and stored in a freezer (−20 °C) until it was analyzed. Analysis was obtained by GLC with ethylbenzene as the internal standard. Yields of products were obtained by comparison to a standard mixture which contained the internal standard and authentic samples of the products. Peak areas were determined with a planimeter. The GLC analysis was carried out with a 20% polypropylene glycol on Chromosorb W column (5 ft × 0.125 in.) under the following conditions: injector 95 °C, column 150 °C, detector 160 °C, nitrogen carrier gas 20 ml/min, chart speed 4 in./min, and sample size 0.5 μl. The retention times for acetone, *tert*-butyl alcohol, toluene, and ethylbenzene were 0.7, 1.0, 2.0, and 3.0 min, respectively.

To check for products resulting from trapping of radical **3**, reactions were carried out through one half-life ($t_{1/2}$) and through 10 half-lives (t_∞). The analysis for cumyl *tert*-butyl peroxide was made by GLC on a 3% SE-30 on Varaport-30 column (5 ft × 0.125 in.) under the following conditions: injector 95 °C, column 70 °C, detector 75 °C, nitrogen carrier gas 22 ml/min, and sample size 0.5 μl. Neither the $t_{1/2}$ nor the t_∞ reaction mixtures showed GLC peaks with a retention time greater than that of benzene (8 min). The retention time of cumyl *tert*-butyl peroxide was 26 min. It was estimated that at least a 1% yield of this peroxide could have been detected.

Analysis for 2-chloro-2-*tert*-butylperoxypropane, which is a possible trapping product from radical **3** in the presence of sodium chloride or carbon tetrachloride solvent, was made with a 15% XF-96 (5 ft × 0.125 in.) on Chromosorb W column. The conditions for trapping **3** with sodium chloride/LTA in benzene were injector 75 °C, column 25 °C, detector 125 °C, nitrogen carrier gas 25 ml/min, and 0.5-μl sample size. It was estimated that the retention time for the chloroperoxide would be somewhat greater than that of di-*tert*-butyl peroxide, based on expected boiling points. No product peaks were observed after benzene (14 min). Under these conditions, di-*tert*-butyl peroxide was found to have a retention time of 33 min. The GLC conditions for analysis of the chloroperoxide from the LTA oxidation of **1** in carbon tetrachloride were injector 110 °C, column 30 °C, detector 90 °C, nitrogen carrier gas 20 ml/min, and sample size 0.5 μl. No product peaks with retention times greater than that of carbon tetrachloride (11 min) were observed.

Kinetic Method. All glassware was dried at 140 °C in an oven for 12 h and then cooled in a vacuum desiccator over silica gel or in a stream of dry nitrogen. The reaction vessel consisted of a 150-ml round-bottomed flask, to which was sealed a condenser and a long stoppered tube into which a pipet could be placed to withdraw aliquots. The reaction vessel, wrapped with aluminum foil, was flushed with purified nitrogen and placed in a constant-temperature bath controlled to ±0.01 °C. A benzene solution of LTA was thermally equilibrated (at least 20 min) in the reaction vessel and then a thermally equilibrated benzene solution of the carboxylic acid was added. The timer was started and 10-ml aliquots were periodically withdrawn. An infinity aliquot was withdrawn after 10 half-lives. The aliquots were added to 10 ml of a potassium iodide solution, which were contained in nitrogen-swept 250-ml Erlenmeyer flasks. The potassium iodide solution was prepared from 15 g of potassium iodide, 25 g of sodium acetate, and 10 g of sodium carbonate per 100 ml of doubly distilled water solution. After the reaction solution aliquot was added to the potassium iodide solution, 20 ml of acetic acid was added, and the flask was swept with nitrogen and allowed to stand in the dark for 20 min. Now 150 ml of water was added, and if a precipitate formed, 0.5 g of sodium carbonate was added. The solution was then titrated with 0.0100 N standardized (with standard sodium dichromate solution) thiosulfate solution to a straw yellow–colorless end point.

The data were processed with a least-squares first-order computer program. The activation parameters for carboxylic acid **7** were obtained by a least-squares computer program as well.

Acknowledgment. We thank the U.S. Army Research Office (Durham) for support of this research.

Registry No.—**1**, 16424-69-4; **6**, 75-98-9; **7**, 13836-62-9; lead tetraacetate, 546-67-8.

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Phosphorus-Containing Products from the Reaction of Propargyl Alcohols with Phosphorus Trihalides. 4. Alkyl Substituent Effects on Oxaphospholene Formation[1,2]

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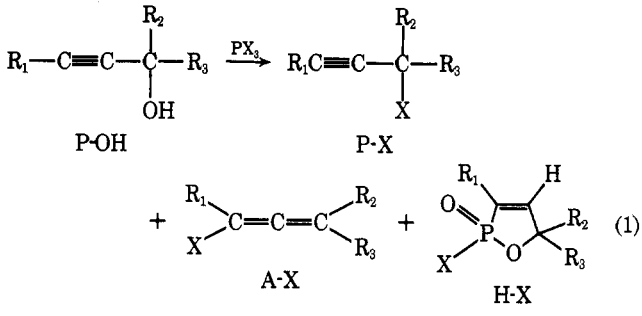
The reactions of eight propargyl alcohols ($R_1C{\equiv}C{-}CR_2R_3OH$) with one or more molar equivalents of phosphorus trichloride have been examined in detail. Each of the alcohols reacts immediately to give the corresponding propargyl dichlorophosphite. If the hydrogen chloride formed during this reaction is efficiently *removed* (not neutralized), the phosphites [except when $R_1 = R_2 = C(CH_3)_3$ and $R_3 = C(CH_3)_3$ or CH_3] rearrange to allenic phosphonyl dichlorides, hydrolysis of which gives crystalline allenic phosphonic acids. These [except when $R_1 = R_2 = R_3 = H$ and $R_1 = R_2 = C(CH_3)_3$; $R_3 = H$] undergo acid-catalyzed cyclization to the novel oxaphospholenes. The relative rates of both the rearrangement and the cyclization follow the order $R_1 = H, R_2 + R_3 = (CH_2)_4 > R_1 = H, R_2 + R_3 = (CH_2)_5 > R_1 = H, R_2 = R_3 = CH_3 > R_1 = C(CH_3)_3, R_2 = R_3 = CH_3 \gg R_1 = R_2 = C(CH_3)_3, R_3 = H > R_1 = R_2 = R_3 = H$. The isolated percent yields of allenic phosphonic acid from propargyl alcohol, and oxaphospholene from phosphonic acid for the above series are 40, 36; 60, 38; 45, 85; 32, 69; 68, 0; 66, 0, respectively. The mechanisms of these reactions as gauged by their response to substituent effects are discussed. The ^1H NMR spectra of these compounds are also described.

During the preparation of 3-bromo-2,2,6,6-tetramethyl-4-heptyne (P_1-Br) and its allenic isomer (A_1-Br) from the reaction of the corresponding propargyl alcohol (P_1-OH) with phosphorus tribromide (PTB) in chloroform, we isolated in

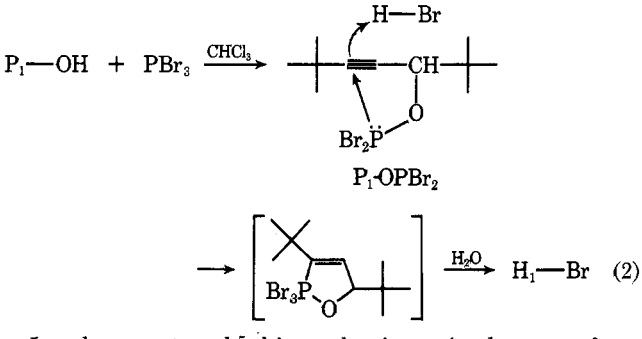
ca. 10% yield a crystalline side product to which we assigned[3] heterocyclic structure H_1-Br. We proposed[3] that the heterocycle resulted from acid-promoted cyclization of intermediate dibromophosphite P_1-$OPBr_2$:[4]



P-OH P-X A-X H-X

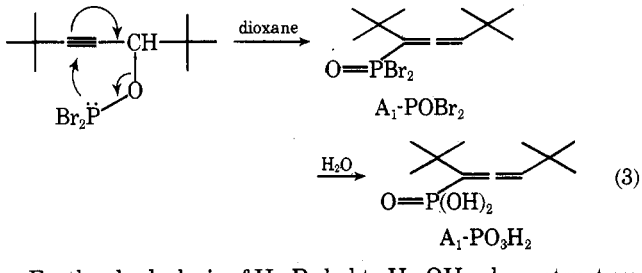
(1)

1, $R_1 = R_2 = C(CH_3)_3$; $R_3 = H$
2, $R_1 = R_2 = C(CH_3)_3$; $R_3 = CH_3$
3, $R_1 = R_2 = R_3 = C(CH_3)_3$
4, $R_1 = H$; $R_2 = R_3 = CH_3$
5, $R_1 = H$; $R_2 + R_3 = (CH_2)_5$
6, $R_1 = H$; $R_2 + R_3 = (CH_2)_4$
7, $R_1 = C(CH_3)_3$; $R_2 = R_3 = CH_3$
8, $R_1 = R_2 = R_3 = H$



(2)

In subsequent work[5] this mechanism gained support from the direct observation of intermediates P_1-$OPBr_2$ by low-temperature ^1H NMR, and the fact that changing the solvent to the more basic dioxane diverted the intermediate via a [3,2] sigmatropic shift to allenic phosphonic acid A_1-PO_3H_2.[6] Phosphorus trichloride (PTC) provided comparable results.[5]



(3)

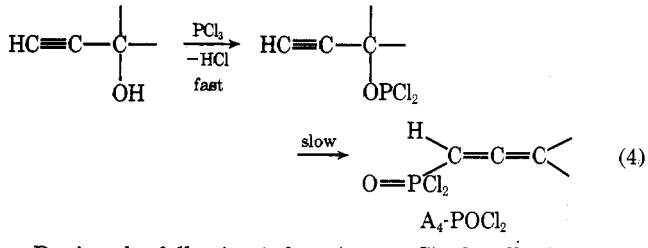
Further hydrolysis of H_1-Br led to H_1-OH, whose structure was confirmed[5] by x-ray crystallographic analysis. Significantly, isomers H_1-OH and A_1-PO_3H_2 could *not* be interconverted under acidic, basic, thermal, or electron impact conditions.

We have now extended this work to seven other propargyl alcohols to assess the effect of alkyl substitution on the formation of phosphorus-containing products. These results not only establish the generality of these reactions but also shed new light on the mechanism of heterocycle formation.

Results

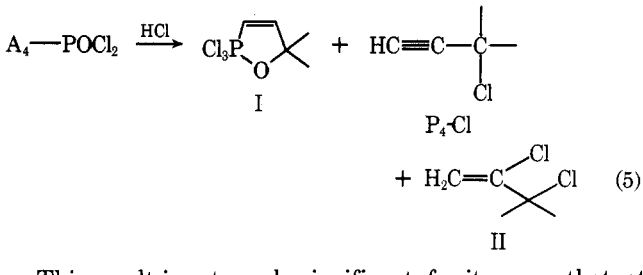
Our initial approach in this study was to incorporate substituents that would minimize formation of propargyl and allenic halides, thereby rendering formation of phosphorus-containing products more competitive. We first examined P_2-OH and P_3-OH, where the methine hydrogen in P_1-OH had been replaced by a methyl and *tert*-butyl group, respectively. These preliminary results proved disappointing; no phosphorus-containing compounds could be isolated, only the simple substitution products and those arising from addition and elimination of HX. (Subsequent work on these compounds is described more fully below.) However, preliminary studies with P_4-OH encouraged us to examine it in detail.

When equimolar amounts of P_4-OH and PTC (in methylene chloride or deuteriochloroform) were combined at 25 °C, ^1H NMR revealed that the original absorptions [δ 1.55 (s, 6 H), 2.45 (s, 1 H), 3.08 (s, 1 H, OH)] had shifted to δ 1.57, 2.45, and 2.75, respectively.[7] Over the next 37 min (at 35 °C), these absorptions were completely replaced by those of a single new species [δ 1.95 (d of d, $J_{HH} = 3$, $J_{PH} = 12$ Hz, 6 H), 5.95 (d of septet, $J_{HH} = 3$, $J_{PH} = 28.5$ Hz, 1 H)], to which we assign structure A_4-$POCl_2$. An infrared spectrum of this compound exhibited strong bands at 1955 (C=C=C) and 1270 cm^{-1} (P=O), confirming the assignment.



(4)

During the following 5 days (at 25 °C), the allenic proton absorptions decreased by ca. 80%, and were replaced by peaks characteristic[3,5] of the oxaphospholene skeleton[8] [δ 1.57 (s, 6 H), 6.40 (d of d, $J_{HH} = 8.5$, $J_{PH} = 39$ Hz, 1 H), 7.21 (d of d, $J_{HH} = 8.5$, $J_{PH} = 56$ Hz, 1 H)]. We assign these to I, the unhydrolyzed precursor[4] of H_4-OH. The spectrum also showed the presence of P_4-Cl [δ 1.84 (s, 6 H), 2.70 (s, 1 H)] and addition product II [δ 1.71 (s, 6 H), 6.31 (AB quartet, 2 H)]. The ratio of these three products was 6:1:2, respectively, and this remained constant over the next 5 days (at 25 °C).



(5)

This result is extremely significant, for it proves that, at least in the case of P_4-OH, the oxaphospholene arises via the allenic intermediate, *not* directly from P_4-$OPCl_2$ as previously suggested for P_1-OH.[3,5] This represented the first observation of an allenic phosphonyl compound cyclizing to an oxaphospholene.

Repetition of this reaction on the preparative scale proved frustratingly complex, until it was discovered that removing the hydrogen chloride formed in the first step (reaction 4) with a stream of nitrogen afforded A_4-$POCl_2$ (a liquid with phosgenelike odor) in 84% yield, the reaction requiring 2 h at 25 °C. *The entire success of this step, and the similar ones described later, rests on the efficient removal of the hydrogen chloride.* Simple neutralization leaves Cl^- in the medium to react with the dichlorophosphite giving undesired propargyl and allenic chlorides. Because PTC has bp 76 °C, an excess must generally be used to compensate for that which evaporates into the nitrogen stream.

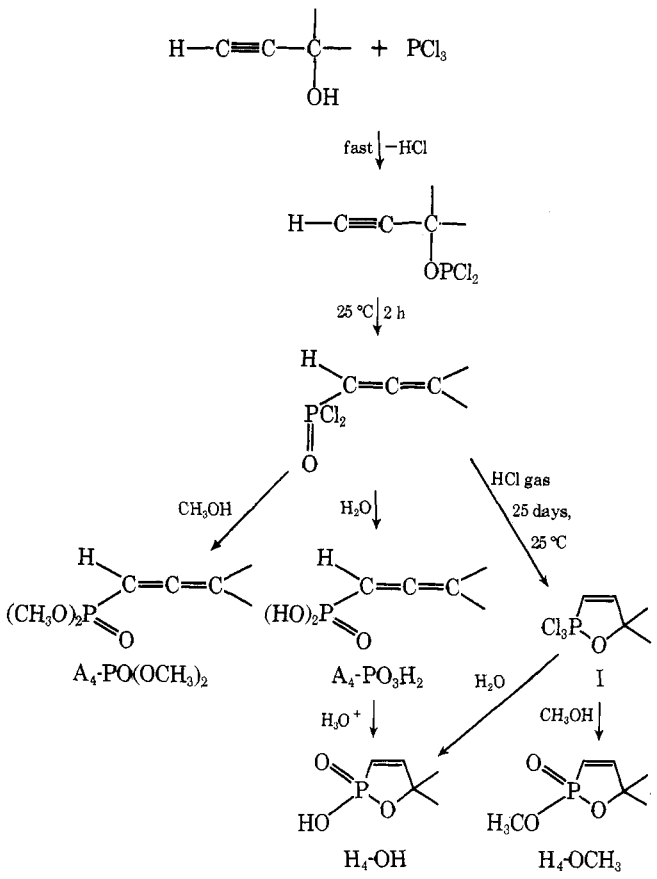
Although A_4-$POCl_2$ underwent uncomplicated methanolysis to give A_4-$PO(OCH_3)_2$ in 64% overall yield, attempts to hydrolyze the former compound under a variety of conditions

gave A_4-PO_3H_2 contaminated inseparably with varying amounts of H_4-OH. It was eventually found that *partial* neutralization of the hydrogen chloride formed during *hydrolysis* gave stable crystalline A_4-PO_3H_2 in 45% overall yield.

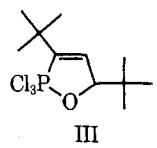
Confirming the occurrence of reaction 5, and the partial isomerization during hydrolysis (vide supra), A_4-PO_3H_2 was found to cyclize cleanly in 2 M aqueous hydrochloric acid to H_4-OH (85% yield), with a half-life of 10.3 h at 66 °C.

Although the above sequence provided a convenient method for the preparation of H_1-OH, we wished to repeat reaction 5 on the preparative scale. Indeed, passage of dry gaseous hydrogen chloride through a methylene chloride solution of A_4-$POCl_2$ for 25 days (25 °C) gave the same product mixture as seen in the ^1H NMR experiment. Hydrolysis or methanolysis of this mixture gave H_4-OH or H_4-OCH_3. These results are summarized in Scheme I.

Scheme I



Armed with these results, we reexamined the reaction of P_1-OH with PTC.[5] When equimolar amounts of the reactants in deuteriochloroform were combined at 25 °C, the ^1H NMR spectrum showed only P_1-$OPCl_2$ [δ 1.01 (s, 9 H), 1.24 (s, 9 H), 4.87 (d, J_{PH} = 12.5 Hz, 1 H)], analogous to P_1-$OPBr_2$.[5] Over the next 27 h, 50 times slower than for P_4-$OPCl_2$, these absorptions were replaced by those of four products, A_1-$POCl_2$ [δ 1.17 (s), 1.36 (s), 5.82 (d, J_{PH} = 17.5 Hz)]; III [δ 1.03 (s), 1.36 (s), 4.78 (d of d, J_{HH} = 1.8, J_{PH} = 6 Hz), 6.82 (d of d, J_{HH} = 1.8, J_{PH} = 54 Hz)];[4] P_1-Cl^3 [δ 1.09 (s), 1.23 (s), 4.33 (s)] and A_1-Cl^3 [δ 1.17 (s), 1.24 (s), 6.59 (s)], in the ratio 4:2:2:1. This remained unchanged after 22 h (25 °C).



III

Table I. Half-Lives of Acid-Catalyzed Cyclization of Allenic Phosphonic Acids

Reactant	$t_{1/2}$, min: Aq acetonitrile,[a] 65 °C	Aq dioxane,[b] 64 °C
A_6-PO_3H_2	40	30
A_5-PO_3H_2	200	90
A_4-PO_3H_2	250	180
A_7-PO_3H_2		2000
A_1-PO_3H_2	∞	∞
A_8-PO_3H_2	∞	∞

[a] Ca. 30 mg of reactant dissolved in 0.35 ml of solvent consisting of CD_3CH, D_2O, and concentrated HCl in volume ratio 5:1.2:1. When attempts were made to cyclize A_1- and A_8-PO_3H_2 at 95 °C in ~50% aqueous acetonitrile containing ~20% (v/v) perchloric acid, crystalline ammonium perchlorate precipitated slowly. [b] Ca. 45 mg of reactant dissolved in 0.34 ml of solvent consisting of dioxane-d_8, D_2O, and concentrated HCl in the volume ratio 1.2:1.2:1.

Repetition on the preparative scale, removing the hydrogen chloride with nitrogen, gave A_1-$POCl_2$ quantitatively, and hydrolysis afforded A_1-PO_3H_2 in 68% overall yield (four times greater than before[5]). Passage of gaseous hydrogen chloride through a methylene chloride solution of A_1-$POCl_2$ gave a complex mixture of products from which only A_1-PO_3H_2 could be isolated. Most importantly, A_1-PO_3H_2 could not be made to cyclize, even when heated to 90 °C for 11 days (2 M hydrochloric acid in 80% aqueous diglyme).

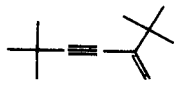
Thus, the rearrangement of P_1-$OPCl_2$ to A_1-$POCl_2$ is about $\frac{1}{50}$ as fast as the rearrangement of P_4-$OPCl_2$, and the cyclization of A_1-PO_3H_2 must be infinitely slower than for A_4-PO_3H_2, suggesting that both reactions respond similarly to substituent changes. Since neither A_1-PO_3H_2 nor A_1-$POCl_2$ could be made to cyclize, the originally observed H_1-Br^3 and H_1-Cl^5 must arise (inefficiently) from P_1-OPX_2, not via allenic phosphonyl compounds, and the best entry into the H_1 system continues to be the original one.[3]

Cyclic alcohols P_5-OH and P_6-OH behaved very similarly to P_4-OH. Both reacted with PTC to produce the phosphonyl dichlorides A_5-$POCl_2$ (91% after 2 h at 25 °C) and A_6-$POCl_2$ (68% after 1.5 h at 25 °C). These could be hydrolyzed to phosphonic acids A_5-PO_3H (68%) and A_6-PO_3H_2 (58%). The latter pair of compounds underwent acid-catalyzed cyclization in a number of solvents, as did A_4-PO_3H_2. These rearrangements were readily followed by ^1H NMR, and they seemed to proceed quantitatively. However, the darkening of the reaction solution (especially in the case of A_6-PO_3H_2) and the relatively low isolated yields (H_5-OH, 38%; H_6-OH, 36%) suggested that other reactions may have competed. At any rate, the relative rates of cyclization (by ^1H NMR) are given in Table I.

To determine if R_1 played any role in the rearrangement and cyclization reactions, P_7-OH,[10] with the methyl groups of P_4-OH and the *tert*-butyl group of P_1-OH, was examined. Preliminary investigation by ^1H NMR showed that the only significant product was P_7-Cl,[10] suggesting that the *tert*-butyl group hindered the [3,2] sigmatropic shift, thus favoring attack by external halide. However, when addition was carried out over 2.6 h at 0 °C with a copious nitrogen flow, A_7-$POCl_2$ could be isolated in 47% yield, along with P_7-Cl. The rearrangement of P_7-$OPCl_2$ required about 8 h, longer than P_4-$OPCl_2$, but shorter than P_1-$OPCl_2$. Hydrolysis led in 32% overall yield to A_7-PO_3H_2, which in turn underwent acid-catalyzed cyclization to H_7-OH (quantitative by ^1H NMR, 69% isolated yield). Most interesting, however, was that this cyclization was only *ca.* one-tenth as fast as that of A_4-PO_3H_2

(Table I), confirming the retarding effect of $R_1 = C(CH_3)_3$ on both reactions.

Alcohol P_2-OH[11] (vide supra) was next reexamined in detail. Its reaction with PTC led after 3 h at 25 °C to a mixture of P_2-Cl and elimination product IV in approximately equal



IV

amounts, together with a trace of A_2-$POCl_2$. The latter was in too small an amount to allow isolation of A_2-PO_3H_2. When P_3-OH[12] was allowed to react with PTC, A_3-Cl could be isolated in 92% yield and no phosphorus-containing products could be detected. The results with these two compounds suggest that if R_2 and R_3 are sterically repulsive enough, ionization of the $-OPCl_2$ group takes place to allow rehybridization ($sp^3 \rightarrow sp^2$) and reduction in nonbonded interaction. The resulting carbonium ions then suffer attack by Cl^- (or elimination of an α hydrogen in the case of P_2^+) in preference to the attack by the bulkier $O{=}PCl_2^-$. This can be taken as evidence that the propargyl phosphite → allenic phosphonyl rearrangement is a concerted sigmatropic shift and does not occur via an SN1′ ion-pair mechanism.

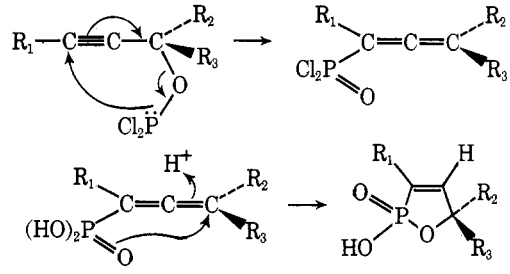
Finally, propargyl alcohol (P_8-OH) itself was examined. Preliminary NMR analysis showed that although formation of P_8-$OPCl_2$ was immediate, its rearrangement to A_8-$POCl_2$ was very slow. On the preparative scale, the reaction gave initially a 72% yield of P_8-$OPCl_2$ [δ 2.62 (t, J_{HH} = 2.6 Hz, 1 H), 4.83 (d of d, J_{HH} = 2.6, J_{PH} = 8.0 Hz, 2 H); 3280, 2120 cm^{-1}]. This material rearranged to A_8-$POCl_2$ [δ 5.51 (d of d, J_{PH} = 18, J_{HH} = 6.6 Hz, 2 H), 6.02 (d of t, J_{PH} = 22, J_{HH} = 6.6 Hz, 1 H),[8] 1940, 1260 cm^{-1}], but the reaction required 10 h at 60 °C, approximately one-fifth as fast as P_1-$OPCl_2$ (vide supra). Hydrolysis led to A_8-PO_3H_2 (66% yield based on P_8-OH) as a slowly crystallizing oil which could not be further purified. Methanolysis gave A_8-$PO(OCH_3)_2$ as a readily distilled liquid. Most importantly, a solution of A_8-PO_3H_2 in acidic aqueous dioxane was heated to 94 °C for 46 h, and although there was some decomposition (evidenced by darkening), ^1H NMR showed only starting material. No absorptions attributable to H_8-OH (vide infra) were observed. Thus, A_1- and A_8-PO_3H_2 were the only two of six allenic phosphonic acids that failed to cyclize, even under harsh conditions.

Discussion

All eight propargyl alcohols examined in this study reacted with PTC instantaneously at 0 or 25 °C to give the corresponding propargyl dichlorophosphites. When the hydrogen chloride formed during this reaction was efficiently *removed* with a stream of nitrogen, the dichlorophosphites rearranged more slowly to the isomeric allenic phosphonyl dichlorides. Exceptions were P_2- and P_3-$OPCl_2$, where steric repulsion between R_2 and R_3 accelerated ionization of the $-OPCl_2$ group at the expense of rearrangement. Compound P_8-$OPCl_2$ was so slow to rearrange that it could be isolated.

Hydrolysis of the phosphonyl dichlorides gave the allenic phosphonic acids as crystalline solids in yields ranging from 32 to 68%. With the exception of A_1- and A_8-PO_3H_2, these compounds underwent acid-catalyzed cyclization to highly crystalline oxaphospholenes, indicating the greater stability of the latter. This reaction could be conveniently monitored by ^1H NMR, and it generally appeared to take place quantitatively, although isolated yields ranged from 35 to 85%. This represents the first general syntheses of allenic phosphonic acids and oxaphospholenes. These compounds are moderately to highly soluble in polar organic media, and relatively insoluble in nonpolar media.

The relative rates of dichlorophosphite → allenic phosphonyl dichloride seemed to parallel the rate of cyclization: system 6 > 5 > 4 > 7 ≫ 1 > 8. This may seem somewhat paradoxical, because substituent interaction between R_1, R_2, and R_3 which would accelerate the first reaction should inhibit the



second one. In the cases where these reactions occur spontaneously, they must be exoergic, and thus have early (reactant-like) transition states by Hammond's postulate. The first reaction should be accelerated by sterically small R_1, and by fairly large R_2 and R_3 which, by virtue of their interaction, decrease the ≡C–C–O angle and favor sp^2 hybridization at the initially saturated carbon. However, if R_2 and R_3 are too large (vide supra) ionization of $-OPCl_2$ occurs more readily than the sigmatropic shift. These expectations agree essentially with the observations except that P_6-OH, with $R_2 + R_3$ constituting a five-membered ring, might be expected to be *slower* than P_5- and P_4-OH.

If the second reaction is stepwise, protonation of the double bond followed by nucleophilic ring closure, its rate should reflect the stability of the intermediate carbonium ion. Thus, $R_2 = R_3$ = alkyl (to give a tertiary carbonium ion) should be faster that R_2 = alkyl, R_3 = H, faster than $R_2 = R_3$ = H, as observed. Here, partial relief of angle strain during rehybridization might explain the relative rates A_6-$PO_3H_2 > A_5 > A_4$.

Probably the strangest finding was that $R_1 = C(CH_3)_3$ *decelerates* cyclization by a factor of 10 compared to R_1 = H. The R_1–C–P angle in H_1-OH (125°[5]) suggests that cyclization might be *facilitated* by large R_1. Perhaps, however, if $R_1 = C(CH_3)_3$ the angle is too large in the allenic precursor. Whatever its source, the deceleration by $R_1 = C(CH_3)_3$, coupled with the lack of sufficient carbonium ion stabilization by $R_2 = C(CH_3)_3$, R_3 = H, renders A_1-PO_3H_2 extremely unreactive toward cyclization. To support these various conclusions, system 8 ($R_1 = R_2 = R_3$ = H) not only rearranges slowest of all compounds in this study, but it also fails to cyclize even in 25% perchloric acid at 94 °C.

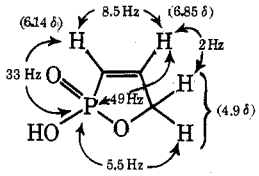
Further work on the generality of these reactions, as well as the chemistry of the oxaphospholenes and allenic phosphonic acids, is underway.

NMR Spectra of Allenic Phosphonic Acids and Oxophospholenes.[8] Several interesting observations can be made regarding the ^1H NMR spectra of the compounds in this study. Compounds H_4-OH and H_7-OH show singlets for the *gem*-dimethyl groups, even though the methyls may be diastereotopic by virtue of the phosphorus substituents. We have explained this type of observation[5] as being due to extremely rapid exchange of the acidic proton between the oxygens on phosphorus. In support of this, it was observed that H_4-OCH_3, where the configuration of phosphorus is fixed, gives rise to two methyl singlets separated by 2.5 Hz.

The two-bond (geminal) P–H coupling in compounds $A_{4,5,6}$-$POCl_2$ averages 28 ± 1 Hz (22 Hz in A_8-$POCl_2$), but it drops to 6 ± 2 Hz in $A_{4,5,6,8}$-PO_3H_2. Similarly, the five-bond P–H coupling in $A_{4,7}$-$POCl_2$ (12 Hz) drops to 7 ± 1 Hz when the Cl groups are hydrolyzed, and the four-bond constant in A_8-$POCl_2$ (18 Hz) drops to 13.4 Hz. Thus, the electronegativity of the phosphorus substituent strongly influences the mag-

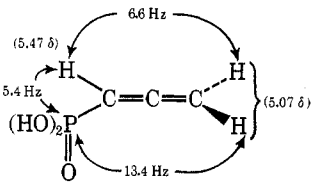
nitude of both short- and long-range coupling interactions.

The predicted chemical shifts and coupling constants for the unsubstituted oxaphospholene H_8-OH (as yet unknown), based on the data for $H_{1,4,5,6,7}$-OH, are given below.



Note that $^3J_{PH}$ always exceeds $^2J_{PH}$ and that $^2J_{PH}$ for the oxaphospholenes always exceeds ^2J for the isomeric allenic phosphonic acids, presumably a consequence of the smaller H–C–P angle in the latter compounds.

The ^{1}H NMR data for isolated A_8-PO_3H_2 are given below.



Experimental Section

General. The instrumentation and techniques were as described previously.[3,5] Except as noted, all reagents were commercially available. Microanalyses[13] were performed by Chemalytics, Tempe, Ariz. PTC was freshly distilled; all solvents were dried over molecular sieve.

Reaction of P_4-OH with PTC. With a small gas dispersion tube, dry nitrogen (200 ml/min) was passed through a solution of 3.45 g (25 mmol) of PTC in 25 ml of CH_2Cl_2, maintained at 25 °C in a water bath. Over 14 min a solution of 2.10 g (25 mmol) of P_4-OH in 25 ml of CH_2Cl_2 was added dropwise. With nitrogen flow continuing, the solution was stirred for 2.0 h. Rotary evaporation (10 mm, 35 °C) left 3.87 g (21 mmol, 84%) of A_4-$POCl_2$ as a colorless liquid. Its spectra are described in the text. This material was added dropwise over 30 min to 15 ml of water at 0 °C. During the addition sodium bicarbonate (exactly 1.76 g, 21 mmol) was added portionwise. The mixture was warmed to 35 °C, 5 ml of water was added, and it was swirled until homogeneous. Complete evaporation of solvent ($P \rightarrow 0.1$ mm, $T <$ 35 °C) left a colorless solid which was treated with 30 ml of hot acetone. After filtration (mass NaCl 1.14 g), evaporation left 3.03 g of crude A_4-PO_3H. Two recrystallizations from $CHCl_3$ gave 1.65 g (45% overall) with mp 101.5–103.0 °C. Prolonged heating during recrystallization causes rearrangement, rendering purification impossible. Acid A_4-PO_3H_2 was highly soluble in water and acetone. ^{1}H NMR (acetone-d_6) δ 1.75 (dd, J_{HH} = 3.5, J_{PH} = 7.5 Hz, 6 H), 5.33 (overlapping d of septet, J_{HH} = 3.5, J_{PH} = 5.4 Hz, 1 H), 11.07 (s, 2 H); ir (mull) 3500–1800 (v br), 1960 (m), 1470 (s), 1370 cm^{-1} (s); MS (70 eV) *m/e* 148 (molecular ion and base).

Anal. Calcd for $C_5H_9O_3P$: C, 40.55; H, 6.13. Found: C, 40.55; H, 6.05.

Methanolysis of A_4-$POCl_2$. A solution of 3.90 g of A_4-$POCl_2$ in 18 ml of CH_2Cl_2 was added dropwise over 10 min to 20 ml of anhydrous CH_3OH at 0 °C. The solution was stirred for 2 h at 25 °C, then rotary evaporated and distilled to give 2.80 g (76%) of A_4-$PO(OCH_3)_2$: bp 48–51 °C (0.09 mm); ^{1}H NMR (CCl_4) δ 1.80 (dd, J_{PH} = 7.3, J_{HH} = 3.5 Hz, 6 H), 3.85 (d, J_{PH} = 11 Hz, 6 H), 5.09 (d of septet, J_{PH} = 7.8, J_{HH} = 3.5 Hz, 1 h); ir (CCl_4) 1970 (sh), 1260 cm^{-1} (vs); MS (20 eV) *m/e* 176 (mi), 81 (base). A satisfactory elemental analysis could not be obtained.[18]

Rearrangement of A_4-PO_3H_2 to H_4-OH. A 456-mg sample of the allenic acid was dissolved in 1.00 ml of water, 249 mg of concentrated HCl was added, and this solution was heated to 67 °C for 43.5 h. (A ^{1}H NMR kinetic study showed that the rearrangement was clean, giving only H_4-OH, with a half-life of 10.3 h.) Upon cooling to room temperature the slightly colored solution deposited two crops totalling 387 mg (85%), mp 156.0–157.5 °C. Spectral data for H_4-OH: ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 6 H), 6.17 (d of d, J_{PH} = 33, J_{HH} = 8.5 Hz, 1 H), 7.13 (d of d, J_{PH} = 48.5, J_{HH} = 8.5 Hz, 1 H), 11.20 (s, 1 H); ^{31}P (CHCl) δ −41.9 (d of d, J = 48.5, 33 Hz); ir ($CHCl_3$) 3000–2600 (br), 3010 (m), 2950 (s), 1600 (s), 1330 (s), 1210 cm^{-1} (s); MS (70 eV) *m/e* 148 (mi), 81 (base).

Anal. Calcd for $C_5H_9O_3P$: C, 40.55; H, 6.13; P, 20.91. Found: C, 40.83; H, 6.16; P, 21.27.

Direct Preparation of H_4-OH. A 1.59-g sample of A_4-$POCl_2$ was hydrolyzed with half-neutralization (vide supra), and this solution was heated to 66.5 °C for 40 h. The resulting solution was decanted to remove a dark, insoluble oil, rotary evaporated (to 0.1 mm), and the residue recrystallized from water to give 0.86 g (68%) of H_4-OH. This represents a 22% (absolute) increase compared to the route via isolated A_4-PO_3H_2.

Reaction of A_4-$POCl_2$ with HCl. Dry gaseous HCl was passed through a stirred solution of 7.40 g (40 mmol) of A_4-$POCl_2$ in 50 ml of CH_2Cl_2 for 25 days at room temperature, replenishing solvent as necessary. At this point ^{1}H NMR indicated 90% conversion to heterocycle. Rotary evaporation left 6.62 g of a brown crystallizing oil. Half of this material was dissolved in 15 ml of dioxane and added to 20 ml of 60% aqueous dioxane at 0 °C. This solution was stirred for 3 h at 25 °C, rotary evaporated to dryness, and recrystallized from water to give 1.78 g (60% from A_4-$POCl_2$) of H_4-OH. This route to H_4-OH, however, considerably less convenient and more costly than the route via A_4-PO_3H_2 (vide supra).

The other half (3.31 g) was dissolved in 20 ml of CH_2Cl_2 and added to 10 ml of anhydrous methanol at 0 °C. After stirring for 2.5 h at room temperature, rotary evaporation left 3.03 g of a green oil. Short-path distillation at 0.05 mm gave 2.11 g of impure H_4-OCH_3 (bp 56–58 °C). The main impurity was A_4-$PO(OCH_3)_2$ (vide supra). A second short-path distillation at 0.70 mm provided 800 mg of 95% H_4-OCH_3, bp 81–83 °C. Larger scale preparations with spinning band distillation would provide higher purity and better recovery. ^{1}H NMR data for H_4-OCH_3 (CCl_4): δ 1.46 (s, 3 H), 1.50 (s, 3 H), 3.71 (d, J_{PH} = 12 Hz, 6 H), 6.07 (d of d, J_{HH} = 8.5, J_{PH} = 32.5 Hz, 1 H), 7.19 (d of d, J_{HH} = 8.5, J_{PH} = 47.5 Hz, 1 H).

Reaction of P_5-OH with PTC. Using the same procedure as described for P_4-OH, 2.48 g (20 mmol) of P_5-OH was reacted with 2.94 g (21 mmol) of PTC. Addition (10 min, 23 °C) was followed by stirring (130 min, 24 °C) and rotary evaporation left 4.09 g (91%) of crude A_5-$POCl_2$ (ir 1955 cm^{-1}; ^{1}H NMR δ 5.86, d of quintet, J_{PH} = 29, J_{H-H} ~ 2 Hz). This was added dropwise over 10 min to 25 ml of 50% aqueous dioxane at 0 °C. This was accompanied by portionwise addition of 1.55 g of sodium bicarbonate. Exhaustive rotary evaporation ($T <$ 30 °C, $P <$ 0.05 mm) left 4.14 g of colorless solid. The product was taken up in 2 × 20 ml of hot dioxane, filtered (giving 1.01 g of sodium chloride), and again rotary evaporated to dryness to give 3.22 g of crude A_5-PO_3H_2. Two recrystallizations from 35 ml of acetonitrile gave 2.26 g (60% based on P_5-OH) with mp 138–139 °C; ^{1}H NMR (acetone-d_6) δ 1.62 (s, $\Delta\nu_{1/2}$ = 10 Hz, 6 H), 2.20 (m, 4 H), 5.31 (heptet, 1 H), 6.80 (s, 2 H, exchanges fairly rapidly with solvent); ir (KBr disk) 3000–2700 (br), 2925 (s), 2845 (s), 1970 (m), 1130 (vs), 1005 (vs), 955 cm^{-1} (vs); mass spectrum (70 eV) *m/e* 188 (mi), 133 (base).

Anal. Calcd for $C_8H_{13}O_3P$: C, 51.06; H, 6.91; P, 16.49. Found: C, 51.25; H, 6.87; P, 16.54.

Isolation of H_5-OH. NMR experiments described in the text indicated that A_5-PO_3H_2 rearranged cleanly to H_5-OH under a variety of conditions. However, isolated yields were well below quantitative. The highest isolated yields were obtained as follows. A_5-PO_3H_2 (1.467 g) was dissolved in 30 ml of 50% aqueous dioxane and 6 ml of concentrated HCl. The solution was heated to 63 °C for 25 h, at which point ^{1}H NMR showed only H_5-OH. The golden solution was rotary evaporated (0.1 mm, 25 °C) to dryness, dissolved in 20 ml of acetone, and again evaporated to dryness (0.1 mm overnight). The remaining dark oil (1.65 g) was dissolved in 3 ml of acetone, cooled, the vessel scratched, and the mixture allowed to stand at −25 °C overnight. The resulting two crops (0.72 g) were recrystallized from acetone to give 0.55 g (38%): mp 151–152.5 °C; ^{1}H NMR ($DCCl_3$) δ 1.68 (s, $\Delta\nu_{1/2}$ = 4 Hz, 10 H), 6.14 (dd, J_{HH} = 8.5, J_{PH} = 32.5 Hz, 1 H), 6.95 (dd, J_{HH} = 8.5, J_{PH} = 47.5 Hz, 1 H), 11.65 (s, 1 H); ^{31}P NMR ($HCCl_3$, external H_3PO_4) δ −43.4 (dd, J = 32 and 47 Hz); ir ($CHCl_3$) 3000–2600 (br), 3000 (w), 2940 (s), 2860 (m), 1600 (m), 1460 (m), 1330 (m), 1210 (s), 1000 (s), 955 (s), 910 (m), 860 (m), 750 cm^{-1} (vs); MS (70 eV) *m/e* 188 (mi), 133 (base).

Anal. Calcd for $C_8H_{13}O_3P$: C, 51.06; H, 6.91; P, 16.49. Found: C, 50.85; H, 6.94; P, 16.40.

Direct Preparation of H_5-OH. Crude A_5-$POCl_2$ (4.00 g) was dissolved in 25 ml of 50% aqueous dioxane and 2 ml of concentrated HCl, and the solution heated to 64 °C for 89 h. Workup as above and two recrystallizations from acetone gave 1.16 g (35%) of H_5-OH. This exceeds the yield via isolated A_5-PO_3H_2 (25% overall).

Reaction of P_6-OH with PTC. Using the same procedure as with P_4-OH and P_5-OH, 2.78 g (25.3 mmol) of the alcohol was reacted with 3.58 g (26 mmol) of PTC, both in 40 ml of CH_2Cl_2. Addition (50 min,

23 °C),[14] stirring (85 min, 24 °C), and rotary evaporation gave 3.63 g (68%) of crude A_6-$POCl_2$ (ir 1950 cm^{-1}; ^1H NMR d of quintet, J_{PH} = 28 Hz). This was added over 10 min to 20 ml of 50% aqueous dioxane (0 °C) along with 1.45 g of sodium bicarbonate. Exhaustive rotary evaporation (0.1 mm) gave 3.61 g of solid which was treated with 35 ml of hot dioxane, filtered (mass NaCl = 0.97 g), and concentrated, and the residue was recrystallized from acetone to give 2.07 g of A_6-PO_3H_2 (40% from P_6-OH): mp 142–143 °C dec; ^1H NMR (dioxane-d_8, D_2O) δ 1.70 (m, 4 H), 2.50 (m, 4 H), 4.80 (s, 1 H as HOD), 5.37 (apparent septet, 1 H); ir (KBr) 3000–2600 (br), 2950 (s), 1960 (m), 1125 (vs), 1000 (vs), 960 cm^{-1} (vs); MS (70 eV) *m/e* 174 (mi), 148 (base).

Anal. Calcd for $C_7H_{11}O_3P$: C, 48.28; H, 6.32. Found: C, 48.58; H, 6.22.

Isolation of H_6-OH. As with H_5-OH, isolated yields were always considerably lower than theoretical, although NMR indicated clean conversion. A solution of 503 mg of A_6-PO_3H_2 in 10 ml of 50% aqueous dioxane and 2.0 ml of concentrated HCl was heated to 62 °C for 4.0 hr. (When carried out for 22 h at 45 °C, the cyclization gives slightly lower yields.) The dark brown solution was rotary evaporated (0.1 mm, 25 °C) to dryness, and the resulting dark oil (530 mg) dissolved in 1.5 ml of hot acetone. The solution was seeded or the vessel vigorously scratched, and then placed at −25 °C. Two crops were collected (235 mg), redissolved in 3 ml of hot dioxane, treated with Norite, filtered, and evaporated. Recrystallization from acetone gave two crops (181 mg, 36%) of H_6-OH: mp 159.5–161 °C; ^1H NMR ($CDCl_3$) δ 1.90 (s, $\Delta\nu_{1/2}$ = 3 Hz, 8 H), 6.10 (dd, J_{HH} = 8.5, J_{PH} = 32 Hz, 1 H), 6.94 (dd, J_{HH} = 8.5, J_{PH} = 47.5 Hz, 1 H), 12.03 (s, 1 H); ^{31}P NMR ($CHCl_3$, external H_3PO_4) δ −43.9 (dd, *J* = 32, 47 Hz); ir ($CHCl_3$) 3000–2600 (br), 3010(s), 2965 (s), 2870 (m), 1600 (s), 1350 (s), 1205 (vs), 1000 (vs), 975 cm^{-1} (vs); MS (70 eV) *m/e* 174 (mi), 146 (base).

Anal. Calcd for $C_7H_{11}O_3P$: C, 48.28; H, 6.32; P, 17.82. Found: C, 48.37; H, 6.28; P, 18.47.

Reaction of P_7-OH with PTC. The usual procedure was used with 2.80 g (20 mmol) of P_7-OH and 4.50 g (33 mmol) of PTC in a total of 40 ml of CCl_4. Addition period: 2.6 h at 0 °C; stir for 5.5 h at 25 °C.[14] Rotary evaporation (10 mm, 25 °C) left 2.84 g of a mixture comprised of 80% A_7-$POCl_2$ [δ (CCl_4) (s, 9 H), 1.85 (d, J_{PH} = 11.5 Hz, 6 H); ir 1950, 1260 cm^{-1}] and 10% P_7-Cl[15] [δ 1.22 (s, 9 H), 1.78 (s, 6 H); ir 2225 cm^{-1}].

The mixture was dissolved in 10 ml of dioxane and the solution was added dropwise to 10 ml of water at 0 °C over 15 min. Rotary evaporation to dryness (0.1 mm overnight) left 2.30 g of the crude product which was recrystallized slowly from CH_3CN to give 1.30 g (32%) of material with mp 175–176 °C.

Spectral data: ^1H NMR (acetone-d_6) δ 1.23 (s, 9 H), 1.73 (d, *J* = 6.4 Hz, 6 H), 8.15 (s, 2 H); ir (acetone-d_6) 3600–2000 (br), 2940, 1945, 1225, 1190, 1000 cm^{-1}; MS (20 eV) *m/e* 204 (mi), 148 (base).

Anal. Calcd for $C_9H_{17}O_3P$: C, 52.93; H, 8.39. Found: C, 52.71; H, 8.50.

Rearrangement of A_7-PO_3H_2. The allenic phosphonic acid (380 mg) was dissolved in 10 ml of 50% aqueous dioxane and 2.0 ml of concentrated HCl and the solution heated to 88 °C for 10 h (4 half-lives). The yellow solution was rotary evaporated to dryness (0.1 min, 40 °C), leaving ~400 mg of crude H_7-OH. This was recrystallized from acetone/heptane (3/2 v/v) to give 260 mg (69%), mp 235–236 °C.

Spectral data: ^1H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 1.46 (s, 6 H), 6.50 (d, J_{PH} = 47 Hz, 1 H), 12.2 (s, 1 H); ir ($CDCl_3$) 3300–1900 (very broad), 2990, 1470, 1380, 1305, 1280, 1230 (vs), 1165, 1000, 840 cm^{-1}; MS (30 eV) *m/e* 204 (mi), 189 (base).

Anal. Calcd for $C_9H_{17}O_3P$: C, 52.93; H, 8.39. Found: C, 52.71; H, 8.63.

Reaction of P_2-OH with PTC. The usual procedure was used with 2.73 g (15 mmol) of the alcohol[11] and 6.18 g (45 mmol) of PTC in a total of 200 ml of CH_2Cl_2. Addition time: 220 min at 0 °C, stir for 3.5 h at 25 °C. Rotary evaporation and centrifugation to remove a highly unstable oily solid[14] gave 2.32 g of a mixture of IV, P_2-Cl, and A_2-POCl in the ratio 5:5:1. The first two of these could be separated by preparative TLC (silica gel, pentane). Spectral data: IV, ^1H NMR (CCl_4) δ 1.10 (s, 9 H), 1.25 (s, 9 H), 5.08 (s, 2 H); ir (CCl_4) 2210, 1670, 1600 cm^{-1}; uv (cyclohexane) λ_{max} 222 nm (ε 1230), 232 (1045); MS (70 eV) *m/e* 164 (mi), 57 (100); P_2-Cl, ^1H NMR (CCl_4) δ 1.15 (s, 9 H), 1.20 (s, 9 H), 1.73 (s, 3 H); MS (70 eV) virtually superimposable on that of IV, no molecular ion; A_2-$POCl_2$, ^1H NMR (CC_4) δ 1.15 (s), 1.30 (s), 1.83 (d, *J* = 11 Hz); ir (CCl_4) 1950, 1280 cm^{-1}. Attempts to hydrolyze this mixture and recover A_2-PO_3H_2 were unsuccessful.

Reaction of P_3-OH with PTC. The usual conditions were employed with 0.70 g (5.0 mmol) of PTC and 1.12 g (5.0 mmol) of P_3-OH[12] in a total of 15 ml of CH_2Cl_2. Addition period: 24 min at 25 °C, stir for 75 min at 30 °C. Rotary evaporation (10 min, 25 °C) left 1.11 g (92%) of A_3-Cl: ^1H NMR (CCl_4) δ 1.15 (s, 9 H), 1.22 (s, 18 H); ir ($CHCl_3$) 2960 (vs), 1940 (m), 1395 (m), 1360 (s), 1240 (s), 1040 (m), 995 (m), 920 cm^{-1} (s); MS (70 eV) *m/e* 242, 244 (mi), 150 (base).

Reaction of Propargyl Alcohol (P_8-OH). In the usual way 2.24 g (40 mmol) of the alcohol in 80 ml of CH_2Cl_2 was added to 16.48 g (120 mmol) of PTC in 80 ml of CH_2Cl_2 over 145 min at 0 °C. After addition, rotary evaporation (10 min, room temperature) left 4.52 g (72%) of P_8-$OPCl_2$, whose spectra are given in the text. This was redissolved in 30 ml of hydrocarbon-stabilized chloroform and heated to 61 °C for 10.5 h. Rotary evaporation left 2.45 g (71%) of crude A_8-$POCl_2$, whose spectra are given in the text.

Hydrolysis of A_8-$POCl_2$. The allene (2.23 g, 1.42 mmol) was added dropwise to 20 ml of 50% aqueous dioxane at 0 °C over 5 min. Rotary evaporation (0.1 min, 40 °C) left 1.58 g (93% based on A_8-$POCl_2$, 66% based on P_8-OH) of a pale yellow oil which crystallized upon standing at −25 °C, mp 43–55 °C. It could not be recrystallized: ^1H NMR (acetone-d_6)[8] δ 5.07 (~dd, $^4J_{PH}$ = 13.4, J_{HH} = 6.6 Hz, ~2 H), 5.47 (~dt, $^2J_{PH}$ = 5.4, J_{HH} = 6.6 Hz, ~1 H), 10.5 (s, 2 H); ir (CH_3CN) 3500–1800 (v broad), 1940 (br), 1210 (br).

Methanolysis of A_8-$POCl_2$. The allene (2.22 g, 1.42 mmol) was added over 15 min to 20 ml of anhydrous methanol at 0 °C. Rotary evaporation (10 mm, 30 °C) left 2.16 g of a pale yellow liquid. Distillation gave 1.26 g (43% based on P_8-OH): bp 46–47 °C (0.08 mm); ^1H NMR (CCl_4) δ 3.70 (d, J_{PH} = 11 Hz, 6 H), 5.03 (~dd, J_{PH} = 12.8, J_{HH} = 6.6 Hz, 2 H), 5.22 (~dt, J_{PH} = 5.6, J_{HH} = 6.6 Hz, 1 H);[8] ir (CCl_4) 3045, 2950, 2840, 1970, 1940,[17] 1470, 1265, 1180, 1040, 835 cm^{-1}; MS (20 eV) *m/e* 148 (mi, 100%), 109 (base). A satisfactory elemental analysis could not be obtained.[18]

Attempted Cyclization of A_8-PO_3H_2. A solution of the allenic acid (40 mg), 0.10 ml of D_2O, 0.10 ml of dioxane, and 0.10 ml of 70% perchloric acid was heated to 94 °C for 46 h. Although the solution had darkened, ^1H NMR showed only solvent and starting material.

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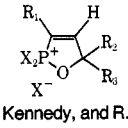
Registry No.—A_2-$POCl_2$, 59474-10-1; A_3-Cl, 37892-65-2; A_4-$POCl_2$, 13337-33-2; A_4-PO_3H_2, 1831-37-4; A_4-$PO(OCH_3)_2$, 17166-43-7; A_5-$POCl_2$, 59474-11-2; A_5-PO_3H_2, 1831-36-3; A_6-$POCl_2$, 59474-12-3; A_6-PO_3H_2, 59474-13-4; A_7-$POCl_2$, 59474-14-5; A_7-PO_3H_2, 59474-15-6; A_8-$POCl_2$, 17166-36-8; A_8-PO_3H_2, 34163-96-7; A_8-$PO(OCH_3)_2$, 18356-17-7; H_4-OH, 59474-16-7; H_4-OCH_3, 59474-17-8; H_5-OH, 59474-18-9; H_6-OH, 59474-19-0; H_7-OH, 59474-20-3; P_2-Cl, 59474-21-4; P_2-OH, 36187-02-7; P_3-OH, 36187-03-8; P_4-OH, 115-19-5; P_5-OH, 78-27-3; P_6-OH, 17356-19-3; P_7-OH, 1522-16-3; P_8-$OPCl_2$, 17166-44-8; P_8-OH, 107-19-7; PTC, 7719-12-2; IV, 59474-22-5.

References and Notes

(1) Part of this work was taken from the Ph.D. Thesis of E.R.K., University of Cincinnati, 1975.
(2) Previous paper in the series: E. R. Kennedy and R. S. Macomber, *J. Org. Chem.*, **39**, 1952 (1974).
(3) R. S. Macomber, *J. Org. Chem.*, **36**, 2713 (1971).
(4) The unhydrolyzed precursors of H–X might exist as salts.[3]



(5) R. C. Elder, L. R. Florian, E. R. Kennedy, and R. S. Macomber, *J. Org. Chem.*, **38**, 4177 (1973).
(6) Several other solvents were found[5] to give inferior results.
(7) During the subsequent reaction the "O–H" absorption moved steadily downfield, reaching δ 4.98 after 4 h (35 °C).
(8) For several of the compounds in this study, the ^1H NMR coupling schemes cannot be uniquely determined by first-order analysis. In such cases, the spectra were simulated (LAOCOON III[9]) to extract the true chemical shifts and coupling constants. Copies of the ^1H NMR spectra of any compound described in this paper will be supplied upon request.
(9) S. Castellano and A. A. Bothner-By, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, No. 111.
(10) R. S. Macomber, *J. Org. Chem.*, **38**, 816 (1973).
(11) A. I. Zehkarova and G. M. Murashov, *Zh. Obshch. Khim.*, **23**, 1981 (1953); *Chem. Abstr.*, **49**, 3783*i* (1955).
(12) M. D. Schlavelli, R. P. Gilbert, W. A. Boynton, and C. J. Boswell, *J. Am. Chem. Soc.*, **93**, 6989 (1971); R. S. Macomber, *J. Org. Chem.*, **37**, 1205 (1972).
(13) Samples of the oxaphospholenes and allenic phosphonic acids were vacuum dried before analysis.
(14) These reactions also produced an insoluble oily solid. Attempted isolation gave highly unstable materials whose ^1H NMR spectra did not resemble the desired phosphorus-containing products. This accounts in part for the lower yield.
(15) Some P_7-Cl (bp 81 °C, 100 mm)[16] is lost during rotary evaporation.

(16) G. F. Hennion and T. F. Banigan, Jr., J. Am. Chem. Soc., 68, 1202 (1946).
(17) The doublet out-of-phase allene stretch is uncommon, but known: N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N.Y., 1975, p 237.
(18) Both A_4-$PO(OCH_3)_2$ and A_8-$PO(OCH_3)_2$ gave low values for C, H analysis: A_4, C, 45.27; H, 7.11 (theory, C, 47.23; H, 7.44); A_8, C, 39.18; H, 6.00 (theory, C, 40.54; H, 6.13). Both compounds appeared homogeneous by spectroscopy and chromatography. The low values may be due to facile hydrolysis or hygroscopicity.

α-Substituted Toluenes and 3-Substituted Propenes. Evaluation of Substituent Effects via Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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The ^{13}C NMR shielding effects for 12 α-substituted toluenes and nine 3-substituted propenes have been determined. The substituent effects were analyzed by the Taft σ_I and σ_R and by the Swain–Lupton **F** and **R** parameters. No significant difference was observed between the two methods. In the α-substituted toluenes substantial substituent shifts were observed at C_4 (para to methylene), five bonds removed from the substituent. Excellent correlation between the toluenes and propenes was obtained for the methylene and C_1 carbons. A substantial resonance interaction was found to be important to describe the substituent effects at C_1 in toluene and C_2 in propene.

The correlation of the effects of substituents on carbon-13 shieldings is an important facet of the current research in ^{13}C NMR spectroscopy.[1] Once determined, these substituent effects can, in principle, be used to predict chemical shifts and thus lend valuable aid to the interpretation of complex spectra. Substituent effect studies have also played a significant role in the correlation of chemical and physical properties with molecular structure.[2] From the studies of substituent effects on fluorine-19, proton, and carbon-13 chemical shifts in substituted benzenes, it is apparent that the substituent is capable of altering the electronic structure of the aromatic ring in a predictive fashion.[3] Recently, a significant carbon-13 substituent effect through eight covalent bonds was observed for substituted biphenyls.[4] Similar results have been reported using ^{19}F NMR where the substituent effect was transmitted through an "insulating" methylene cavity.[5]

The nature of the transmission of substituent effects in α-substituted toluenes, particularly the halogenated cases, has been addressed by various methods. It has been shown that α-substitution, even by a nitro group, does not markedly affect the ortho–para directability in these systems.[6] The acidity of α-substituted *p*-toluic acids as a function of the α substituent indicated that a π-inductive mechanism was operating.[7] Other studies, including PES spectra, have attributed the substituent effect to a hyperconjugative mechanism.[8,9] Since it has been established that the carbon-13 chemical shift is sensitive to π-charge density,[3a] it would be of interest to see how the carbon-13 chemical shifts behave with respect to a variety of substituents at the benzylic position. Additionally, it should prove informative to compare the substituent effects obtained from aromatic systems to those of the ethylene derivatives, in this instance 3-substituted propenes.

The use of linear free energy relationships has found great utility in the study of substituent effects in NMR spectroscopy.[3b,c] In general, the contributions to the chemical shift changes induced by the substituent are attributable to either inductive or field and resonance effects.[10] In order to obtain the relative importance of these interactions a two (or more) parameter equation such as eq 1 can be used[11]

$$\Delta\delta = aA + bB + i \qquad (1)$$

where $\Delta\delta$ is the chemical shift difference for a particular carbon in the parent compound vs. the same carbon in the substituted case; A is the inductive and field parameter taken together, and B is the resonance parameter. For the purpose of the study herein two different but equally diagnostic forms of eq 1 will be evaluated: that of Swain and Lupton,[11b] where A = **F** and B = **R**, and that of Taft,[11a] where $A = \sigma_I$ and $B = \sigma_{R^\circ}$. The terms a and b (correlation factors) are determined by a minimization of the difference between the experimental chemical shifts and the chemical shifts calculated on the basis of eq 1. The term i is the intercept of the regression analysis and corresponds to the calculated shift of a particular carbon in the parent system.[12] The percent of contribution for each of the correlation factors can be obtained by the relative magnitudes of the absolute a and b values.[11b]

Results

The ^{13}C NMR spectra were recorded in deuteriochloroform solution, and all chemical shifts were determined from proton decoupled spectra using Me_4Si as internal reference.

The carbon-13 chemical shifts for the α-substituted toluenes are given in Table I. The aromatic assignments were determined as follows. The C_1 carbon (methylene substituted carbon) was readily identified by its low intensity and its singlet nature in the proton coupled spectrum. Likewise the assignment of the C_4 carbon could be easily established via intensity considerations since it is only ca. one-half the area of the other two signals. The $C_{2,6}$ and $C_{3,5}$ carbon shift assignments were more difficult to make, and in those cases where the chemical shifts are close, the assignments given in Table I may be reversed. However, when the $C_{2,6}$ and $C_{3,5}$ carbon shifts are separated by more than ca. 0.5 ppm and no overlap with the C_4 resonance occurs, the assignments could be obtained from inspection of the proton coupled spectrum. The $C_{2,6}$ carbon resonance appears as a broad multiplet owing to two different three-bond couplings (protons meta to $C_{2,6}$), a two-bond coupling (protons ortho to $C_{2,6}$) and a four-bond coupling (from the proton para to $C_{2,6}$), while the $C_{3,5}$ carbon resonance appears as a broad doublet owing to one three-bond, two two-bond, and one four-bond couplings.[13] The assignments, see Table III, for the 3-propenes are straightforward,