (Figure 3). When C-4 was substituted with a phenoxy and a hydrogen [instead of methyl] elimination of phenol occurred spontaneously. These results suggest that steric hindrance inhibits the removal of the C-5 proton in compound **18i**. When **18i** was heated with a catalytic amount of *p*-toluenesulfonic acid, elimination of phenol took place to form the pyrazolo[1,5-*a*]pyridine **19c**.

The products isolated from the reactions of phosphoranes **12a–c** with ketenes are consistent with the intermediacy of resonance-delocalized zwitterions **17** which are analogous to intermediates implicated or isolated in a number of other azine cycloaddition reactions. This suggests that the 4,5-dihydropyrazolo[1,5-*a*]pyridines **18** are produced from the allenylazines **16** via ring closure from the zwitterionic intermediates **17b**.

We have recognized since the inception of this series that a number of the products which have been described in the introduction may occur via intramolecular concerted cycloaddition reaction pathways. In the present series the formation of **18** (or **24**) [We thank the referees for pointing out our consistent omission of any mention of these possibilities.] directly from **16** (or 22) would obviate the necessity of invoking the zwitterionic intermediate **17** (or **23**). We have, however, consistently invoked the intermediacy of charge-separated resonance forms, similar to **17**, or **23**, because they can be used to explain *all* of the products found. Bimodal reaction pathways from a single cumulated azine are being explored.

Ring closures to produce pyrazoloisoquinolines (such as **20**) have been previously observed (see **4**) in the reaction of phosphorane **1a** with diphenylketene.[1,3] However, reactions of phosphoranes **12a–c** with diphenylketene yielded only the corresponding 4,5-dihydropyrazolo[1,5-*a*]pyridines **18a–c**. The pyrazolo[1,5-*b*]isoquinolines **20** that would be produced by ring closure and a 1,3-hydride shift from the zwitterionic species **17c** were not observed [by TLC or ^{13}C NMR].

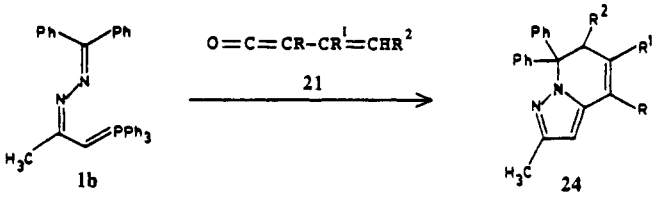
B. Preparation of 6,7-Dihydropyrazolo[1,5-*a*]pyridines 24. The phosphorane **1b** was prepared by a previously reported method.[3] The various vinylketenes **21** used were generated in situ by allowing the appropriate α,β-unsaturated acid chlorides to react with triethylamine. The intermediate allenylazines **22** were too unstable to isolate and the thermolyses were carried out directly by briefly heating the crude reaction mixtures. Products were isolated by column chromatography and identified on the basis of spectral data as the 6,7-dihydropyrazolo[1,5-*a*]pyridines **24** (Table II). No attempts at optimization were made; however the yields were good.

The products isolated are consistent with the intermediacy of the resonance-delocalized zwitterions **23**. The 6,7-dihydropyrazolo[1,5-*a*]pyridines **24** may be produced by ring closure from zwitterionic intermediates **23b**.

Another possible reaction path is ring closure and a 1,3-hydride shift from species **23c** to produce the pyrazolo[1,5-*b*]isoquinolines **25**. Ring closure in this direction was the major pathway observed for the azines produced from the reactions of phosphorane **1b** with simple ketenes.[3] However, pyrazoles **25** were not observed (by TLC or ^{13}C NMR) in the reaction of phosphorane **1b** with vinylketenes.

Thus it has been demonstrated that pyrazolo[1,5-*a*]pyridines **19**, 4,5-dihydropyrazolo[1,5-*a*]pyridines **18**, and 6,7-dihydropyrazolo[1,5-*a*]pyridines **24** may be produced in good yields from the corresponding allenylazines. These

Table II. Reactions of Phosphorane 1b with Vinylketenes 21. Isolated Yields and Melting Points for Preparation of 6,7-Dihydropyrazolo[1,5-*a*]pyridines 24



compd	R	R^1	R^2	yield (%)	mp (°C)[a]	method[b]
24a	H	H	H	69	128–129	B
24b	CH_3	H	H	82	143–144	B
24c	H	CH_3	H	73	125–126	B
24d	H	H	CH_2CH_3	56	*c*	B

[a] Recrystallized from ethanol. [b] See Experimental Section. [c] Compound **24d** was isolated as an oil.

two methods offer the advantage of producing pyrazolo[1,5-*a*]pyridines in which the pyridine ring is not fully aromatized. Most syntheses of pyrazolo[1,5-*a*]pyridines are based on the reactions of *N*-imino pyridinium ylides with electrophiles and thus the pyridine ring of the products is fully aromatic.[9]

Further utility of cumulated azines as synthons for fused pyrazoles will be demonstrated in forthcoming papers.

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), quartet (q), multiplet (m). The numbering scheme for the pyrazolo[1,5-*a*]pyridines is as shown in Figure 2.

Tables III, IV, and V (available as supplementary material) list the ^1H NMR parameters for compounds **18**, **19**, and **24**. The ranges of the ^1H parameters for the 4,5-dihydropyrazolo[1,5-*a*]-pyridines **18** were as follows: δ 2.23–2.30 (C2-CH_3), 5.61–6.67 (C3-H), 2.85–3.71 (C4-H), 3.39–4.29 (C5-H), 5.25–5.89 (C6-H). The ranges of the ^1H parameters for the 6,7-dihydropyrazolo[1,5-*a*]-pyridines **24** were as follows: δ 2.19–2.24 (C2-CH_3), 5.97–6.03 (C3-H), 5.83–6.29 (C4-H), 5.64–5.87 (C5-H), 3.05–3.28 (C6-H).

Tables VI, VII, and VIII (supplementary material) list the ^{13}C NMR parameters for compounds **18**, **19**, and **24**. The ranges of the ^{13}C parameters for the 4,5-dihydropyrazolo[1,5-*a*]pyridines **18** were as follows: 153.7–148.5 (C2), 107.3–101.5 (C3), 143.8–140.9 (C3a), 76.5–29.4 (C4), 55.2–38.1 (C5), 122.3–111.8 (C6) ppm. Peaks at 154.2–154.0 (C2) and 94.9–94.2 (C3) ppm characterize the pyrazole backbone of the pyrazolo[1,5-*a*]pyridines **19**. A pyrazole ring was indicated for the 6,7-dihydropyrazolo[1,5-*a*]pyridines **24** by peaks at 147.5–147.8 (C2), 102.1–103.7 (C3), and 140.1–142.9 (C3a) ppm in the ^{13}C NMR spectrum. In addition there were resonances at 113.5–134.1 (C4, C5), 40.2–47.8 (C6), and 69.6–73.5 (C7) ppm for the dihydropyridine ring and 12.4–13.8 ppm for (C2-CH_3).

Precise mass spectra were recorded by using a Du Pont 21-492 B instrument with a resolution of 3300 or 5000. Table IX (supplementary material) lists the mass spectral data. 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.

Acetonitrile, dried previously over calcium hydride, was distilled over P_2O_5. Toluene and triethylamine were dried and distilled from sodium metal. Eastman Chromatogram (silica gel with a fluorescent indicator on polyethylene) precoated sheets were employed in thin-layer chromatographic (TLC) operations. Baker silica gel (60–200 mesh) and EM7747 silica gel for column chromatography were used throughout for product separation.[10] A Varian Aerograph Model 90-P gas chromatograph with a column (10 ft × 0.25 in.) packed with 10% GDSF-96 silicone fire brick and equipped with a thermal-conductivity detector was used to separate the isomeric pyrazoles **18g** and **18h**.

The following compounds were prepared by known methods: 1-(2-methyl-7-phenyl-3,4-diaza-2,4,6-heptatrienyl)triphenylphosphorane (**12a**),[5] 1-(2,7-diphenyl-3,4-diaza-2,4,6-heptatrienyl)triphenylphosphorane (**12b**),[5] [2-((diphenylmethylene)-hydrazono)propylidene]triphenylphosphorane (**1b**),[3] and (phenylethynyl)triphenylphosphonium bromide.[11] α-Phenoxypropionyl chloride, 3,3-dimethylacryloyl chloride, tiglyl chloride, and 2-hexenoyl chloride were prepared from the corresponding acids with thionyl chloride. Diphenylacetyl chloride β-phenylpropionyl cloride, butyryl chloride, O-acetylmandelyl chloride, and phenoxyacetyl chloride were purchased from the Aldrich Chemical Company. All of these acyl chlorides were purified by distillation prior to use. Hydrazine (95%) was purchased from Eastman Kodak and used as received.

(2,7-Diphenyl-6-methyl-3,4-diaza-1,4,6-heptatrien-1-yl)-triphenylphosphonium Bromide (11c). Hydrazine (1.0 g, 0.03 mol) was added with stirring to a solution of (phenylethynyl)-triphenylphosphonium bromide (**9**) (12.95 g, 0.03 mol) in acetonitrile (60 mL) and stirring was continued at room temperature for 1 h. α-Methylcinnamaldehyde (8.76 g, 0.06 mol) was added and stirring was continued at room temperature for an additional 16 h. A yellow compound precipitated, the mixture was filtered, and the residue was washed with acetonitrile (10 mL). The residue was dissolved in a minimum amount of methylene chloride and the solution was filtered. The filtrate was added dropwise with stirring to anhydrous ether (600 mL), which on filtration gave 15.6 g (86%) of the pure salt **11c**: one spot by TLC; mp 169–170 °C; ^1H NMR for **11c-1** δ 0.75 (s, 3 H, MeC=N), 6.29 (d, J_{PH} = 12.4, 1 H, $CH_2P(Ph)_3$); for **11c-2** δ 0.75 (s, 3 H, MeC=N), 3.93 (d, J_{PH} = 16.1, 1 H, =CHP(Ph)$_3$) 6.55 (s, 1 H, PhCH=), 7.04–8.02 (m, 25 H, Ar), 8.95 (s, 1 H, HC=N), 12.12 (s, 1 H, NH); ^{13}C NMR for **11c-1** 15.6 (s, MeC=N) 38.4 (d, J_{CP} = 61.8, $CH_2P(Ph)_3$), 117.9 ppm (d, J_{CP} = 86.4, C ipso); for **11c-2** 12.2 (s, MeCN), 58.5 (d, J_{CP} = 111.5, =CHP(Ph)$_3$), 118.0 (d, J_{CP} = 86.5, C ipso P(Ph)$_3$), 129.4 (d, J_{CP} = 12.4, C meta P(Ph)$_3$), 133.3 (d, J_{CP} 11.3, C ortho P(Ph)$_3$), 133.4 (s, C para P(Ph)$_3$), 136.4 (s, C6), 156.4 (s, C7), 161.6 (s, C5) ppm; ^{31}P NMR for **11c-1** 20.8 ppm (15%), for **11c-2** 16.7 and 15.4 ppm (85%). Anal. Calcd for $C_{36}H_{32}BrN_2P$: C, 71.64; H, 5.35. Found: C, 71.40; H, 5.42.

(2,7-Diphenyl-6-methyl-3,4-diaza-2,4,6-heptatrienylidene)triphenylphosphorane (12c). The salt **11c** (8.12 g, 15

(9) For recent reviews of the synthesis of pyrazolo[1,5-*a*]pyridines, see: Hardy, C. P. *Adv. Heterocycl. Chem.* **1984**, *36*, 343. Tamura, Y.; Ikeda, M. *Adv. Heterocycl. Chem.* **1981**, *29*, 71. Uchida, T.; Matsumoto, K. *Synthesis* **1976**, 209.

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

(11) Dickstein, J. I.; Miller, S. I. *J. Org. Chem.* **1972**, *37*, 2168.

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).

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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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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.

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

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