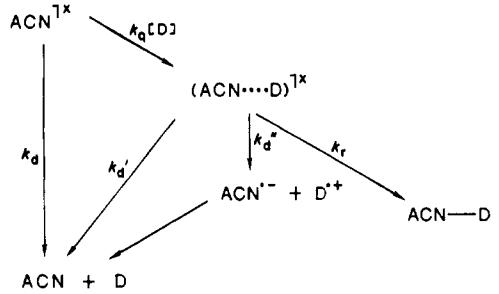
Scheme I



Photochemical Reactions. A solution of 9-anthracenecarbonitrile (ACN, 200 mg) and naphthalene (2 g) in 300 mL acetonitrile was deaerated by boiling and cooling while flushing with argon and irradiated at 17 °C by means of a high-pressure mercury arc (Philips HPK 125 W) through Pyrex for 30 min. Evaporation of the solvent and chromatography on a silica gel column, eluting with cyclohexane–ethyl acetate mixture yielded 10 mg of unreacted ACN, 63 mg (33%) of 9-anthracenecarbonitrile homodimer (**1**), and 118 mg (38%) of 9-cyano-9,10,11,14-tetrahydro-9,10-[1,4]naphthalenoanthracene (**2**), colorless crystals from hexane, which decomposes on rapid heating at ca. 135 °C: NMR δ 3.35 (11-H, ddd), 3.95 (10-H, d), 4.2 (14-H, dd), 5.75 m (12-H, 13-H) [J_{11-12} = 11 Hz, J_{12-14} = 2 Hz, J_{13-14} = 6 Hz); IR 2235 cm^{-1}. Crystals of this compound become visibly yellow after several days, and the presence of ACN and napthalene can then be detected. The other photoreactions were carried out as reported in Table I. New photoproducts are the following. 9-Cyano-12-methyl-9,10,11,14-tetrahydro-9,10-[1′,4′]naphthalenoanthracene (**3**), colorless crystals from hexane (decomposes on rapid heating at ca. 130 °C): NMR δ 3.2 (11-H, d), 3.9 (10-H, d), 4.15 (14-H, d), 5.35 (13-H, d) [J_{10-11} = 10.5 Hz, J_{13-14} = 7.5 Hz]; IR 2235 cm^{-1}. 9-Cyano-9,10,11,16-tetrahydro-9,10-[9′,10′]anthracenoanthracene (**4**), colorless crystals from cyclohexane: mp 154–155 °C on rapid heating (with decomposition); NMR δ 4.05 (10-H, 11-H, s), 4.9 (16-H, s); IR 2239 cm^{-1}.

Fluorescence Quenching. Fluorescence measurements were carried out on solutions degassed by five freeze–degas–thaw cycles by means of an Aminco Bowman MPF spectrophotofluorimeter linear Stern–Volmer plots were obtained in every case.

Reaction Quantum Yield. Reaction quantum yield was measured at 366 nm on ACN solutions (2 × 10^{-4} M) degassed by five freeze–degas–thaw cycles on a optical bench fitted with a super-high-pressure mercury arc (Osram 200 W/2). Light was collimated by means of quartz lenses and monochromatized by means of an interference filter. Light flux (10^{-7} einstein min^{-1} cm^{-2}) was measured by ferrioxalate actinometry.

Acknowledgment. This work was supported by CNR, Progetto Finalizzato Chimica Fine e Secondaria.

Registry No. 1, 33998-38-8; 2, 105598-00-3; 3, 105597-98-6; 4, 105597-99-7; 9-anthracenecarbonitrile, 1210-12-4; naphthalene, 91-20-3; 2-methylnaphthalene, 91-57-6; anthracene, 120-12-7; 1-methylnaphthalene, 90-12-0; 2-cyanonaphthalene, 613-46-7; 2-methoxynaphthalene, 93-04-9.

Synthesis and Reactivity of New Pentacoordinated Phosphoenolpyruvate Derivatives

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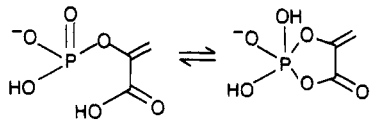
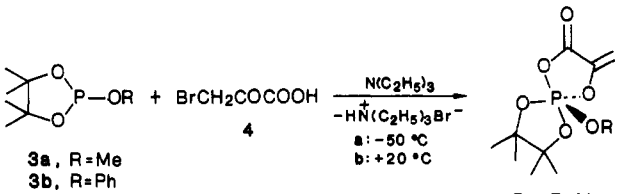
Pentaoxyphosphoranes are thought to be closely related intermediates to the biologically important phosphate ester reactions.[1,2] Thus, the hydrolysis of phosphoenolpyruvate **1**, a strong phosphorylating agent,[3,4] proceeds most probably via the formation of the cyclic acyloxyphosphorane[5] **2** (eq 1).



(1)

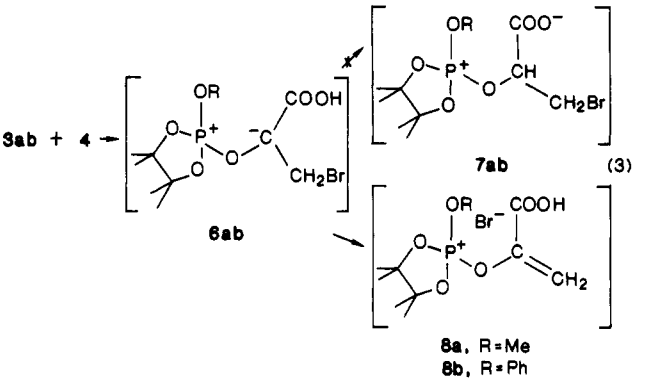
To our knowledge, structures of type **2** have not yet been isolated. So, it becomes important to prepare well-defined species having a structure as close as possible of the structure of **2**.

The synthesis (eq 2) involves the first step of a Perkow reaction followed by a ring closure. Since no reaction



(2)

occurs at room temperature between **3a** or **3b** and an equivalent amount of triethylammonium bromopyruvate, the first step is probably the attack of the phosphite **3** on the acid **4**. This step proceeds without any proton transfer, as observed with α-keto acids,[6] in the phosphonium oxyanions **6a** and **6b** (eq 3). Moreover, despite the elimi-



(3)

nation of Br$^-$, no Arbuzov reaction takes place in the case of **8a** (R = Me), although it is the major reaction with trimethyl phosphite.[3a] However, the presence of the dioxaphospholane ring in **3** facilitates the ring closure[6] of **8** to give the spirophosphoranes[7] **5**.

(1) Reviews on oxyphosphoranes: (a) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168. (b) Westheimer, F. H. *Ibid.* **1968**, *1*, 70. (c) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillepsie, P.; Ramirez, F. *Ibid.* **1971**, *4*, 288. (d) Hudson, R. F.; Brown, C *Ibid.* **1972**, *5*, 204. (e) Ramirez, F. *Synthesis*, **1974**, 90.

(2) For recent compilations with many references, see: (a) Mc Ewen, W. E., Berlin, K. D., Eds.; *Organophosphorus Stereochemistry*, Dowden, Hutchinson and Ross: Stroudsburg, PA, 1975; Vol. 1, 11. (b) Luckenbach, R. *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*; Thieme-Verlag Stuttgart, 1973.

(3) (a) Hirschbein B. L.; Mazenod, F P.; Whitesides, G. M. *J. Org. chem.* **1982**, *47*, 3765. (b) Wong, C. H.; Haynie, S. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 115.

(4) Kazlauskas, R. J.; Whitesides, G. M. *J. Org. Chem.* **1985**, *50*, 1069.

(5) (a) Clark, V. M.; Kirby A. J. *J. Am. Chem. Soc.* **1963**, *85*, 3705. (b) Benkovic, S J.; Schray, K. J. *Ibid.* **1969**, 91, 5653. (c) Ramirez, F.; Glaser, S. L.; Stern, P.; Ugi, I.; Lemmen, P. *Tetrahedron* **1973**, *29*, 3741. (d) Smith, G. D.; Caughlan, C. N.; Ramirez, F.; Glaser, S.; Stern, P. *J. Am. Chem. Soc.* **1974**, *96*, 2698. (e) Ramirez, F.; Stern, P.; Glaser, S.; Ugi, I.; Lemmen, P. *Phosphorus*, **1973**, *3*, 165.

(6) (a) Saegusa, T.; Kobayashi, S. *J. Macromol. Sci. Chem.* **1979**, *A13*, 295. (b) Saegusa, T.; Kobayashi, S.; Kimura, Y.; Yokoyama, T. *J. Org. Chem.* **1977**, *42*, 2797; *J. Am. Chem. Soc.* **1976**, *98*, 7843.

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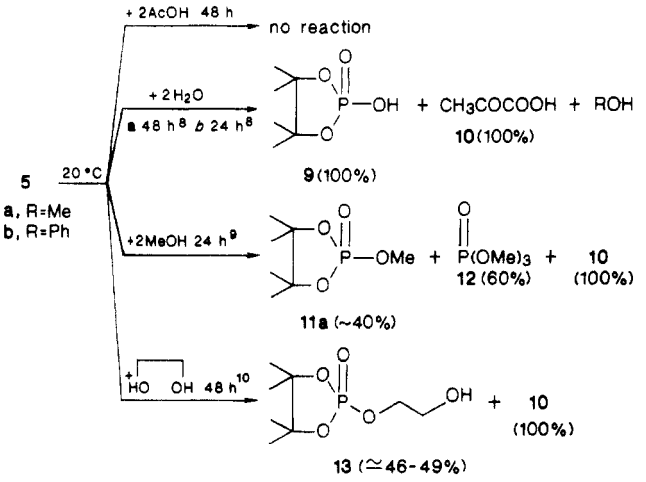
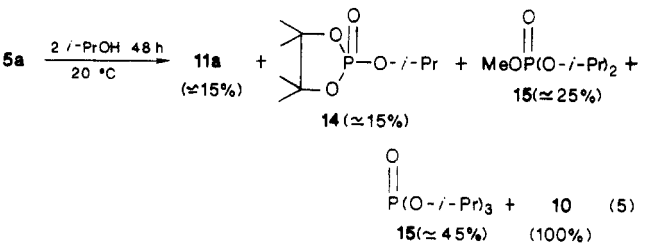
The reactivity of **5a** and **5b** is studied at 20 °C. With glacial acetic acid, no reaction occurs, but with water or alcohols **5a** and **5b** disappear within 24 to 48 h. Two equivalents of the protic reagent are required for a complete transformation of **5a** and **5b**. The results of the NMR study are the following (eq 4 and 5).



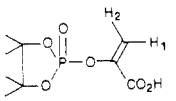
(4)



(5)

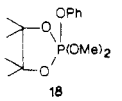
(7) With $C_6H_4\overline{OP(OMe)O}$, in the same conditions as for **3b**, no evolution is observed with **4**, even after 8 days at 20 °C, due to the lower nucleophilic character of the phosphorus atom.

(8) The hydrolysis (1 H_2O, 2 h) shows the formation of the intermediate phosphates **11a** or **11b** and **17** observed together with **9**, **10**, and **5a**



or **5b**. All these compounds, except **9** and **10**, disappear with a second equivalent of H_2O. **17** $\delta^{31}P$ = 7.3 (s); ^1H NMR ($CDCl_3$, 100 MHz) 9.80 (s, OH), 6.06 (dd, $J \lesssim 4$ Hz, H_1), 5.70 (dd, id, H_2), 1.47 (s) and 1.43 (s) Me of dioxaphospholane.

(9) Methanolysis of **5b** yields first **5a** + PhOH; with 1 MeOH (24 h), ≃41% of **5a** is detected beside **11a** (≃27%) and **12** (≃32%); in the case of **5a** and beside **11a** (~16%), **12** (≃26%), **18** (≃10%; $\delta^{31}P$ = −42.0, hept, $^3J_{PH}$ = 14.0 Hz), **19** (≃8%, $\delta^{31}P$ = −41, 3, d, $^1J_{PH}$ = 700 Hz) in the case of **5b**.



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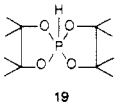

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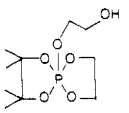
(10) With **5a**, after 2 h, there is 20% of **20** ($\delta^{31}P$ = −35.8 hept, $^3J_{PH}$ =

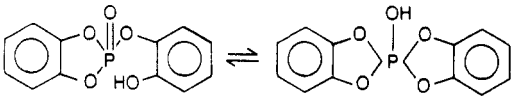


20

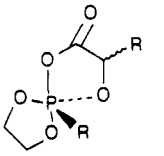
9.2 Hz), ≃10% of **11a** and ≃70% of **5a**. With **5a**, after 48 h, **11a** (≃34%) and an unidentified product (≃20%) at $\delta^{31}P$ = +12.4 are also observed. With 5b (48 h), the unidentified product still appears (≃25%).

(11) Ramirez, F.; Nowakowski, M.; Marecek, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4515.

The results show that **5a** and **5b** are phosphorylating agents, since R'OH (R' = H, Me, *i*-Pr, $HOCH_2CH_2$) selectively attack the phosphorus atom. No ester resulting from an attack of R'OH on the carbonyl group of the phosphoacyl chain is detected. Finally, this study provides additional data in favor of the existence of **2**, and thus, is related to the results obtained by Ramirez and Coll[11] and further by Saegusa and Coll[6] who respectively reported the existence of the dynamic equilibrium between the two forms **20** ⇄ **21** and the synthesis of several (acyloxy)-phosphoranes **22**.



20 21



22
R = Ph, Me
R' = Ph, PhO

Experimental Section

Commercial bromopyruvic acid (Flucka) is dried by azeotropic distillation (toluene) and then recrystallized in dry $CHCl_3$. Crystals are dried 48 h at 20 °C (0.5 torr P_2O_5). Melting points were taken with a Büchi SMP-20 instrument. A JEOL MH100 and a Bruker WP250 instruments were used for the ^1H NMR measurements. Me_4Si was the internal reference. The ^{31}P and ^{13}C NMR spectra were recorded on a JEOL FX90Q instrument. For the ^{31}P NMR spectra, H_3PO_4 85% was introduced in the instrument as an electronic reference. For the ^{13}C NMR spectra, Me_4Si was used as an internal reference. IR spectra were recorded on a Perkin-Elmer 157G instrument.

Spirophosphoranes 5ab. Bromopyruvic acid (1.67 g, 10 mmol) in 5 mL of dry acetone is added under N_2 at −50 °C (**a**, R = Me) or +20 °C (**b**, R = Ph) to a solution of phosphite (1.78 g of **3a** or 2.40 g of **3b**, 10 mmol) and dry triethylamine (1.40 mL, 10 mmol) in 5 mL of dry acetone. The mixture is then allowed to stir 1 h at 20 °C. Triethylammonium bromide is filtered and the solution is evaporated at 20 °C under reduced pressure. The residue analyzed in ^{31}P NMR shows only one peak (yield 100%). **5a** is a white crystalline compound which can be recrystallized in ethyl acetate (yield 75%, mp = 114–5 °C). **5b** is a yellow oil.

5a: ^{31}P NMR ($CDCl_3$): δ −46.0 (ddq, 1.9, 2.4, and 14.0 Hz). For the two doublets, the weak coupling constants are approximative, due to the bad resolution of the apparatus. ^1H NMR (250 MHz) is more available. ^1H NMR ($CDCl_3$, 250 MHz): 3.78 (d, $^3J_{HP}$ = 14.3 Hz) P-OMe; 5.45 (dd, $^2J_{H1H2}$ = 2.4, $^4J_{H1P}$ = 3.6 Hz) *trans*-POCH=CH_1H_2; 5.12 (dd, $^2J_{H2H1}$ = 2.3, $^4J_{H2P}$ = 1.5 Hz) *cis*-POCH=CH_1H_2; 1.36 and 1.33 (2 s) Me of dioxaphospholane. IR film (cm^{-1}); 1750 s C=O of α,β unsaturated γ-lactone, 1665 C=C, 1380 s and 890 s C=CH_2, 1155 s and 1075 s POC and COC.

5b: ^{31}P NMR ($CDCl_3$): δ −50.2 s (wide); ^1H NMR ($CDCl_3$, 250 MHz): 7.50–6.83 (m, aromatic H), 5.48 (dd, $^2J_{H1H2}$ = 2.5 and $^4J_{H1P}$ = 3.6 Hz) H_1, 5.25 (dd, $^2J_{H2H1}$ = 2.5 and $^4J_{H2P}$ = 1.4 Hz) H_2, 1.52 (s), 1.44 (s), and 1.35 (s) Me of dioxaphospholane. IR film (cm^{-1}): 1758 s (C=O), 1588 m C=C; 1385 s and 895 s C=CH_2, 1210 s and 1140 s POC.

The hydrolysis of **5a** or **5b** is carried out in 2 mL of acetone with 2 mmol of the phosphorane and 4 mmol of H_2O. At the end of the reaction, the solvent is removed at 20 °C under reduced pressure and the oil is analyzed in ^{31}P NMR, ^1H NMR (100 MHz), and ^{13}C NMR in $CDCl_3$. The alcoholyses are carried out in $CDCl_3$ (2 mL) with 2 mmol of **5a** or **5b** and 4 mmol of R'OH.

^{31}P NMR (non decoupled spectrum): **9**, +13.1 (s); **11a**, +13.5 (q, $^3J_{PH}$ = 11.6); **11b**, +7.0 (s); **12**, +1.7 (dec. $^3J_{PH}$ = 11.6); **13**, +12.7 (t, $^3J_{PH}$ = 9.2); **14**, +11.2 (d, $^3J_{PH}$ = 6.7); **15**; −2.6 (tq, $^3J_{PH}$ = 6, 7, $^3J_{PH}$ = 11.6); **16**, −4.4 (q, $^3J_{PH}$ = 6.7).

Characteristic peaks in ^1H NMR: **10**, 2.46 (s); **9**, 1.44 (s), 11.84 (s, 2 OH belonging to **10** and **9**) in the case of **5a** or 9.42 (s, 3 OH belonging to **10**, **9** and PhOH) in the case of **5b**; **11a**, 3.87 (d, $^3J_{HP}$ = 12.0); **12**, 3.83 (d, $^3J_{HP}$ = 12.0)

Characteristic peaks in ^{13}C NMR: **9**, 89.6, 23.8, 23.6; **10**, 197.7, 161.9, 26.1; **11a**, 89.8; 55.5 (d, $^2J_{CP}$ = 6.0); **12**, 54.5 (d, $^2J_{CP}$ = 5.3).

Acknowledgment. We thank the C.N.R.S. for financial support (U.A. 473).

Substituent Effects on the ^{31}P, ^{15}N, and ^{13}C NMR Spectra of *N*-(Arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes and on the ^{15}N and ^{13}C NMR Spectra of the Corresponding Arenesulfonamides

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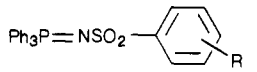
Received July 28, 1986

As part of our ongoing program in the synthesis and study of phospha-λ⁵-azenes,[2-5] we have examined, and report on, the ^{31}P, ^{15}N, and ^{13}C NMR spectra of a series of *N*-(arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes **1**.



RC6H4N=PPh3

1a, R = *p*-NO_2
b, R = *m*-NO_2
c, R = *p*-CN
d, R = *p*-CO_2CH_3
e, R = *p*-Br
f, R = *p*-Cl
g, R = *p*-F
h, R = H
i, R = *p*-CH_3
j, R = *p*-OCH_3
k, R = *p*-NH_2

2a, R = *p*-NO_2
b, R = *p*-CN
c, R = *m*-NO_2
d, R = *p*-CF_3
e, R = *p*-Cl
f, R = *p*-F
g, R = H
h, R = *p*-CH_3
i, R = *p*-OCH_3
j, R = *p*-$N(CH_3)_2$

This work stems from our study of a series of *N*-aryl-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes **2**[2,3] where we examined the ^{31}P, ^{13}C, and ^{15}N NMR spectra, oxidation, and reduction by cyclic voltammetry (CV) and carried out PRDDO molecular orbital calculations. The observations were, in general, explained by inductive and resonance effects and were aided and reinforced by the calculations. The observed correlations between experimentally measured parameters and Hammett substituent constants were explained by contributions of resonance forms A, B, and C to the resonance hybrid, and it was suggested that the

$$\underset{A}{Ph_3P^+N^-Ar} \leftrightarrow \underset{B}{Ph_3P^+N{=}Ar^-} \leftrightarrow \underset{C}{Ph_3P{=}NAr}$$

double bond in form C was not necessarily completely of the pπ-dπ type but could also involve overlap of a nitrogen electron pair with a σ* orbital of the P–C(Ar) bond.[2,3] The present work was undertaken to see if this explanation is equally applicable to the substituent effects shown by the series of *N*-(arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes **1**.

Our initial expectation was that since the SO_2 group insulates the nitrogen lone pair from direct resonance interaction with the ring but does allow for ready transmission of inductive effects, the dependence of the majority of NMR parameters, particularly chemical shifts, would be on the Hammett σ_p and σ_m substituent constants and not on σ^- as had been observed with the series **2**. In addition, we thought that the dependence of $^1J_{PN}$ on σ_R or σ_R^+ which was observed with **2** would not be observed in this case, but a solid prediction here is difficult to make.

In this paper we report on the ^{31}P, ^{15}N, and ^{13}C NMR spectra of the sulfonylphospha-λ⁵-azenes **1**, including both chemical shifts and coupling constants and the correlation of these parameters with Hammett substituent constants.

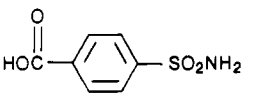
Results and Discussion

Syntheses. The phospha-λ⁵-azenes **1a–k** were synthesized by our previously described procedure[4] using the corresponding arenesulfonamides **3**, triphenylphosphine, and diethyl azodicarboxylate (eq 1). All sulfonamides **3**

$$\underset{3}{RC_6H_4SO_2NH_2} + Ph_3P + C_2H_5O_2CN{=}NCO_2C_2H_5 \xrightarrow{THF} RC_6H_4SO_2N{=}PPh_3 + C_2H_5O_2CNHNHCO_2C_2H_5 \quad (1)$$

a, R = *p*-NO_2
b, R = *m*-NO_2
c, R = *p*-CN
d, R = *p*-CO_2CH_3
e, R = *p*-Br
f, R = *p*-Cl
g, R = *p*-F
h, R = H
i, R = *p*-CH_3
j, R = *p*-OCH_3
k, R = *p*-NH_2

were either from commercial sources or were prepared in the standard way from the corresponding sulfonyl chlorides. **3d** was prepared by esterification (CH_2N_2) of sulfonamide **4** and **3c** was made by diazotization of sulfanilamide followed by a Sandmeyer reaction using $NiCl_2$ and NaCN.[6] Table I lists some of the properties of those *N*-sulfonylphospha-λ⁵-azenes not reported in ref 4 and that have not been prepared previously. It should also be pointed out that the melting point of **1k** reported previously[4] is incorrect and the correct value is 196–198 °C.



4

In order to obtain ^{15}N NMR spectra, a series of ^{15}N-labeled compounds (67% ^{15}N) was prepared (**1a***, **e***, **f***, **g***, **h***, **i***, **j***, **k***). These were made from the labeled sulfonamides that had been synthesized, in turn, from the corresponding sulfonyl chlorides and $^{15}NH_3$. Table I also lists these labeled compounds along with some properties.

p-$RC_6H_4SO_2{}^{15}N{=}PPh_3$

1a*, R = NO_2
1e*, R = Br
1f*, R = Cl
1g*, R = F
1h*, R = H
1i*, R = CH_3
1j*, R = OCH_3
1k*, R = NH_2

NMR Spectroscopy. In Table II are listed the ^{31}P, ^{15}N, and ^{13}C chemical shifts for the series of *N*-(arylsulfonyl)-phospha-λ⁵-azenes **1a–k**. As was done previously,[2,3] the

(1) On leave from the Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland.
(2) Pomerantz, M.; Marynick, D. S.; Rajeshwar, K.; Chou, W.-N.; Throckmorton, L.; Tsai, E. N.; Chen, P. C. Y.; Cain, T. *J. Org. Chem.* **1986**, *51*, 1223.
(3) Pomerantz, M.; Ziemnicka, B. T.; Merchant, Z. M.; Chou, W.-N.; Perkins, W. B.; Bittner, S. *J. Org. Chem.* **1985**, *50*, 1757.
(4) Bittner, S.; Assaf, Y.; Krief, P.; Pomerantz, M.; Ziemnicka, B. T.; Smith, C. G. *J. Org. Chem.* **1985**, *50*, 1712.
(5) Bittner, S.; Assaf, Y.; Pomerantz, M. *J. Org. Chem.* **1982**, *47*, 99.
(6) Andrews, C. H.; King, H.; Walker, J. *Proc. R. Soc. London, Ser. B* **1946**, *B133*, 20.

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