the endo proton of the aziridino methylene. The lone-pair anisotropy of N-3 (in 6) or N-1 (in 8) would account for this chemical shift difference, so H-3 is expected to have a preferred axiallike orientation in the bicyclic compound 6. This position would result from the repulsive nonbonded interaction between the aziridine " π -electron" system and the N-3 lone pair. (ii) The N-1 lone pair in 8 has an upfield shifting effect on the antiperiplanar exo H-2¹² and an increasing effect on the algebraic value of the H-2 geminal coupling¹³ with respect to the corresponding protons of 6.

EI (or CI) spectra confirm the structure of compounds 5, 6, and 8. These products exhibit a molecular ion (or protonated ion), and the base peak is the 1-aza-3-azoniabicyclo[3.1.0]hex-2-ene cation (9) for 5 and 6 and the tetrahydropyridinium cation (10) for 8.

Experimental Section

All melting and boiling points are uncorrected. Basic nitrogen analyses were performed by titration, controlled by potentiometry, with a solution of perchloric acid in acetic acid. Infrared spectra were obtained from a Perkin-Elmer 21 or Beckman 4210 spectrometer. ¹H NMR spectra were recorded on a Cameca 350, Varian XL 200, or Bruker WP 80 instrument. The naturalabundance ¹³C NMR spectra were obtained by Fourier transformation carried out on a Bruker WP 80 spectrometer operating at 20.15 MHz and using a 2-2.5-kHz spectral width, 8K memory points, and a flip angle of 30°. Mass spectrometry was performed on a Ribermag R 10-10 quadrupole spectrometer equipped with a Sydar 121 data system. GLC analyses were carried out on a Girdel 30 instrument equipped with a 60-m glass capillary column coated with Carbowax 20M or with a 2-m glass column packed with 3% OV-17 (or 2.75% Carbowax 4000M and 0.75% potassium hydroxide) on Chromosorb W HP (100-120 mesh).

2-(4-Hydroxybutyl)-1,3-diazabicyclo[3.1.0]hexanes 5 and 6. A mixture of 2-(dimethylamino)tetrahydropyran¹⁴ (12.9 g, 0.1 mol) and 2-(aminomethyl)aziridine¹⁵ (7.6 g, 0.106 mol) was stirred at room temperature for 48 h and then heated at 65 °C under reduced pressure for 8 h to yield a mixture of the amines 5 and 6: 13.1 g (84%); bp 128 °C (0.4 mm); $n^{21}{}_{\rm D}$ 1.5050; IR (neat) 3280 (OH), 3055 and 3030 (aziridine) cm⁻¹; EI mass spectrum, m/z(relative intensity) 83 (9, 100), 155 (M - 1), 156 (M⁺·); CI (isobutane) mass spectrum, m/z (relative intensity) 157 (M + 1, 100), 197 (M + 41), 213 (M + 57). Anal. Calcd for C₈H₁₆N₂O: N, 17.95. Found: N, 17.78.

1,5-Diazatricyclo[4.4.0.0^{3,5}]**decane (8).** A mixture of the amines 5 and 6 (6 g 0.038 mol) was treated with triphenylphosphine (13.6 g, 0.052 mol), carbon tetrachloride (9.4 g, 0.061 mol), and triethylamine (4 g, 0.039 mol) in 35 mL of acetonitrile as previously described⁶ for 2-(4-hydroxybutyl)tetrahydro-1,3-thiazole to yield 8: 1.10 g (21%); bp 62 °C (7 mm); $n^{18}{}_{\rm D}$ 1.4990; IR (neat) 3060, 3025, 2985 cm⁻¹; EI mass spectrum, m/z (relative intensity) 84 (10, 100), 138 (M⁺-); CI (isobutane) mass spectrum, n/z (relative intensity) 139 (M + 1, 100). Anal. Calcd for $C_{2}H_{14}N_{2}$ N, 20.27. Found: N, 20.16. Dipicrate, mp 138 °C. Anal. Calcd for $C_{20}H_{20}N_8O_{14}$: basic N, 4.70. Found: basic N, 4.65.

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Registry No. 1, 37019-50-4; **2**, 55099-23-5; **5**, 82165-82-0; **6**, 82165-83-1; **8**, 82165-84-2.

Supplementary Material Available: Homonuclear correlated two-dimensional ¹H spectrum of compound 8 (1 page). Ordering information is given on any current masthead page.

Bicyclic Dioxaphosphoranes. 2. Spectral Properties Indicative of a Karplus Relationship in Phosphoranes

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In 1964 Denney reported the first reaction of a trivalent phosphorus compound, triethyl phosphite, with a dialkyl peroxide, diethyl peroxide.¹ The product of that reaction was a stable phosphorane, pentaethoxyphosphorane (1).



Since that initial report the reactions of trivalent phosphorus with several $acyclic^2$ and $cyclic peroxides^3$ have been reported. The reaction of triphenylphosphine (2) with tetramethyldioxetane (3) has been extensively investigated from a mechanistic point of view;⁵ however, it is remarkable how very little is known about the effect of structure on the mechanism of insertion of phosphorus into the oxygen-oxygen bond.

We have recently reported⁶ that 2 reacts with the prostaglandin endoperoxide model,⁷ 2,3-dioxabicyclo-[2.2.1]heptane (4) to produce a stable phosphorane 5. (eq 1). We have suggested that this reaction is a concerted



insertion of phosphorus into the oxygen-oxygen bond. Evidence was also presented which suggested that phosphorane 5 hydrolyzed in nonpolar media by an outersphere mechanism (attack at carbon) rather than by the established innersphere mechanisms⁸ (attack at phosphorus). The interest in this ring system⁹ has prompted us to report the synthesis of three more phosphoranes, kinetic data for their formation, and their interesting spectral properties.

The addition of methyl diphenylphosphinite, dimethyl phenylphosphonite, and trimethyl phosphite to 4 dissolved

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Table I.	Spectral	Data for	Dioxaphos	phoranes 5	, 6,	7.	, and	8 ^{a,}	t
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	5	6	7	8	
¹³ C NMR ^c					
C ₄₆ ppm	79.5	78.1	77.9	77.5	
J_{P-C} , Hz	11.1	9.1	10.9	9.5	
J_{C-H} , Hz	157	157	157	161	
$C_{7,8}$, ppm	32.7	32.8	32.8	32.5	
J_{C-H} , Hz	132	129	133	131	
C ₅ , ppm	37.8	37.5	37.5	37.2	
J_{P-C} , Hz	12.7	10.9	14.6	11.1	
J_{C-H} , Hz	129	137	125	127	
C _{OCH} , ppm		50.7	53.2	54.7	
$J_{\rm P-C}$, Hz		9.1	10.9	12.7	
$J_{\rm C-H}$, Hz		140	143	146	
$^{31}P NMR^{d}$	-64.0	-49.2	-55.4 ^e	-72.4	
¹ H NMR ^{<i>c</i>}					
H_{5s}, H_{5a}, ppm	2.02, 0.64	2.20, 0.70	2.11, 0.80	2.12, 0.81	
$J_{\rm H-H}$, Hz	12.5	13.3	7.9	11.9	
$H_{4.6}, ppm$	4.56	4.48	4.38	4.42	
\vec{J}_{P-H} , Hz	19.8	19.3	17.1	23.1	
$H_{7n,8n}, H_{7x,8x}, ppm$	1.90, 1.28	2.10, 1.36	2.13, 1.37	2.15, 1.38	
$J_{\rm H-H}, {\rm Hz}$	7.9	8.9	6.6	8.1	
$H_{OCH_{2}}$, ppm		3.29	3.63	3.66	
J_{P-H} , Hz		10.5	12.5	13.4	

^a All spectral data reported in benzene. ^b The aromatic carbon and proton data are not reported because of serious overlap with solvent absorbance in several cases. ^c Chemical shifts reported vs. Me₄Si. ^d Chemical shifts reported vs. 85% H_3PO_4 by substitution. ^e In CDCl₃.

Table II. Activation Parameters for the Reaction of Triphenylphosphine with Peroxides

 compd	<i>T</i> , ^{<i>a</i>} °C	$10^{2}k$, ^b M ⁻¹ s ⁻¹	ΔH^{\ddagger} , kcal/mol	ΔS^{\ddagger} , eu	ΔG^{\ddagger} , kcal/mol
 5 ^b	24	1.58 ± 0.04			
	29	2.26 ± 0.05			
	33.5	2.80 ± 0.10			
	38	3.88 ± 0.23			19.9 ± 0.02 (25 °C)
	43	5.21 ± 0.22	11.0 ± 0.67	-29.6 ± 2.2	20.2 ± 0.02 (35 °C)
9°	33.5	0.46 ± 0.01			
	38	0.64 ± 0.02			
	43	0.95 ± 0.05			
	47	1.37 ± 0.09			$21.1 \pm 0.07 (25 \degree C)$
	50	1.66 ± 0.06	14.9 ± 1.2	-20.6 ± 3.9	21.3 ± 0.03 (35 °C)
10 ^{d,e}			9.2^{f}	-28	17.6 (25 °C)

^a Temperatures are controlled to ±0.5 °C. ^b Obtained from pseudo-first-order rate constants by dividing by the concentration of the peroxide. ^c In *n*-decane. ^d Baumstark, A. L.; Barrett, M.; Kral, K. M. J. Heterocycl. Chem., submitted for publication. ^e In xylenes. ^f Calculated from E_a , using $\Delta H^{\ddagger} = E_a - RT$.

in dry benzene resulted in an exothermic reaction producing phosphoranes 6-8. These phosphoranes like 5^6



decompose only slowly in a dry inert atmosphere. Removal of benzene from a solution of phosphorane 5 resulted in the isolation of a solid. The spectral data obtained by redissolving this solid in CDCl₃ indicated that only 25% of the phosphorane decomposed during this manipulation.

The ¹³C, ¹H, and ³¹P NMR spectral data of 6-8 are compared with the spectral data for phosphorane 5 in Table I. Examination of this table produces several interesting observations. (1) The ³¹P NMR resonances of all four of the phosphoranes are between -49 and -72 ppm. This is the chemical shift region where five-coordinate phosphorus is expected to be observed.¹⁰ (2) Only

three-bond phosphorus-hydrogen coupling to $H_{4.6}$ and the methoxy hydrogens is observed. The striking similarity in the NMR spectra of phosphoranes 5-8 indicate that no significant geometry changes occur upon substitution of the extracyclic ligands. (3) Phosphorus coupling to $C_{4.6}$, C_5 , and the methoxy group is observed in all the phosphoranes, while coupling to $C_{7,8}$ is totally absent. Examination of molecular models indicates that compounds 5-8 can exist in two bicyclic ring conformations. These two conformations and a Newman projection down the O-(3)-C(4) bond in which the oxygen is represented to a first approximation as sp³ hybridized are depicted in Scheme I. The angles θ and Φ are very insensitive to the geometry around phosphorus. Changing the two phosphorus-oxygen bonds from equatorial-equatorial to apical-equatorial in a trigonal bipyramid or by forcing the phosphorus into a square-pyramidal geometry produces only minor variations in θ and Φ . Analysis of the two Newman projections indicate that only C_5 is in a favorable Karplus relationship¹¹

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for phosphorus-carbon coupling similar to that observed in P(III) and P(IV) phosphorus derivatives.¹² Construction of an accurate Karplus curve¹³ from this data is not possible because of the limited amount of data and the absence of accurate structural information from X-ray crystallography.

We have also examined this reaction kinetically and report the activation barriers for the formation of phosphoranes 5, 9, and 10^{14} in Table II. The reaction is en-



thalpy controlled. The activation entropies are approximately the same for all three bimolecular reactions. The increasing ring strain in the peroxides is reflected in a decreasing enthalpy of activation.

Experimental Section

Materials. The synthesis of bicyclic peroxide 4 and 2,3-dioxabicyclo[2.2.2]octane was accomplished as reported previously.¹⁵ Both compounds gave satisfactory spectral and physical data. The triphenylphosphine, methyl diphenylphosphinite, and dimethyl phenylphosphonite were obtained from Aldrich and used without further purification. Trimethyl phosphite was received from Eastman Kodak and distilled off of sodium before use. Benzene was distilled in a N₂ atmosphere off of benzophenone ketyl and then stirred over the disodium salt of EDTA. The *n*-decane was distilled at 5 mmHg and then stirred over EDTA.

Dioxaphosphoranes 5-8. These compounds were synthesized by addition of triphenylphosphine, methyl diphenylphosphinite, dimethyl phenylphosphonite, and trimethyl phosphite via syringe to a serum-capped 10-mm NMR tube containing 4 and benzene at -78 °C. The reaction mixture was then allowed to warm slowly to room temperature and the spectral data was collected.

NMR Measurements. The ³¹P NMR measurement were made on a JEOL-FX270 MHz instrument at 109.13 MHz. A total of 16 384 points were collected over a spectral width of 50 000 Hz, utilizing a pulse delay of 5 or 10 s. All the chemical shifts are reported relative to 85% H_3PO_4 by substitution. The proton and ¹³C NMR data were also collected on a JEOL-FX270 MHz instrument and the data referenced to tetramethylsilane by substitution.

Kinetic Measurements. A 1.7-mL sample of 2.0×10^{-2} M 4 in *n*-decane was mixed with 1.7 mL of 2.0×10^{-4} M PPh₃ also in *n*-decane in a 1-mm curvette thermostated at the desired temperature. The psuedo-first-order disappearance of PPh₃ was monitored at 290 nm for at least 3 half-lives.

Data Treatment. Each rate constant was determined by following the decrease in absorbance of PPh₃ at 290 nm for at least 3 half-lives and plotting $\ln (A_0 - A_{\infty})$ vs. time. All rate constants were obtained by linear regression analysis of the experimental data and resulted in correlation coefficients (r) of greater than -0.997 in each case. The reported rate constants were obtained by dividing the pseudo-first-order rate constants by the concentration of 4 and are the average of three independent determinations.

The activation parameters were determined by plotting $\ln (k/T)$ vs. 1/T and the confidence limits in the slope and intercept were calculated with the equations of Bennett and Franklin¹⁶ and propagated into the activation parameters at the 95% confidence level.

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Registry No. 4, 279-35-6; **5**, 78870-51-6; **6**, 81898-36-4; **7**, 81898-37-5; **8**, 81898-38-6; **9**, 81898-39-7; **10**, 49595-63-3; triphenylphosphine, 603-35-0; methyl diphenylphosphinite, 4020-99-9; dimethyl phenylphosphonite, 2946-61-4; trimethyl phosphite, 121-45-9.

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Phenylmercuric Hydroxide. A Highly Selective Reagent for the Hydration of Nonconjugated Terminal Alkynes¹

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We herein describe an unusual and highly selective method for hydrating nonconjugated terminal alkynes based on the use of phenylmercuric hydroxide (1) as a reagent. Unlike classical mercury catalyzed procedures, σ -bonded mercury acetylides are formed initially as stable intermediates and subsequently reacted with water under neutral pH to form the corresponding methyl ketone.^{3,4} Isolated yields which have been obtained by using this approach lie in the range of 49–65%.

Addition of phenylmercuric hydroxide to a chloroform (or carbon tetrachloride) solution of 1-heptyne followed by heating for 2 h at 60 °C produced a pale yellow solution. Direct examination by IR, ¹H NMR, and ¹³C NMR indicated complete conversion to the acetylide (eq 1), accom-

$$PhHgOH + CH_{3}(CH_{2})_{4}C \equiv CH \xrightarrow[CHCl_{3}]{CHCl_{3}}$$
$$PhHgC \equiv C(CH_{2})_{4}CH_{3} + H_{2}O (1)$$

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