A Study of 1-Methylphosphole as a Heteroaromatic Substance[1]

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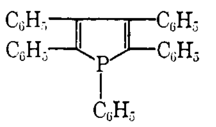
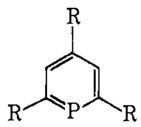
Abstract: A new phosphole synthesis was devised to provide 1-methylphosphole. 1-Methyl-3-phospholene 1-oxide was converted to the 3,4-dibromide, which was then reduced to the phosphine with trichlorosilane. Dehydrohalogenation with potassium *t*-butoxide provided the phosphole. Physical evidence suggested considerable cyclic delocalization of the ring π systems, *e.g.*, the nmr spectra revealed strong deshielding of ring and P–CH$_3$ protons as well as of ^{31}P, and the ultraviolet spectrum showed strong resemblance to that of N-methylpyrrole. Chemically, the phosphole was exceptionally weak as a base and was not prone to undergo certain phosphine complexation reactions; it did, however, react with oxidizing agents and quaternizing halides. The system seems best described as possessing considerable delocalization but retaining the highly characteristic reducing and nucleophilic properties of phosphines.

Until 1959, no phosphorus analog of an aromatic monocyclic nitrogen compound had been prepared. The question of whether such systems could exist was answered with the synthesis of pentaphenylphosphole (I),[2] where the ring system is analogous to pyrrole. A few other phospholes have been synthesized in recent years.[3] A striking new development is the construction of the phosphorus analog of the pyridine system, in the form of several 2,4,6-trisubstituted derivatives (II).[4]



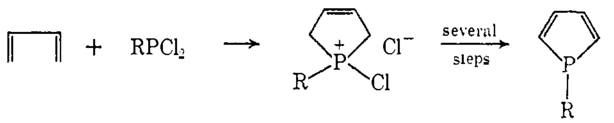
I



II

Thus, there no longer seems to be reason to doubt that a family of phosphorus counterparts of the well-known nitrogen systems is possible. Versatile synthetic methods remain to be developed, however, and the picture with regard to possible aromaticity of these systems is incomplete. In this paper, the phosphole system will receive consideration from these two standpoints.

The phosphole system has frequently been formed in a single ring-closing reaction between a trivalent phosphorus compound and a 1,3-diene derivative or a 1,3-diyne. The intermediates needed for these syntheses limit their versatility. We will describe in this paper a new method which employs the useful condensation of phosphonous dihalides and simple dienes[5] to close the ring in the dihydrophosphole (phospholene) stage, and the subsequent conversion to the phosphole.[6] The specific synthetic objective was 1-methylphosphole; this would be the simplest possible phosphole save for the parent itself, and should be useful in studies on aromaticity of the ring system.



The extent of delocalization of the lone electron pair on phosphorus in phospholes has not been well defined experimentally. HMO calculations (assuming a planar ring) have given a pπ–pπ conjugation energy of 1.49β for the parent phosphole (*cf.* 1.37β for pyrrole), and suggest the presence of a small amount of d$_\pi$–p$_\pi$ resonance.[7] However, it has been difficult to confirm such a substantial degree of resonance stabilization experimentally. This has been due primarily to the lack of suitable compounds for study. When our work was started, every authenticated phosphole had from three to five phenyl substituents; only recently have less highly phenylated compounds (1-phenyl-2,5-dimethylphosphole[8a] and 1-phenylphosphole[8b]) become available. A phenyl substituent is undesirable, as it may contribute conjugative effects tending to obscure the characteristics of the phosphole ring. The best prior evidence in favor of describing the phosphole ring as aromatic was (1) the low heat of oxidation of pentaphenylphosphole to its oxide,[9] 39 kcal/mol less than for the oxidation of trimethylphosphine, and (2) the low-field position (δ 6.39 ppm) of the ring protons in the nmr spectrum of 1-phenyl-2,5-trimethylphosphole.[8a] The former observation suggests the presence of considerable stabilization in the phosphole, in part, however, due to conjugative effects of the phenyl group; the latter shows the deshielding of ring protons characteristic of aromatic systems. Other evidence is conflicting; the phosphorus atom is rather easily oxidized, complexed or quaternized, and the ring undergoes the Diels–Alder reaction with greater ease than might be expected for an aromatic system (for a more detailed discussion, see ref 3).

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(1) Taken from the Ph.D. Dissertation of J. G. B., Duke University, 1968. Inquiries should be directed to L. D. Q. at Duke University. Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute.

(2) E. H. Braye and W. Hübel, *Chem. Ind.* (London), 1250 (1959) [see also E. H. Braye, W. Hübel, and I. Capier, *J. Am. Chem. Soc.*, **83**, 4406 (1961)]; F. C. Leavitt, T. A. Manuel, and F. Johnson, *ibid.*, **81**, 3163 (1959) [see also F. G. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehmann, *ibid.*, **82**, 5099 (1960)].

(3) For a brief review, see G. Märkl, *Angew. Chem.*, 77, 1109 (1965).

(4) G. Märkl, *ibid.*, **78**, 907 (1966).

(5) W. B. McCormack, U. S. Patents 2,663,736 and 2,663,737 (Dec 22, 1953). The subject has been reviewed: L. D. Quin in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

(6) Preliminary communication: L. D. Quin and J. G. Bryson, *J. Am. Chem. Soc.*, **89**, 5984 (1967). Essentially the same method was later reported for the synthesis of 1-phenylphosphole (see ref 8b).

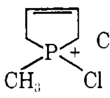
(7) D. A. Brown, *J. Chem. Soc.*, 929 (1962).

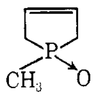
(8) (a) G. Märkl and R. Potthast, *Angew. Chem.*, **79**, 58 (1967); (b) G. Märkl and R. Potthast, *Tetrahedron Letters*, 1755 (1968).

(9) A. P. Clayton, P. A. Fowell, and C. T. Mortimer, *J. Chem. Soc.*, 3284 (1960).

Synthetic Studies

The cycloaddition of butadiene and methylphosphonous dichloride has been reported previously, as has the hydrolysis of adduct III to the phospholene oxide IV and the reduction of III to the phospholene V.[10]


III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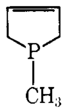
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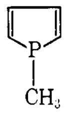
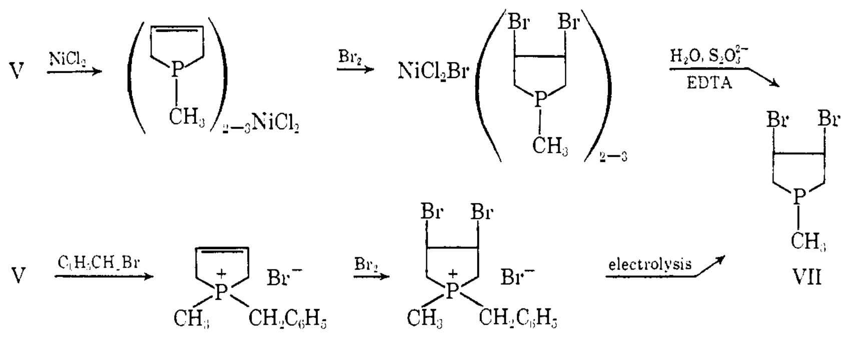
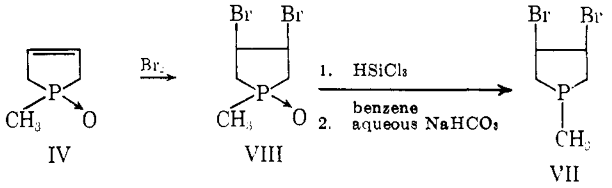

VI



Both IV and V have been considered as precursors of 1-methylphosphole (VI). The most obvious way of obtaining the necessary degree of unsaturation in the ring is to add halogen to the double bond, and perform twofold dehydrohalogenation. Although use of phosphine V in this scheme would be desirable, it cannot be used directly, as halogens add very readily to trivalent phosphorus. Two indirect approaches to utilizing V were unsuccessful, and will be mentioned only briefly. Both consisted of blocking phosphorus with a group hopefully impervious to halogenation, to be removed after the addition of halogen to the double bond. Nickel chloride, which readily forms complexes with phosphines, was tried for this purpose. It did not provide adequate protection of the phosphorus. Although some of the desired product (VII) was indeed obtained (after breaking the complex with EDTA in a reducing medium), the yield was poor and erratic. Another approach employed quaternization to block phosphorus, followed by electrolytic dequaternization.[11] The salt from quaternization of V with benzyl bromide underwent smooth addition of halogen to the double bond. However, attempted debenzylation by electrolysis gave dehalogenation instead, and none of the desired product was obtained.

Oxide IV already contains phosphorus in a form inert to halogen, and the dibromide VIII has been prepared.[10] Deoxygenation of the dibromide would give the desired phosphine VII. Until recently, however, no feasible method for converting a phosphine oxide to a phosphine was known. In 1965, it was announced that certain silane derivatives effected this transformation,[12] and we have used trichlorosilane for the conversion of VIII to VII in acceptable yield (34.5%). A small amount of phospholene V was detected in the reaction mixture, presumably a result of dehalogenation of VII. A trace amount of another product, gas chromatographing as 1-methylphosphole but not otherwise characterized, was also obtained.

Compound VII was a low-melting solid; it was stable at room temperature and could be recrystallized. As a bromophosphine, however, it would be expected to undergo ready self-quaternization or dehydrohalogenation, and in refluxing toluene it rapidly formed a precipitate containing ionic bromine. The product appeared to be a mixture resulting from the occurrence of both reactions and was not further examined. The structure of VII was confirmed by its conversion to a benzyl bromide salt, and by its proton and ^{31}P nmr spectra. The proton spectrum contained methyl, methylene, and methine signals in the proper ratio, and had no vinyl signals. The ^{31}P signal appeared at +41.5 ppm (85% H_3PO_4 standard), consistent with phosphine character (*cf.* to +41.8 for V).



Compound VII was not usually isolated; pentane solutions were subjected to dehydrohalogenation with potassium *t*-butoxide to form phosphole VI. In working up the product, it was necessary to remove an impurity of 1-methyl-3-phospholene (V), carried along as a by-product from the preceding step. This was accomplished by extraction of the pentane solution with 1 *N* hydrochloric acid, which did not noticeably affect the 1-methylphosphole (VI). The basicity of VI is thus revealed to be lower than that of a normal tertiary phosphine, a point of considerable interest to be discussed later. Another feature of importance in the work-up is that 1-methylphosphole is somewhat unstable at elevated temperatures; it can be successfully distilled if prolonged heating is avoided, but considerable loss was encountered on attempts to fractionate the product. Consequently, most of our work was done on a specimen containing a few per cent of residual pentane, the resultant of a rapid distillation without a column. The presence of pentane did not interfere with experiments defining some of the physical and chemical properties of the phosphole. The yield of VI in the dehydrohalogenation was determined by titration of the pentane solution with iodine, assuming that a 1:1 oxidation reaction occurred. This procedure has been found effective for assay of other phosphine solutions. The over-all yield of the phosphole from the dibromophospholane oxide VIII has generally been about 13–15%. Further study of the

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(10) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, 33, 1034 (1968).

(11) L. Horner, F. Rottger, and H. Fuchs, *Chem. Ber.*, **96**, 3141 (1963).

(12) H. Fritzsche, U. Hasserodt, F. Korte, G. Friese, and K. Adrian, *ibid.*, **98**, 171 (1965).

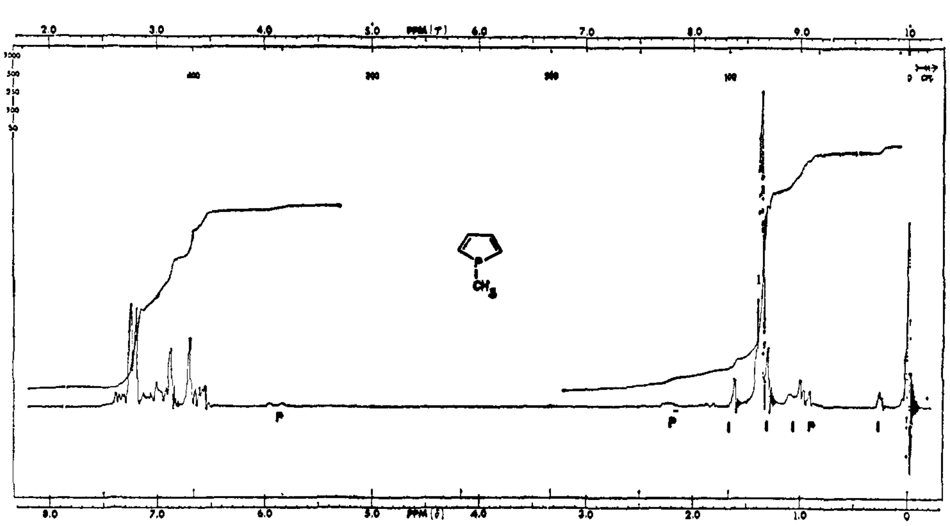


Figure 1. 60-MHz ^1H nmr spectrum of 1-methylphosphole in $CDCl_3$: I, impurity; P, 1-methyl-3-phospholene.

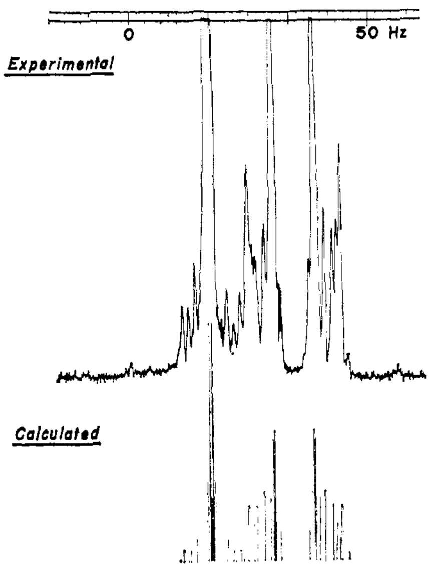


Figure 2. Experimental and calculated 100-MHz ^1H nmr spectrum of neat 1-methylphosphole.

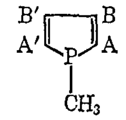
dehydrohalogenation step should improve this figure; no attempts were made to find optimum conditions or reagents.

1-Methylphosphole is a colorless, mobile liquid. A fraction of about 87% purity distilled at 82–83° (317 mm). It is quite soluble in organic solvents but only slightly soluble in water. A sample maintained in a sealed nmr tube showed no change in its spectrum over a period of several months at room temperature, although a trace of yellow gum deposited on the tube walls.

Physical Properties

Proton Nmr Spectrum. The ^1H nmr spectrum of 1-methylphosphole in $CDCl_3$ with internal TMS at 60 MHz is shown in Figure 1. The methyl protons appear as a singlet at δ 1.38 ppm. This apparent lack of coupling appears to be due to a coincidental cancellation of the positive and negative terms which contribute to the spin–spin interaction between ^{31}P and ^1H in the P–C–H group. It does not seem unreasonable that J_{PCH} could be near zero for 1-methylphosphole, since J_{PCH} is positve (but small) for $(CH_3)_3P$ and $(CH_3)_2C_6H_5P$ but negative for $(CH_3)(C_6H_5)_2P$.[13,14]

Table I. Calculated[15] Nmr Parameters for Ring Protons of 1-Methylphosphole



$\Delta\nu_{AB}$ = 7.43 ± 0.10 Hz at 100 MHz
$J_{AA'}$ = 3.01 ± 0.14 Hz
J_{AB} = $J_{A'B'}$ = 7.24 ± 0.11 Hz
$J_{AB'}$ = $J_{A'B}$ = 1.12 ± 0.07 Hz
J_{AX} = $J_{A'X}$ = 38.49 ± 0.21 Hz
$J_{BB'}$ = 1.96 ± 0.13 Hz
J_{BX} = $J_{B'X}$ = 13.77 ± 0.20 Hz

The ring protons at δ 6.5–7.5 ppm give a second-order spectrum which has been analyzed as an AA'BB' part of an AA'BB'X system, where X = ^{31}P. The spectral analysis was performed with a 360 IBM Model 75 computer and the LAOCN3 iterative program.[15] The calculated values of the spectral parameters are given in Table I. There is very good agreement between the observed and calculated spectrum as seen in Figure 2. The calculations do not indicate whether A (and A') or B (and B') are the α- or the β-protons of 1-methylphosphole. However, the value of J_{BX} is close to values of 12.5 and 10.8 Hz obtained for $J_{PH\beta}$ in 2,5-dimethyl-1-phenylphosphole[8] and 1,2,5-triphenylphosphole,[16] respectively. Also, in 3-methyl-1-phenyl-2-phospholene, $J_{PH\alpha}$ is 42 Hz,[10] and in selenophene $J_{SeH\alpha}$ and $J_{SeH\beta}$ have been reported[17] as 48 and 9.5 Hz, respectively. These similarities strongly suggest that B and B' are the β-protons and that A and A' are the

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(13) S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966).

(14) G. Mavel in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. I, by J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, England, 1966, p 266.

(15) S. Castellano, C. Sun, and R. Kostelnik, *J. Chem. Phys.*, **46**, 327 (1967).

(16) C. G. Moreland, unpublished results. Comparison of the 60- and 100-MHz spectra of 1,2,5-triphenylphosphole in THF solution shows a doublet (independent of frequency) in the center of the phenyl region with J_{PH} = 10.8 Hz.

(17) M. L. Hefferman and A. A. Humffray, *Mol. Phys.*, 7, 527 (1963).

α-protons. In acyclic organophosphorus compounds $|J_{PH\alpha}|$ is generally less than $|J_{PH\beta}|$,[18] but our assignments would make $|J_{PH\alpha}$ considerably greater than $|J_{PH\beta}|$ for 1-methylphosphole. It should be noted that this assignment leads to a value of 1.96 Hz for $J_{H\beta H\beta}$ and 3.01 Hz for $J_{H\alpha H\alpha}$, both values being different from similar values reported for pyrroles.[19] A calculated spectrum using $J_{H\beta H\beta}$ as 3.50 Hz (the usual value for five-membered heteroaromatics[17, 19]) did not fit the experimental spectrum as well as the one reported in Figure 2. Also, the value of 7.24 Hz for $J_{H\alpha H\beta}$ is significantly larger than values reported for $J_{H\alpha H\beta}$ (2.4–3.1 Hz) for pyrroles.[19] These couplings constants are also different from the respective coupling constants reported for thiophene,[20] furan,[21] and selenophene.[17] According to the work of Abraham and Bernstein,[22] this would seem to imply a difference in the angles of 1-methylphosphole from these five-membered heterocycles.

The chemical shift of the α- and β-protons of 1-methylphosphole (~7.00 ppm from TMS) is close to the chemical shift of the ring protons in thiophene (7.13–7.35 ppm).[23] This similarity suggests that the deshielding of the ring protons in 1-methylphosphole results from the anisotropic magnetic susceptibility of the ring, *i.e.*, "ring-current" effect. Also the chemical shift of P–Me protons (1.38 ppm from TMS) is at lower field than the P–Me protons of 1-methyl-3-phospholene (0.92 ppm). This difference is close to the 0.55-ppm difference between the methyl protons of 2-methylthiophene and 4,5-dihydro-2-methylthiophene.[23]

The ^1H nmr resonances for neat 1-methylphosphole differ only slightly from those obtained after dilution with $CDCl_3$ or TMS. This indicates that the molecules of 1-methylphosphole are not associated in the neat liquid.

^{31}P Nmr Spectrum. The ^{31}P nmr spectrum of neat 1-methylphosphle at 40.5 MHz is shown in Figure 3. The ^{31}P chemical shift of the neat liquid is +8.7 ± 0.1 ppm relative to external 85% phosphoric acid. The small splitting of each of the 11 lines is due to the weak coupling of the phosphorus with the methyl protons.

The ^{31}P chemical shifts of 1-methyl-3-phospholene, ethyldivinylphosphine, and trivinylphosphine were found to be +41.8 ± 0.1, +20.8 ± 0.5, and 20.7 ± 0.5 ppm, respectively, relative to external 85% phosphoric acid. The low-field shift of phosphorus in 1-methylphosphole relative to these compounds can possibly be attributed to the delocalization of the lone pair of electrons on phosphorus into the cyclic π system.

Ultraviolet Spectrum. The uv spectrum is quite simple, and possesses a single maximum at 286 mμ (log ε 3.89, f_i = 0.17) in isooctane. The peak shows no vibrational fine structure; this is also lacking in the vapor spectrum (λ_{max} 280.6 mμ). There is strong end absorption.

This spectrum is totally unlike that of a tertiary phosphine, where the $n \rightarrow \sigma^*$ transition for an electron of the lone pair would fall below 210 mμ.[24] Nor does it resemble a divinylalkylphosphine; very recently, data have been published for a number of such phosphines,[24] and bands attributed to promotion of an n electron to a π* vinyl orbital were observed in the 200–246-mμ range. Ethyldivinylphosphine, the closest noncyclic analog of 1-methylphosphole for which data are available, absorbs at 236 mμ (log ε 3.719).[24] Data are not available for a dialkyl(butadienyl)phosphine, but it seems unlikely that the phosphino group would shift the butadiene maximum from 214 mμ to the observed range. The 286-mμ band of 1-methylphosphole is therefore unique, and cannot be accounted for if the compound is considered simply as a cyclic divinylphosphine. Furthermore, the spectrum resembles that of N-methylpyrrole, λ_{max} 280 mμ (log ε 2.06),[25] suggesting that similar electronic excitations occur for the two ring systems.

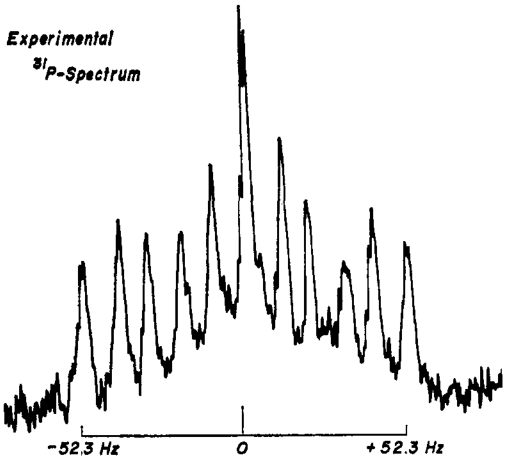

Figure 3. 40.5-MHz ^{31}P nmr spectrum of neat 1-methylphosphole.

Mass Spectrum. The mass spectrum of VI has several features in common with the related heterocycles furan, thiophene, and N-methylpyrrole. The spectrum at 70 eV is reported in Table II. The molecular ion peak (M^+) of *m/e* 98 is the strongest signal, with a relative abundance of 12.6%. Strong M^+ peaks are characteristic of the related heteroaromatics,[26] and

Table II. Prominent Peaks in the Mass Spectrum of 1-Methylphosphole[a]

m/e	Ion	Abundance[b]
99 (M^+ + 1)	$C_5H_8P^+$	14
98 (M^+)	$C_5H_7P^+$	100
97	$C_5H_6P^+$	98
96	$C_5H_5P^+$	26
83	$C_4H_4P^+$	47
71	$C_3H_4P^+$	26
70	$C_3H_3P^+$	26
57	$C_2H_2P^+$	87
56	C_2HP^+	31
45	CH_2P^+	33
39	$C_3H_3^+$	36

[a] Interference by peaks due to impurities of pentane and *t*-butyl alcohol has been accounted for. [b] Relative to M^+ as 100.

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(18) Reference 14, p 269.

(19) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Oxford, England, 1966, p 788.

(20) Reference 19, pp 804.

(21) Reference 19, pp 782–783.

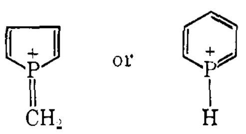
(22) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961).

(23) R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, *B*, 127 (1966).

(24) M. A. Weiner and G. Pasternack, *J. Org. Chem.*, **32**, 3706 (1967).

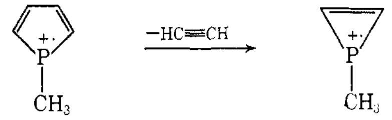
(25) Sadtler UV Catalog, Sadtler Research Laboratories, Philadelphia, Pa., spectrum no. 6851 U, p 1911.

attest to the stability of the ring system. Cleavage of methyl from M^+ might account for the peaks at *m/e* 83 of rather high intensity (47% of M^+). Loss of a hydrogen radical from M^+ accounts for the strong *m/e* 97 peak (98% of M^+); a similar peak is of equal importance in the spectrum of N-methylpyrrole, where it is believed that the methyl group is the source of the hydrogen. As in the pyrrole case, the fragment could conceivably have either a five- or six-membered ring, but no evidence bears on this point.



m/e 97

Ring-opening fragmentations of M^+ could include loss of acetylene to form the ion of *m/e* 72 (11% of M^+).



M^+ *m/e* 72

Fragments of analogous structure are postulated for N-methylpyrrole and thiophene; the prominent *m/e* 57 peak may arise from loss of methyl from this fragment. A *m/e* 39 fragment, prominent in the spectra of furan, thiophene, pyrrole, and N-methylpyrrole, is believed to be the cyclopropenium ion.[26,27] Such a peak also appears in the spectrum of VI.

Chemical Properties

Basicity. It has already been noted that 1-methylphosphole is less basic than 1-methyl-3-phospholene; it was not extracted from pentane even by 2 *N* hydrochloric acid, whereas the phospholene was readily extracted. With stronger acid (6 *N*), however, the phosphole was removed from the pentane. On neutralization, a brown precipitate formed, and the solution turned yellow. None of the phosphole was recovered; it had presumably been converted to polymeric material. The general behavior is similar to that well known for simple pyrroles; their basicity is quite low due to the high degree of resonance stabilization, and their stability in acid is notoriously poor.

When the very dilute (10^{-3} *M*) solution resulting from saturating water with VI was strongly acidified, the characteristic peak in the uv spectrum of the phosphole (284 mμ) disappeared, and was not replaced by new absorption near this region. This observation suggested that a pK_a value could be obtained readily from measurements of absorbance due to unprotonated phosphole (A_{VI}) in water and in dilute acid, using eq 1.

$$pK_a = pH - \log\frac{(A_{VI} \text{ in } H_2O)}{(A_{VI} \text{ in } H_2O) - (A_{VI} \text{ in acid})} \qquad (1)$$

The denominator in the log function is a measure of the concentration of the protonated phosphole. Activity effects are ignored. A complicating factor is the instability of the acidic solutions; the absorbance dropped almost instantaneously on addition of acid, presumably due to the protonation process, and then decreased slowly as decomposition occurred. The plot of log *A vs.* time was linear for the first few minutes of the decomposition process. To obtain the absorbance of unprotonated phosphole at the moment when acid was added, the linear portion of the curve was extrapolated to zero time. Measurements were made at two different acid concentrations; results are given in Table III. The average pK_a was 0.5. The value is below that expected for a saturated tertiary phosphine by about 7–8 pK_a units. More appropriate models for comparison, however, would be divinylphosphines, for which no pK_a data are available. Approximate values may be calculated from the expression

Table III. Determinations of pK_a of VI

[HCl], *N*	Absorbance of VI In H_2O	 In HCl	pK_a
0.124	0.202	0.148	0.57
0.250	0.665	0.419	0.49
0.250	0.513	0.316	0.51

$$pK_a = 7.85 - 2.67\sum\sigma^*$$

where $\Sigma\sigma^*$ is the sum of the Taft σ^* values for the substituents on phosphorus.[28] Thus, for $CH_3P(CH{=}CHCH_3)_2$ a value for pK_a of 5.73 may be calculated. Conjugation of the phosphorus lone pair with the π system(s) of the substituents will probably lower this value slightly. For example, the experimental pK_a of triphenylphosphine is 0.5 p*K* unit less than that calculated from the above equation.[28] If it is assumed that a resonance effect of similar importance prevails for the divinyl model, then a value of 5.2 is suggested. On this basis, the pK_a of VI is still about 5 pK_a units low; the best explanation for this property appears to be that the ring system is highly resonance stabilized, as in the pyrrole system.

The site of protonation of the phosphole ring has not been established. It now seems clear that carbon, rather than nitrogen, is protonated in pyrroles,[29] and it will be of interest to consider this point in the phospholes.

Quaternization. 1-Methylphosphole readily reacts with methyl iodide or benzyl bromide to form quaternary salts. The rate of the reaction has not been quantitatively determined, but qualitatively shows no reduction relative to the rate expected for a tertiary phosphine. This property would appear to conflict with the general picture, evident in the preceding discussion, that electron delocalization is extensive in the phosphole ring. However, it is necessary to recall that tertiary phosphines are extremely potent nucleophiles, even more so than tertiary amines, and perhaps this property will not be very greatly affected even in systems where the ground-state energy is reduced through delocalization. This point is certainly due further con-

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[26] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectroscopy of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapters 22–24.

[27] H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman, and J. M. Wilson, *J. Chem. Soc.*, 1949 (1964).

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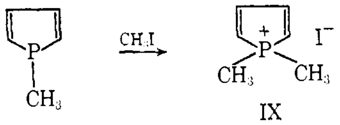
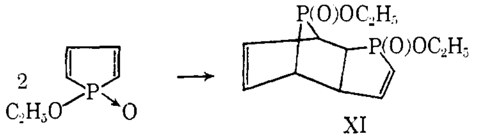
sideration; energy parameters are required for the quaternization of phospholes and related, but not delocalized, systems before meaningful discussion can take place.

The structure of the methiodide of VI deserves comment. While it gives the correct analysis, there is some doubt that its structure is that of the monomeric species IX. Since IX no longer has six π electrons, it should be a highly reactive diene, and polymerization might be expected. This has been observed in the somewhat analogous case of compound X, which rapidly dimerizes to XI.[30] The nmr spectrum of the methiodide of VI was not consistent with structure IX.



VI IX



X XI

In the P–CH$_3$ region, there should be a sharp 6 H doublet. While two broad peaks separated by 14 Hz do appear in the expected position (δ 2.67 ppm), there are a number of smaller broad peaks leading to a complex multiplet in the same region. The number of vinyl protons is also lower than expected for IX. These discrepancies are accentuated after the solution (deuteriochloroform) has been warmed. While it seems likely that the sample is undergoing polymerization in solution, it is not yet clear if the initially precipitated methiodide is monomeric.

When N-methylpyrrole is treated with methyl iodide, attack occurs at the α position rather than at nitrogen.[31] This does not appear to be the case for VI. The nmr spectrum of its methiodide does not suggest the presence of a C–CH$_3$ group, which should appear upfield from the P–CH$_3$ signals.

Oxidation. Tertiary phosphines are highly susceptible to oxidation; some preliminary results suggest that 1-methylphosphole is not exceptional in this respect. A sample exposed to air rapidly formed a gummy, hygroscopic solid; similarly, a water solution exposed to air rapidly lost the characteristic uv absorption at 284 mμ.

The ease of oxidation is also evident in the reaction with halogens. A solution of VI in isooctane rapidly decolorized approximately 1 molar equiv of bromine, with simultaneous precipitation of a solid. The solid, presumably the 1,1-dibromide, was hydrolyzed, and a new substance believed to be the oxide of 1-methylphosphole (or a polymer thereof) was obtained. This compound has not been completely characterized and its structure remains unconfirmed. Its infrared spectrum is similar to that of the product of air oxidation of VI; phosphoryl absorption is evident at about 1200 cm^{-1} and olefinic absorptions are present. It appears, therefore, that bromine has added to phosphorus rather than to the double bonds. Iodine also reacts rapidly with VI, again presumably at phosphorus.

As in the case of quaternization, oxidation destroys the 6π-electron system, and it may seem surprising that oxidation reactions occur so readily. Again, however, the great ease of oxidation of trivalent phosphorus (in the case of air oxidation, with the formation of the very strong phosphoryl bond) must be taken into consideration. A study of the relative rates of oxidation of VI *vs.* suitable model compounds would reveal any diminution of phosphine character in VI through delocalization. In this connection, it was found by gas chromatography that, when iodine was added in small protions to a solution containing both VI and 1-methyl-3-phospholene, the latter was completely consumed before loss of VI could be detected.

A further example of the oxidizability of VI was encountered on reaction with mercuric acetate, where metallic mercury was formed. Tri-*n*-butylphosphine was found to give a similar reaction. This may be contrasted to the behavior of thiophene, which undergoes substitution of a ring proton by the acetoxymercuri group.[32]

Complexation. Another characteristic feature of phosphine chemistry is the tendency to form complexes with metal salts. Thus nickel chloride usually forms highly colored complexes with phosphines in ethanol solution. However, addition of nickel chloride to VI in ethanol resulted in no color formation, and the uv maximum of VI in the solution was unchanged. In benzene solution on adding solid nickel chloride, a change did occur in the uv spectrum of VI, but without typical color formation. Maxima developed at 295, 363, and 475 mμ. A complex thus may have been formed, but not of the normal type. It has not yet been isolated.

Carbon bisulfide also forms red complexes readily with most tertiary phosphines. However, those bearing strongly electronegative groups react slowly or not at all, as is true for trivinylphosphine.[33] On the other hand, ethyldivinylphosphine was found to react, although slowly, to give the usual red complex. 1-Methylphosphole formed no complex with carbon bisulfide, indicating a lower order of reactivity than predicted for a divinyl system.

Conclusions

We believe the bulk of the evidence gathered so far points to a substantial degree of delocalization in 1-methylphosphole, and that the phosphole ring system may be properly included in the family of heteroaromatics, with suitable allowance for the unique character of phosphorus. Evidence supporting this suggestion includes the following. (1) The stability of the system is greater than that expected for a conjugated diene. When protonated, the compound undergoes decomposition, suggesting that this stability depends on the presence of a 6π-electron system. (2) The downfield position of the ring protons in the nmr spectrum accords with that of the related heteroaromatics, and is explainable on the usual basis of anisotropic effects due to a

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ring current. The methyl substituent is similarly displaced downfield. (3) The ^{31}P spectrum suggests a low electron density on phosphorus, relative to a noncyclic divinyl compound, as expected for a delocalized system. (4) The ultraviolet spectrum is very similar to that of N-methylpyrrole and unlike that of a divinylphosphine. (5) The mass spectrum reveals high stability for the molecular ion, in keeping with the related heteroaromatics. The fragmentation pattern is also similar. (6) The basicity of VI is remarkably low, indicating an unusually high energy difference between neutral and protonated forms, possibly attributable to delocalization in the former species. (7) Unsuccessful attempts with VI to form the typical colored complexes with ethanolic nickel chloride and with carbon bisulfide suggest reduced phosphine character.

Qualitatively, it appears that VI retains the high reactivity of a tertiary phosphine to oxidizing agents and to quaternizing halides, as has been noted for other phospholes.[3] However, reduced reactivity toward oxidation by iodine relative to a tertiary phosphine has been detected, and a quantitative study may reveal that the phosphine character of the ring system is diminished beyond that attributable to divinyl substitution. These reactions appear at present to constitute the only evidence against considering VI to be stabilized by delocalization, and their significance must be further evaluated. It should be noted that oxidation and sulfonium ion forming reactions of thiophenes are known; perbenzoic acid oxidizes 2,5-diphenyl- and 2,5-dimethylthiophenes to the nonaromatic 1,1-dioxides in good yield at room temperature,[34] and thiophene forms 5-methyl derivatives with trimethyloxonium fluoroborate or methyl iodide in the presence of silver perchlorate.[35]

In continuing studies of the chemical properties of alkylphospholes, it will be important to examine their behavior in the Diels–Alder reaction, as well as to reactions known to effect substitution of ring protons in the related heteroaromatics. The Diels–Alder reaction is known to take place with some of the phenyl-substituted phospholes; a recent study[36] on the reaction of 1,2,5-triphenylphosphole with dimethyl acetylenedicarboxylate has confirmed the lower reactivity of the system relative to the phosphole oxide, but has shown that the Diels–Alder reaction occurs to a smaller extent than does attack on the triple bond by the phosphorus atom to form a spirobiphosphole with pentacovalent phosphorus. This reaction does not involve the ring double bonds and is analogous to one known to occur with triphenylphosphine.[37] It has been argued that these results indicate 1,2,5-triphenylphosphole to have virtually no aromatic character.[36] However, the data provided suggest that the conditions required to make the phosphole react are more forcing than those required for triphenylphosphine, suggesting diminished phosphine character in the phosphole. As we have already pointed out, the occurrence of phosphine-like reactions does not necessarily prove that significant delocalization is absent in phospholes. However, delocalization would be expected to be accompanied by diminished phosphine-like reactivity.

Experimental Section[38]

Bromination of the Nickel Chloride Complex of 1-Methyl-3-phospholene. A cold solution of 10 g (0.042 mol) of nickel chloride hydrate in 75 ml of absolute ethanol was added to 7.85 g (0.0785 mol) of 1-methyl-3-phospholene.[10] The purple color of the complex developed immediately. After overnight standing, ethanol was stripped, and the residue was washed repeatedly with benzene to extract the complex from nickel chloride. Stripping of the benzene left 10.6 g of crude complex, which was then recrystallized from benzene (yield 7.52 g). Different crops from the crystallization had varying melting point values in the range 111–134° and variable analyses, which indicated a mixture of 2:1 and 3:1 phosphine–nickel chloride complexes. A 5.0-g batch analyzing fairly closely for the 3:1 complex in 200 ml of benzene was treated with a cold solution of 0.072 mol of bromine in 25 ml of benzene. There was a color change from purple to red. With vigorous stirring, the solution was treated with 25 g (0.099 mol) of solid sodium thiosulfate, followed by a solution of 60 g of EDTA and 50 g of sodium bicarbonate in 500 ml of water. After 5 min, the benzene layer was removed and extracted with 4 *N* hydrochloric acid. The acid layer was neutralized with sodium bicarbonate and extracted with ether. The ether was partially stripped, and the residue was treated with a solution of 2 ml of benzyl bromide and 3 ml of ether. The precipitated benzyl bromide salt of 1-methyl-3,4-dibromophospholane (1.97 g, about 15% from the complex) after two recrystallizations from ethyl acetate–methanol had mp 172°.

Anal. Calcd for $C_{12}H_{16}PBr_3$: C, 33.52; H, 3.75; P, 7.20. Found: C, 33.56; H, 3.95; P, 7.40.

The process was not reproducible and occasionally gave none of the desired product.

Bromination of the Benzyl Bromide Salt of 1-Methyl-3-phospholene. The same salt as above was obtained by a different route. A solution of 11.6 g (0.043 mol) of the benzyl bromide salt[10] of 1-methyl-3-phospholene in 100 ml of chloroform was treated slowly with a solution of 5.8 ml (about 0.1 mol) of bromine in 30 ml of chloroform. A red oil, believed to be the benzyl perbromide salt of 1-methyl-3,4-dibromophospholane, was formed; this oil was converted to the benzyl bromide salt by slowly dripping it into acetone. The desired salt formed as a white precipitate in an exothermic reaction. The crude product was washed with acetone and recrystallized from methanol–chloroform, yielding 10.8 g (58.6%) of white crystals, mp 175.5–176.5°, having the same infrared spectrum as that of the salt prepared from the nickel chloride route. Its nmr spectrum in trifluoroacetic acid with external TMS had a phenyl singlet at δ 7.49, a broad 2 H doublet (J = 32 Hz) at δ 5.01 for the protons at the 3 position, a 2 H doublet (J = 15.5 Hz) at δ 4.10 for the benzylic protons, a 4 H methylene multiplet at δ 3.32 (J = 14.5 Hz) and a P–CH_3 doublet (J = 14.5 Hz) at δ 2.24.

1-Methyl-3,4-dibromophospholane Oxide (VIII). This compound was prepared as described previously[10] by adding bromine (0.31 mol) in 50 ml of chloroform to 26.7 g (0.23 mol) of 1-methyl-3-phospholene oxide in 200 ml of chloroform. The reaction mixture was worked up by adding 20 g of ice, neutralizing with sodium bicarbonate, and destroying excess bromine with saturated sodium thiosulfate solution. The mixture was filtered, and both residue and filtrate were extracted with chloroform. The extracts were combined and stripped to yield a yellow solid, which was dissolved in the minimum amount of methanol and filtered to remove some sulfur. Chilling of the methanol caused crystallization of 19.6 g of VIII, mp 144–145° (lit.[10] mp 145.5–146°). The filtrate was treated with charcoal, again filtered, and partially evaporated, providing a second crop which was recystallized from chloroform (16.7 g, mp 139–145°). The total yield was 56.8%.

A second method was also used. A suspension of 167 g (0.98 mol) of the methylphosphonous dichloride–butadiene adduct[10] in 1.2 l. of methylene chloride was chilled and treated with 60 ml (1.1

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[38] Melting points are corrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. All operations involving phosphines were conducted in a nitrogen atmosphere. Gas chromatography was performed with a Wilkins Aerograph 202-B instrument using a 5 ft × 0.25 in. column of SE-30 silicone oil on Chromosorb W, 1:4. Infrared spectra were obtained on a Perkin-Elmer Model 237 spectrophotometer. Ethyldivinylphosphine and trivinylphosphine were kindly supplied by M. A. Weiner and G. Pasternack, City College of New York.

mol) of bromine. After 30 min at room temperature, the mixture was again chilled and treated with 100 g of ice. After treatment with sodium bicarbonate and sodium thiosulfate, the mixture was filtered, and both residue and filtrate extracted with chloroform. The combined extracts were dried with Drierite and stripped to leave 200 g of crude VIII. Crystallization from methanol removed sulfur, and provided 130 g (46%) of VIII, mp 139.5–145°, of identical infrared spectrum to that from the other synthesis. This method has occasionally given a dark oily impurity which makes purification of the product difficult. Carrying out the bromination in a nitrogen atmosphere has helped to overcome this problem.

1-Methyl-3,4-dibromophospholane (VII). A suspension of 100 g (0.362 mol) of oxide VIII in 600 ml of benzene was dried by distillation of 150 ml of the benzene, and the flask was then fitted with a short condenser topped with a Dry Ice condenser. Through a dropping funnel, 130 g (0.97 mol) of trichlorosilane was added to the stirred mixture. A large amount of white solid formed. After 30 min at room temperature, the mixture was slowly heated until trichlorosilane refluxed in the Dry Ice condenser, and was held at this condition for 3.5 hr. With ice-bath cooling and vigorous stirring, the mixture was treated slowly with 100 ml of nitrogen-purged water. Considerable foaming was caused by the evolution of hydrogen chloride. The mixture was filtered on a coarse sintered glass funnel; the benzene layer was separated and washed with water, as was the residue on the funnel. The water washes were added to the acidic aqueous layer of the filtrate; this solution of the hydrochloride of VII was neutralized with sodium bicarbonate and continuously extracted with pentane for 22 hr. Titration with aqueous iodine of 1 ml of the pentane extract in 5 ml of ethanol containing 3 g of sodium bicarbonate revealed the solution to contain 0.136 mol of phosphine (37.5%). However, only about 90% of the phosphine was due to VII; gas chromatography at 100° showed the presence of pentane and three other components: 1.25 min (area 1.0), 1.50 min (area 1.4), 18.3 min (area 17.5). The peak at 18.3 min was due to VII; that at 1.50 min was heightened by addition of 1-methyl-3-phospholene, as was the peak at 1.0 min by addition of 1-methylphosphole. Generally, solutions of this type were used directly for dehydrohalogenation to 1-methylphosphole. Compound VII could be isolated as a crystalline solid, mp 47.5–49°, by chilling the pentane solution. It formed a benzyl bromide salt, mp 172.5–174°, in benzene solution, identical (mixture melting point and infrared spectrum) to that obtained previously from bromination of the benzyl bromide salt of 1-methyl-3-phospholene. Structure VII was further established by ^{31}P nmr (in benzene, +41.5 ppm relative to 85% phosphoric acid), and by ^{1}H nmr (2 H multiplet at δ 3.98 for protons at the 3 position, 4 H multiplet for the methylenes at δ 1.87, and a P-CH_3 doublet (J = 4 Hz) at δ 0.70).

The instability of VII was demonstrated by bringing a toluene solution to reflux, whereupon cloudiness developed, and after 10 min a vigorous exothermic reaction occurred, precipitating much solid. From 2.67 g of VII there was formed 2.28 g of this precipitate after refluxing for 1 hr. The solid was water soluble, contained ionic bromine, and released a phosphine odor on neutralization. It exhibited a P-H signal (2400 cm^{-1}) in its infrared spectrum, and vinyl signals (δ 7.08–5.68) in its nmr spectrum. In part, the solid appears to be a hydrobromide of a dehydrobrominated phosphine from VII. The nmr spectrum showed the sample to be more complex than this, however; the P-CH_3 region seemed to consist of three overlapping doublets (δ 2.37–2.80), and the vinyl signals were small (0.6 H relative to the P-CH_3 signal taken as 3 H). The product was not further examined, and seems best described as a mixture of dehydrobrominated and quaternized material.

1-Methylphosphole (VI). A solution of dibromophosphine VII in pentane was prepared as in the preceding experiment. By iodine titration, the pentane (185 ml) was found to contain 0.125 mol of phosphine. The solution was treated with 35 g (0.312 mol) of potassium *t*-butoxide at room temperature. A mildly exothermic reaction occurred; the mixture was stirred at room temperature for 3 hr. The brown mixture was treated with 20 g of ice; the resulting water layer contained most of the colored matter. The pentane layer was separated, and the water layer extracted twice with 20-ml portions of pentane. The pentane layers were combined and washed with 25 ml of 1 N hydrochloric acid, which removed 1-methyl-3-phospholene revealed to be present by gas chromatography. The pentane solution was washed with 20 ml of saturated sodium bicarbonate solution and then with two 25-ml portions of water. By iodine titration, the pentane was found to contain 0.030 mol of phosphine, a 25% yield if all phosphine is considered to be VI. After drying with Drierite, the pentane was removed on a spinning-band column at 289 mm, using a brine-cooled condenser. When no more pentane could be distilled, the boiling flask was connected to a simple distillation apparatus with a 6-cm uncooled condenser, permitting the distillate to be collected in Dry Ice–acetone chilled receivers. Three fractions were collected: A, 52–73° (251 mm), 0.64 g; B, 83–85° (317 mm), 0.41 g; C, 79° (306 mm), 0.58 g. Gas chromatography at 50° indicated the content of VI to be 25% in A, 84% in B, and 87% in C. The latter peak emerged at 4.8 min. The major impurity in B was pentane (10%), along with 1-methyl-3-phospholene at 5.4 min (2.6%), and two other compounds in smaller amounts. Fraction C contained 3.9% pentane and 5.8% 1-methyl-3-phospholene. Attempts to obtain VI in higher purity by continued fractional distillation of the original pentane solution caused extensive destruction of VI with the formation of solid in the still pot. Fractions such as B and C above were used in experiments defining the properties of 1-methylphosphole.

Physical Properties of 1-Methylphosphole (VI). Proton Nmr. The spectrum was obtained on a Varian A-60 spectrometer on a neat sample with internal TMS (see Figure 1). The spectrum was essentially unchanged when obtained on a 10% or 30% solution in TMS or on a 25% solution in deuteriochloroform. The spectrum at 100 MHz was obtained with a Varian HA-100 spectrometer; the vinyl region is shown in Figure 2.

^{31}P Nmr. The spectrum was obtained with a Varian HA-100 spectrometer at 40.5 MHz on a neat sample with external P_4O_6 standard, and is shown in Figure 3. The ^{31}P chemical shift was +121.2 ± 0.1 ppm from external P_4O_6 (+8.7 ppm from 85% H_3PO_4).

Ultraviolet Spectrum. This was obtained with a Cary 14 spectrophotometer. In isooctane, a peak occurred at 285.7 mμ (log ϵ 3.89); there was also end absorption (200 mμ (log ϵ ~4)). The solutions were very sensitive to oxygen, and the absorbance dropped rapidly if care was not exercised. In water, λ_{max} 284 mμ (log ϵ ~4) was observed; in ethanol, λ_{max} 285; vapor, λ_{max} 280.6 (broad, smooth peak).

Mass spectrum was obtained on a Bendix Model 12 Time-of-Flight Mass Spectrometer with a Model 14 source. The spectrum is summarized in Table II.

Chemical Properties of 1-Methylphosphole (VI). Basicity. A saturated solution of VI was prepared by shaking 50 mg with 2 ml of water. Undissolved VI was removed, leaving a solution of about 10^{-3} M (estimated from the intensity of the ultraviolet absorption of the VI). One portion was treated with an equal volume of water, another with an equal volume of 0.248 N hydrochloric acid. Absorbance values at 284 mμ for each solution were read as rapidly as possible after preparation. The log of absorbance of the water solution changed only slightly and in a linear manner on standing for several hours; the absorbance of this solution at the moment the acidified solution was prepared was calculated. Absorbance of the acid solution dropped virtually instantaneously on preparation, and then dropped more slowly, although faster than the water solution. The plot of log A was linear over a period of several minutes. Extrapolation of the linear portion to the moment the acidified solution was prepared gave the initial absorbance. Data from this experiment, as well as for the use of 0.50 N hydrochloric acid, are given in Table III. The pH of the acid solution was assumed to be insignificantly changed from that of a solution of pure hydrochloric acid of the appropriate strength. pK_a was determined from eq 1.

Reaction with Methyl Iodide. A solution of 3.86 mmol of VI in 9 ml of isooctane was treated with 32 mmol of methyl iodide. The solution formed a white precipitate very rapidly; the solid turned slightly yellow on standing, possibly due to exposure to light. After about 10 min, the solid was filtered and washed with pentane; the yield was 0.35 g (38%). More solid, somewhat gummy, formed in the filtrate on standing. The methiodide was dissolved in ethanol; reprecipitation with pentane gave a white solid mp 189° dec. Another sample crystallized from methanol–ethyl acetate had mp 190–194° dec.

Table IV. Titration with Iodine of a Mixture of V and VI

I_2, ml	Area of VI peak[a]	Area of V peak[a]
0.0	1.0	1.8
0.1	0.9	1.1
0.2	1.0	0.6
0.3	1.1	0.0
0.4	0.7	0.0
0.5	0.0	0.0

[a] Peak areas are corrected for dilution.

Anal. Calcd for $C_6H_{10}IP$: C, 30.02; H, 4.20; I, 52.87; P, 12.91. Found: C, 30.15; H, 4.39; I, 52.63; P, 12.63.

Reaction with Iodine. An ether solution containing VI and 1-methyl-3-phospholene (V) was treated with a solution of iodine in ether. The course of the reaction was followed by gas chromatography at 65°; results are in Table IV. Iodine decolorization was very rapid, but at 0.5 ml of iodine the color persisted.

Reaction with Bromine. A solution of 8.69 mmol of VI in 21.4 ml of isooctane was treated with a solution prepared from 1 ml (18 mmol) of bromine in 100 ml of carbon tetrachloride. After 60 ml had been added, the color of the bromine persisted, indicating that about 10 mmol had reacted. The mixture contained much yellow solid, which was filtered off and washed with isooctane. The solid was dissolved in water and neutralized with sodium bicarbonate. The solution was saturated with potassium sulfate and extracted several times with chloroform. Extracts were combined, dried over Drierite, and evaporated to leave 0.932 g of solid. The crude product contained residual bromide ion (positive test with aqueous silver nitrate). It reduced potassium permanganate solution. Its infrared spectrum showed stretching bands for C=C (1570 cm^{-1}), olefinic C—H (3030 cm^{-1}), and phosphoryl (1200 cm^{-1}).

Reaction with Oxygen. The absorbance at 284 mμ of a saturated water solution of VI in a quartz cell sealed with wax was measured over a period of 6.5 hr. The log of the absorbance decreased in a roughly linear fashion from 0.1858 to 0.1098. When the stopper was removed from a solution of log *A* 0.1098, the absorbance dropped much more rapidly and vanished on long standing. Only end absorption was present in the spectrum.

The Barrelene to Semibullvalene Transformation. Correlation of Excited-State Potential Energy Surfaces with Reactivity. Mechanistic and Exploratory Organic Photochemistry. XLIV[1]

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Abstract: A photochemical transformation of barrelene was observed, wherein a C_8H_8 isomer is produced as the major product; cyclooctatetraene was obtained as a minor product. The structure of the C_8H_8 isomer was elucidated as that of bullvalene minus one vinyl bridge, and the compound was named "semibullvalene." The process was demonstrated to proceed *via* the triplet of barrelene in a process subsequently shown to be general. The irradiation of semibullvalene afforded cyclooctatetraene. It was found that semibullvalene undergoes degenerate valence tautomerism at a faster rate than any previously studied system. Barrelene was labeled at all vinyl positions with deuterium, leaving only the bridgehead positions still bearing hydrogen. The method developed for deuteration of barrelene involved treatment with lithium N-deuteriocyclohexylamide in N,N-dideuteriocyclohexylamine; the method promises to be generally useful for preparing deuterated compounds. The location of the hydrogen label in the semibullvalene photolysis product was investigated and found to fit one of two reasonable mechanisms. The reaction mechanism was shown to proceed *via* a unique bicyclic, allylic, triplet biradical having finite lifetime. The rearrangement was considered from a theoretical viewpoint with the use of three-dimensional Hückel theory, and the results were used to correlate the excited-state potential energy surface with observed photochemical behavior.

Interest in our laboratory has been heavily focused on exploratory and mechanistic organic photochemistry. Consequently, when reasonable quantities of barrelene[2] became available,[2,3] the enticing problem of the photochemistry of barrelene presented itself.

Exploratory Studies of the Photochemistry of Barrelene. Our initial efforts dealt with the direct irradiation of barrelene (*i.e.*, without sensitizer). However, cyclooctatetraene appeared to be the only product, as shown by ir, nmr, and vpc analysis, and our attention turned to the sensitized irradiation. Because of the volatility of barrelene, isopentane was chosen as a solvent, and acetone was selected as a sensitizer; this allowed later solvent removal.

Indeed, the sensitized irradiation of barrelene led to an interesting product, whose development could be followed by nmr. Additionally, cyclooctatetraene was formed in lesser quantity. However, separation of the new product proved unusually difficult because of overlap with the cyclooctatetraene on a large variety of vpc columns. Finally, a method of separation was developed which involved liquid-liquid partition chromatography with a stationary aqueous silver nitrate phase.

The cyclooctatetraene was identified by ir, nmr, and vpc retention time comparison with an authentic sample.

The major product was a colorless, volatile liquid with a strong odor, whose nmr consisted of three multiplets at τ 4.92, 5.83, and 7.03 in a 2:4:2 ratio. The nmr and ir spectra are given in Figure 1. The compound was found to be isomeric with barrelene (C_8H_8) by elemental analysis, and the parent ion of mass 104 found in the mass spectrum confirmed the molecular weight.

There are 16 possible C_8H_8 isomers, of which barrelene,[2,3] cubane,[4] and cyclooctatetraene are known. Interestingly, bonding between atoms 5 and 7, 3 and 6,

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