loss of intensity was observed during the experiment as judged by regular monitoring of three reference reflections so that a single scale factor could be used. No corrections for absorption were deemed necessary.

Crystal Data for *o*-Bromobenzoate 6.—$C_{27}H_{31}BrO_7$ had formula weight 547.4, orthorhombic, a = 11.25 (2), b = 26.63 (4), c = 8.96 (2) Å, U = 2685 Å^3, D_m = 1.34 (by pycnometry with an aqueous ZnI solution), Z = 4, D_c = 1.35, F (000) = 1136. Space group $P2_12_12_1$. Precession photography, Mo K_α radiation, λ 0.7107 Å, μ 17 cm^{-1}.

Structure Determination and Refinement.—The structure was solved by the heavy-atom method in the usual way, and five cycles of Fourier refinement with a single, overall, isotropic thermal parameter, B = 4.0 Å^2, gave R = 0.22.

Further refinement of the structural parameters was by block-diagonal least-squares methods. With anisotropic thermal parameters assumed only for the bromine atom, R was 0.118 at convergence. Inclusion of the anomalous dispersion terms[16] for bromine in the structure factor calculations gave R = 0.123 and 0.116 for the two possible enantiomeric structures. By Hamilton's R-factor ratio test[17] a significant distinction is implied between the two absolute configurations at the 99.5% confidence level. The crystal was accidentally dislodged and lost during the measurement of intensity differences in Friedel pairs of reflections. The very few measurements made confirmed the correctness of the choice indicated by the ratio test.[18]

The least-squares refinement was continued for the favored enantiomorph, and with anisotropic thermal parameters assumed for all atoms R was 0.079 at convergence.

The scattering functions used were those for the neutral atoms.[19] The weighting scheme used was based on counting statistics with some allowance for errors of a nonstatistical nature in the stronger intensities.[20] All calculations were performed on an XDS Sigma 2 computer with programs written in this laboratory.

Registry No.—**1**, 34175-79-6; **2**, 38821-16-8; **3**, 38821-17-9; **4**, 38821-18-0; **5**, 34160-71-9; **6**, 34160-72-0; **7**, 34160-73-1; *o*-bromobenzoyl chloride, 7154-66-7; *p*-bromobenzoyl chloride, 586-75-4.

(16) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(17) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(18) J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature (London)*, **168**, 271 (1951).
(19) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
(20) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957); D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Crystallogr., Sect. B*, **25**, 374 (1969).

Synthesis and Spectral Characterization of Some *C*-Alkylphospholes and Phospholecarboxylates[1]

LOUIS D. QUIN,* STEPHEN G. BORLESKE, AND JOHN F. ENGEL

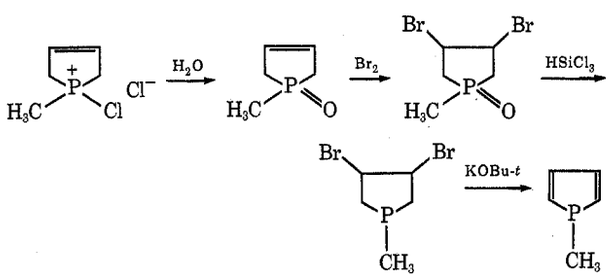
Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Received November 13, 1972

Ten phospholes, bearing either methyl, benzyl, or phenethyl substituents on phosphorus and methyl or carbomethoxy on carbon, have been synthesized by dehydrohalogenation of 3,4-dibromophospholanes or of 1-halophospholenium halides. The two esters prepared are the first phospholes with a reactive functional group. Significant differences were noted in the rates of reaction of phospholes to quaternization with alkyl halides; the fastest reacting phospholes (3,4-dimethyl derivatives) exhibited other differences, including (1) a small blue shift in the characteristic uv maximum of phospholes, (2) diminished allylic coupling between β CH_3 and an α proton, (3) a slight upfield shift of the α proton, and (4) a pronounced upfield shift of the ^{31}P signal. Steric or electronic effects, or a combination of these, are apparently leading to a diminution of electron delocalization from phosphorus in these derivatives. Some of the *P*-methyl phospholes had readily interpreted P–H coupling patterns, permitting experimental verification of computed values made earlier. It was possible to consider the ^{31}P value of the phosphole as derived from definite contributions for the ring fragment and for the P substituent. The phosphorus in phospholes is more strongly deshielded than in 2-phospholenes and in these more than in phospholanes. The carbomethoxy substituent caused quite strong additional deshielding, moderated, however, by steric interaction with a methyl substituent adjacent to it. The sensitivity of the ^{31}P value to conjugative effects is revealed by these observations.

In 1967, we announced[2] the synthesis of 1-methylphosphole, the first phosphole of sufficient structural simplicity to allow a meaningful evaluation[3] of properties of this ring system relative to those of the heteroaromatics thiophene, pyrrole, and furan. This study, as well as subsequent work of others,[4,5] has revealed that the phosphole ring has some of the properties associated with systems partaking of electron delocalization through p_π–p_π bonding. Following our initial work, we proceeded to pursue a synthetic program designed to provide appropriate phospholes for exploring further some unique features present in this system. Some of the results of this study are described in this paper.

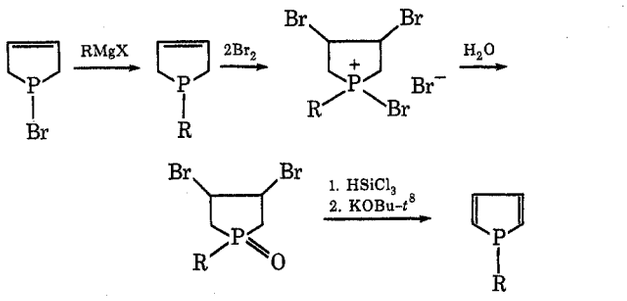
Synthesis.—The phospholene ring system, available from the cycloaddition of dienes and trivalent phosphorus halides,[6] serves as a useful starting point for construction of the phosphole system. Thus, 1-methylphosphole was prepared in our earlier work[2,3] by the following sequence.



(1) Taken from the Ph.D. dissertations of J. F. E. (1971) and S. G. B. (1972). Supported in part by Public Health Service Research Grant CA-05507 from the National Cancer Institute. The National Science Foundation provided funds toward the purchase of the Bruker spectrometer (Grant No. GP 10301), and the AEI spectrometer is sponsored by Special Facilities Grant No. FR-0330-01, National Institutes of Health.
(2) L. D. Quin and J. G. Bryson, *J. Amer. Chem. Soc.*, **89**, 5984 (1967).
(3) L. D. Quin, J. G. Bryson, and C. G. Moreland, *ibid.*, **91**, 3308 (1969).
(4) (a) W. Egan, R. Tang, G. Zon, and K. Mislow, *ibid.*, **92**, 1442 (1970); (b) *ibid.*, **93**, 6205 (1971); (c) A. Rauk, J. D. Andose, U. G. Frick, R. Tang, and K. Mislow, *ibid.*, **93**, 6507 (1971); (d) W. B. Farnham and K. Mislow, *Chem. Commun.*, 469 (1972).
(5) F. Mathey and R. Mankowski-Favelier, *Org. Magn. Resonance*, **4**, 171 (1972).
(6) W. B. McCormack, U. S. Patents 2,663,736 and 2,663,737 (Dec 22, 1953).

Our recent work has provided means for varying the substituent on phosphorus other than that offered by choice of reactants in the cycloaddition process, and has also given access to phospholes with a reactive functional group (*e.g.*, carboxylate). Some of our work has been aided by a new contribution of others to phosphole synthesis: the direct dehydrohalogenation[5] of the McCormack cycloadducts (halophospholenium halides).

Method A.—We have shown[7] that diene–PX_3 cycloadducts can be reduced (dehalogenated) to 1-halophospholenes. These have now been demonstrated to be useful intermediates for the synthesis of dibromophospholane oxide precursors of phospholes.



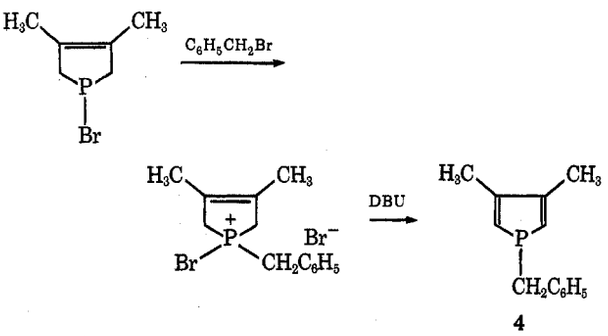
1, R = $CH_2C_6H_5$
2, R = $CH_2CH_2C_6H_5$
3, R = $CH_2CH_2C_6H_4$-*p*-Cl

The first reaction permits the synthesis of a wide variety of P-substituted phospholenes through the Grignard reaction. Addition of 1 mol of bromine to the phospholene occurred selectively at phosphorus; a second 1 mol added to the double bond. The resulting tetrabromo compound could then be hydrolyzed smoothly to the 3,4-dibromo *P*-oxide, which as in our previous work[3] was converted in two steps to the phosphole. One phosphole (1-benzyl, **1**) was also prepared by our earlier[3] route, starting with benzylphosphonous dibromide.

A side reaction, noted previously,[3] leads to contamination of the phosphole with some of the 3-phospholene. Its removal from the phosphole presents no difficulty; the latter is of greatly reduced basicity,[3] and remains in an organic solvent while the 3-phospholene is extracted with 1–2 *N* hydrochloric acid. The 3-phospholene apparently arises from debromination of the 3,4-dibromo system, by either the trichlorosilane[9] or by the phosphine formed in the reduction.[10]

Method B.—The 1-halo-3-phospholenes possess another property of value in phosphole synthesis; phosphorus is of sufficient nucleophilicity that an alkyl group can be added through reaction with an alkyl halide.

Phosphorus halides are generally much less reactive to alkyl halides than are tertiary phosphines, although examples of the alkylation of other phosphinous

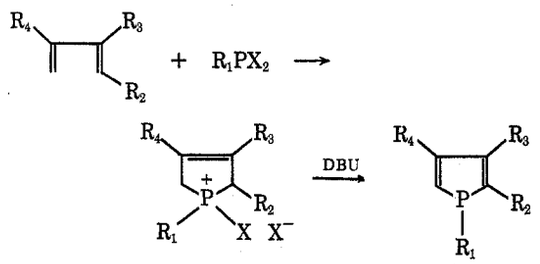


4

halides are known.[11,12] We found that particularly reactive alkyl halides (*e.g.*, benzyl and methyl halides; *n*-butyl bromide failed to react) were required to form phosphonium salts with our cyclic phosphinous bromides. These salts have the same structure as the diene–$RPBr_2$ cycloadducts, and can be converted to phospholes by the steps of our 1-methylphosphole synthesis. Alternatively, dehydrobromination by DBU[5,13] (method C) is possible, and was employed successfully in the synthesis of **4**.

Method B is preferred to method A for the synthesis of 3,4-dimethylphospholes, for the 3,4-dibromo-3,4-dimethylphospholane oxides required in method A are quite susceptible to decomposition *via* dehydrohalogenation.[14]

Method C.—The direct dehydrohalogenation of halophospholenium halides to phospholes[5,13] proceeds with modest yield, but the simplicity of the method makes it attractive where the halides can be readily obtained. We have used it in the synthesis of phospholes **5–8** (10–20% yield).



5–8

Compd	R_1	R_2	R_3	R_4
5	$CH_2C_6H_5$	H	CH_3	H
6	CH_3	CH_3	H	H
7	CH_3	H	CH_3	H
8	CH_3	H	CH_3	CH_3

Method D.—Phospholenecarboxylic esters have been prepared for the first time by the sequence in eq 1 and 2.

The anion from the phospholene oxide is delocalized and is attacked by the electrophile at two sites. Subsequently, rearrangement to the conjugated acids occurs. Sufficient difference in chemical properties of the 2- and 3-phospholene oxide systems existed to allow their separation in useful quantity. The utility of the silane method of oxide reduction is extended by our observation that the presence of an ester function offers no apparent complication. Some other aspects of the synthesis and properties of the products

(7) D. K. Myers and L. D. Quin, *J. Org. Chem.*, **36**, 1285 (1971).

(8) Diazabicycloundecane (DBU) has been successfully used for the corresponding reaction in the synthesis of 1-phenylphosphole [G. Märkl and R. Potthast, *Tetrahedron Lett.*, 1755 (1968)], but it has not given as satisfactory results as *tert*-butoxide in our syntheses.

(9) Trichlorosilane in the presence of triethylamine has been found to debrominate some vicinal dibromides (*e.g.*, *trans*-1,2-dibromocyclohexane): L. D. Quin, R. L. Wells, and R. Maher, unpublished results.

(10) I. J. Borowitz, D. Weiss, and R. K. Crouch, *J. Org. Chem.*, **36**, 2377 (1971).

(11) S. T. McNeilly and J. A. Miller, *J. Chem. Soc. C*, 3007 (1971).

(12) A. P. Stewart and S. Trippett, *ibid.*, 1263 (1970).

(13) F. Mathey, *C. R. Acad. Sci.*, **269**, 1066 (1969).

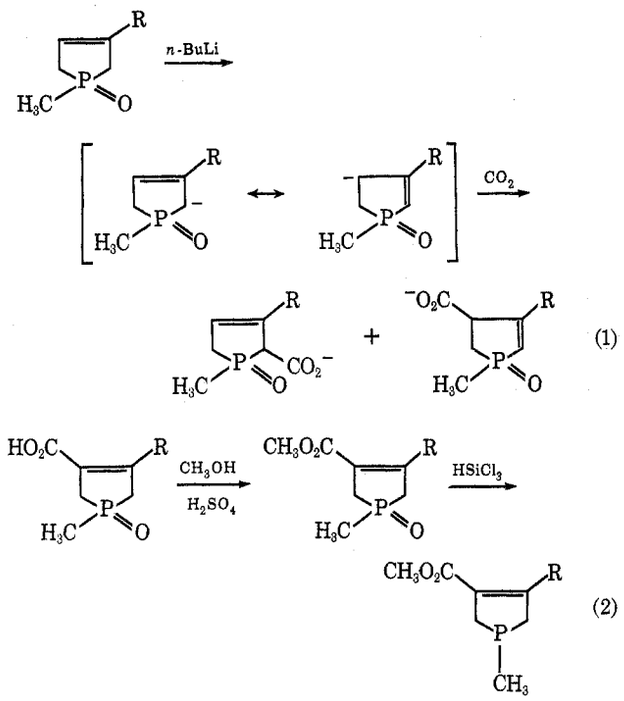
(14) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, **33**, 1034 (1968).

TABLE I

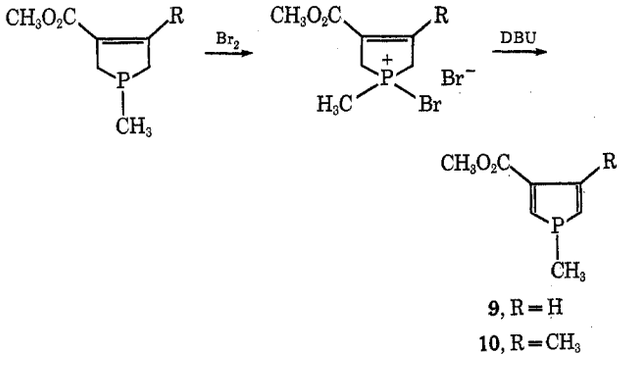
PHOSPHOLES PREPARED AND THEIR SALTS

Phosphole	Synthetic method	Mp, °C	Formula	Quaternary salts C, % Calcd	C, % Found	H, % Calcd	H, % Found	P, % Calcd	P, % Found
1-PhCH$_2$ (**1**)[a]	A	199–201[b,c]	$C_{18}H_{18}BrP$	62.62	62.58	5.26	5.31	8.97	8.74
1-PhCH$_2$-3-Me (**5**)	C	173–176[b,d]	$C_{19}H_{20}BrP$	63.52	62.99	5.61	5.45	8.62	8.78
1-PhCH$_2$-3,4-diMe (**4**)	B	261–264[b,d]	$C_{20}H_{22}BrP$	64.35	64.35	5.94	6.23	8.30	8.43
1,2-diMe (**6**)	C	177–179[c,e]	$C_7H_{12}IP$	33.09	33.02	4.76	4.88	12.19	12.14
1,3-diMe (**7**)	C	193–195[c,e]	$C_7H_{12}IP$	33.09	32.76	4.76	4.66	12.19	11.95
1,3,4-triMe (**8**)	C	181–183[d,e,f]	$C_8H_{14}IP$	35.84	35.80	5.26	5.47	11.55	11.55
1-Ph(CH$_2$)$_2$ (**2**)	A	187–189[b,c]	$C_{19}H_{20}BrP$	63.52	63.24	5.61	5.62	8.62	8.27
1-*p*-ClC$_6$H$_4$(CH$_2$)$_2$ (**3**)	A	116–118[e,g]	$C_{18}H_{15}ClIP$[c]	42.83	42.75	4.15	4.23	8.49	8.32
1-Me-3-COOMe (**9**)	D	*h*							
1,4-diMe-3-COOMe (**10**)	D	*h*							

[a] Calcd for $C_{11}H_{11}P$: C, 75.85; H, 6.37; P, 17.78. Found: C, 75.49; H, 6.74; P, 17.50. [b] Benzyl bromide salt, prepared at room temperature in benzene solution and recrystallized from methanol-ethyl acetate. [c] Dimer.[22] [d] Monomer. [e] Methyl iodide salt, from room temperature reaction in benzene; recrystallized from methanol–ether. [f] Lit.[5] mp 178–180°. [g] The nmr spectrum of a solution of this salt slowly changed to that of the dimer.[22] This implies that the initial solid is monomeric, or largely so. [h] Phosphole decomposition interfered with quaternization. These were characterized by high-resolution mass spectrometry (see Experimental Section).



are more appropriate for discussion elsewhere;[15] the phospholenes were of importance in the present program as precursors of phospholecarboxylates, the first phospholes known with a reactive functional group.



(15) L. D. Quin and S. G. Borleske, manuscript in preparation.

The synthesis depends on the selective addition of bromine to phosphorus, giving salts which are of the same structure as would be formed from the cycloaddition reaction. Phospholes were then obtained by DBU dehydrohalogenation.[16] This general method may have much wider synthetic utility; other substituents can be placed on the phospholene oxide ring *via* their carbanions,[17] and the resulting products may lend themselves to phosphole synthesis as above.

Properties and Reactivity of the Phospholes.—The ten phospholes prepared in this study are listed in Table I with some of their properties. All were purified by distillation;[18] however, the two esters proved to be unstable at room temperature and within a few hours after distillation formed a solid brown mass. On prolonged exposure to high temperature other phospholes showed instability. Thus, in refluxing xylene, 1-benzyl-3,4-dimethylphosphole was about half decomposed after 25 hr, forming insoluble matter of indefinite nature. The phospholes were in general readily oxidized by atmospheric oxygen.

The phospholes were quaternized[22] with alkyl halides to form crystalline salts, useful for analysis (Table I). Distinct differences in the rates of quaternization were noted. 1-Benzylphosphole formed a salt with benzyl bromide very slowly (28% yield after 11 days), while in only 2 days the 3-methyl derivative gave an 83% yield, and the 3,4-dimethyl derivative a quantitative yield. This reactivity difference, noticed also by others,[5] is reflected in rates of complexation as well; neither 1-methyl- nor 1-benzylphospholes undergo

(16) Preliminary communication: L. D. Quin and S. G. Borleske, *Tetrahedron Lett.*, 299 (1972).

(17) F. Mathey and J. P. Lampin, *C. R. Acad. Sci.*, **270**, 1531 (1970); J. P. Lampin, F. Mathey, and B. Bartet, *Bull. Soc. Chim. Fr.*, 317 (1971).

(18) 1-Benzylphosphole (**1**) proved to be a solid (mp 34–34.5°) and was subjected to X-ray analysis. Compounds **2** and **3** were synthesized for continuation of our X-ray studies, but both proved to be liquids. Some results of the analysis of **1** have been published;[19] full details will appear elsewhere.[20] The X-ray analysis of another phosphole (1,2,5-triphenyl-) was published later;[21] the molecular parameters for this more complex derivative show no special effects attributable to delocalization.

(19) P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, **92**, 5779 (1970).

(20) P. Coggon and A. T. McPhail, manuscript in preparation.

(21) W. P. Ozbirn, R. A. Jacobson, and J. C. Clardy, *Chem. Commun.*, 1062 (1971).

(22) In a separate paper, properties of these salts, some of which are dimeric, are discussed: L. D. Quin, S. G. Borleske, and J. F. Engel, *J. Org. Chem.*, **38**, 1954 (1973).

TABLE II

PROTON AND PHOSPHORUS NMR SPECTRA OF PHOSPHOLES

Phosphole	$\delta(^{31}P)$ ppm[a]	$\delta(^1H)$, ppm (J_{PH}, Hz)[b]					
		PCH_2R	CCH_3	2 H	3 H	4 H	5 H
1	−8.0	3.01 (s)[c]		Complex multiplet, 6.31–7.29			
2	−5.8	2.21–2.61 (m)[d,e]		Complex multiplet, 6.67–7.70			
3	−5.9	1.85–2.5[c,d]		Complex multiplet, 6.36–7.37			
4	+3.0	2.97 (s)[c]	1.96 (3)	6.31 (37.2)			6.31 (37.2)
5	−11.5	3.02 (s)[c]	2.03 (3)	Complex multiplet, 5.87–7.21			
6	+7.3	1.36 (1.5)[e]	2.28 (11)			Multiplet, 5.8–7.1	
7	+6.9	1.45 (1.3)[e]	2.31 (3.3)	6.52 (41)		6.93 (12.5)	7.01 (40)
8[i]	+20.2	1.22 (2)[e]	2.03 (3)	6.42 (41)			6.42 (41)
9	−3.0	1.92 (s)[f,g]		8.3 (34.5)		7.8 (17)	7.3 (38)
10	+12.6	1.96 (s)[f,h]	2.93 (3)	8.44 (33)			7.03 (39)

[a] All values are relative to external 85% H_3PO_4; 9 and 10 were run in $CDCl_3$ solution while all others were neat. [b] ^1H–^1H constants are given in Table III. [c] Neat with internal TMS. [d] Overlapped by benzylic CH_2. [e] Neat with external TMS. [f] In $CDCl_3$ with external TMS. [g] CH_3O at δ 4.26 (s). [h] CH_3O at δ 4.37 (s). [i] Reference 5.

the well-known phosphine reaction of complexation with nickel chloride, but 3,4-dimethyl-1-benzylphosphole reacts rapidly to give a typical complex.[23] These reactivity differences can be taken to imply that greater phosphine-like character (diminished electron delocalization from phosphorus) results from introduction of methyls in the two β positions. Other consequences of this substitution pattern will be noted in this paper and it is clear that effects are felt not only in chemical reactivity but in physical properties as well. Whether the influence of the substituents is electronic or steric in nature, or a combination of these, is not clear at this time. The direction of the effect is consistent with the electron-releasing characteristic of methyl,[5] but some observations will be noted that indicate that repulsive interactions occur between the adjacent methyls. If these repulsions caused some distortion of the ring carbons from planarity, or if the position of phosphorus relative to this plane (in **1**, it is out of this plane by 0.18 Å[19]) were modified slightly, then the extent of orbital overlap between the π electrons and the p orbital of phosphorus could differ slightly in the 3,4-dimethyl case. Knowledge of the behavior of phospholes with a variety of substituents seems called for to assess the relative importance of the two influences.

Spectral Properties of Phospholes.—In our study of 1-methylphosphole, some unique ultraviolet, ^1H nmr, and ^{31}P nmr spectral properties were observed. Our continued study has shown that these properties, described in the discussion to follow, are general characteristics of the phosphole system.

Uv Spectra.—In its uv spectrum, a maximum was observed for 1-methylphosphole at 285 nm (log ε 3.89, isooctane). This absorption has been found in every phosphole that we have since examined. The maximum is sensitive to conjugating substituents; the carbomethoxy group caused a pronounced shift (22 nm) to higher wavelength, a strong indication that the maximum is associated with the π electrons of the ring. Placement of a methyl on the other β carbon of the ester (as in **10**) produced a blue shift of 7 nm, in accord with steric inhibition of the conjugation. Relative to a 3-methylphosphole (**5**), the maximum for a 3,4-dimethylphosphole (**4**) is blue shifted by 5 nm. Normally, alkyl substitution in conjugated systems produces red shifts; a blue shift is common, however, when steric interaction is strong between adjacent substituents and affects conjugation, as in ortho-disubstituted benzenes. The blue-shifted uv maximum for the 3,4-dimethylphosphole case therefore is indicative of the repulsions having some effect on conjugation in the ring.

Proton Nmr Spectra.—The olefinic proton nmr spectrum (AA′BB′X) of 1-methylphosphole required computer assistance for interpretation.[3] The presence of substituents on the ring carbons has greatly facilitated the interpretation of the spectra; in many cases, olefinic signals were spread out so that spectra of first-order quality were obtained and chemical shifts and coupling constants could be measured by inspection. This was especially true where $-COOCH_3$ was present (**9** and **10**), for it added strong deshielding to adjacent CH. A methyl substituent, as in **7** and **8**, caused a useful upfield shift of adjacent CH. Phospholes with a benzyl substituent have less readily interpreted spectra, since the protons of the phenyl and the phosphole rings overlapped. The methyl effect did help in this regard, however, and in 1-benzyl-3,4-dimethylphosphole (**4**) the protons at the 2,5 positions were cleanly separated from the phenyl protons.

With the spectra of ten phospholes available (Table II), we have been able to consider in some detail the more unique properties of phospholes. (1) The ring protons, clearly in the "aromatic" region, are sensitive to substituent effects just as are those of benzene, thiophene, etc. Comparison of chemical shifts with those of olefinic protons in 2-phospholenes shows some additional deshielding, as might be expected from operation of a ring current [*cf.* δ 5.74–6.40 in 1-benzyl-2-phospholene to δ 6.31–7.29 in 1-benzylphosphole (**1**), and δ 5.90 in 1,3-dimethyl-2-phospholene[24] to δ 6.52 for the α proton in 1,3-dimethylphosphole]. (2) Values for ^{31}P–^1H coupling in 1-methylphosphole were calculated to be 38.5 Hz, an extraordinary size, and 13.8 Hz. These were assigned to the α and β protons, respectively, although the opposite assignments generally hold for phosphines. As seen especially by **4** and **8** in Table II, these assignments are now fully confirmed. Furthermore, as we have reported elsewhere,[7,14] $^2J_{PH}$ for the α proton in 2-phospholenes is of the same large size. It is not yet possible to account for this effect; it may prove to be a consequence

(23) L. D. Quin, J. G. Bryson, and J. F. Engel, *Phosphorus*, **2**, 205 (1973).

(24) L. D. Quin, J. J. Breen, and D. K. Myers, *J. Org. Chem.*, **36**, 1297 (1971).

of the bonding characteristics (C–P bond order greater than 1 through delocalization), or it may depend on the spatial relation of the α proton to the lone pair as in other cyclic phosphines. That a large value of $^2J_{PH}$ (38 Hz) has been recently reported[25] for phosphabenzene (phosphorin) should be noted in this regard. X-Ray analyses of 1-benzylphosphole[19] and of 2,6-dimethyl-4-phenylphosphorin[26] confirm the reduction in C–P bond length in these systems (1.78 and 1.74 Å, respectively) relative to saturated phosphines (*e.g.*, 1.846 Å in trimethylphosphine[27]). (3) Phosphorus coupling occurs with protons on substituents of the ring. Methyl or benzyl protons attached to phosphorus have quite small (1.3–2.0 Hz) or even unobservable values[3] for $^2J_{PH}$. *C*-methyl protons are more strongly coupled, especially at the α position. Thus, $^3J_{PH}$ for 1,2-dimethylphosphole is 11 Hz; this is a particularly large value but not unexpected from the magnitude of coupling with a proton at the α position. Similar values for α methyls have been observed by others.[4b,28] $^4J_{PH}$, as for the β methyl of 1,3-dimethylphosphole, is much smaller (3.3 Hz). These position-specific coupling constants are an aid in structure elucidation as well as spectra interpretation. (4) From the calculated spectrum[3] of 1-methylphosphole, proton–proton coupling constants were obtained. The directly measured constants of the present study are totally consistent with these values (Table III).

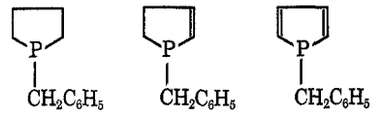
TABLE III
RING PROTON–PROTON COUPLING CONSTANTS[a] (HERTZ) IN PHOSPHOLES AND THIOPHENES

	$J_{H_2H_4}$	$J_{H_2H_5}$	$J_{H_4H_5}$ (or H_2H_3)
Phospholes			
1-Me[b]	1.1	3.0	7.2
1,3-diMe (**7**)	1.3	2.5	7.5
1-Me-3-COOMe (**9**)	1.5	2.5	7.5
1,4-diMe-3-COOMe (**10**)		3.0	
Thiophenes			
Unsubstituted[c]	1.0	2.9	4.7
3-Me[d]	*e*	3.0	4.9
3-COOMe[d]	1.3	2.9	5.1

[a] $J_{H_\alpha CH_3}$ values follow: for **5**, **6**, and **7**, 1.5 Hz; for **4**, **8**, and **10**, *ca.* 0.5 Hz. [b] See ref 3. [c] L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969, p 307. [d] R. A. Hoffman and S. Gronowitz, *Ark. Kemi*, **16**, 515 (1961). [e] Not reported.

Furthermore, the values are not greatly different from those found for the corresponding thiophenes. A comparison of values for the carboxylates of the two ring systems is included in Table III. That a similarity in values should exist for these systems is not unexpected, for X-ray studies[19] have shown that bond angles and lengths in the two systems are similar and that the phosphole ring atoms deviate only slightly from coplanarity (at phosphorus). Agreement with values for pyrrole and furan would not be expected (and are not observed), for the smaller heteroatom in these rings leads to quite different molecular parameters. (5) Allylic coupling has been observed between β CH_3 groups and the α protons, causing the CH_3 doublet (from ^{31}P coupling) to split again. The magnitude of this coupling is greatest (1.5 Hz) when only one β CH_3 group is present (as in **5** and **7**); it is less than 0.5 Hz when two β CH_3 groups are present (as in **4** and **8**). Allylic coupling is well known[29] to be sensitive to geometric factors and the smaller value for the 3,4-dimethyl derivatives may imply a deviation from coplanarity for the α proton and β methyl. The suspected steric interactions between 3- and 4-methyls could cause such a deviation. Another nmr manifestation of the 3,4-dimethyl effect is the upfield shift for the α proton from a 3-methylphosphole to a 3,4-dimethylphosphole (*e.g.*, from **7** to **8**, 0.1 ppm; a larger difference, 0.4 ppm, has been reported[5] for the *n*-butylphospholes). In searching for an understanding of the origin of the 3,4-dimethyl effect, it is of importance to consider its possible occurrence among other heterocyclics where d_π–p_π conjugation cannot be implicated.[5] It is then found, for example, that for pyrroles the effect is also present (3-methylpyrrole,[30a] δ 6.42; 3,4-dimethylpyrrole,[30b] δ 6.27). The proposal[5] that dimethyl substitution on phospholes increases the extent of d_π–p_π conjugation relative to p_π–p_π conjugation[5] receives no support from this observation.

Phosphorus Spectra.—The ^{31}P nmr signal for 1-methylphosphole was located at +8.7 ppm, a value showing considerable deshielding relative to an acyclic vinylphosphine (*e.g.*, ethyl divinylphosphine, +20.8 ppm).[3] No suitable cyclic vinylphosphines were available at that time to test for the effect of the cyclic structure, however. We have now prepared the series of cyclic derivatives shown below to permit evaluation of the effect of introduction of unsaturation into a five-membered ring.



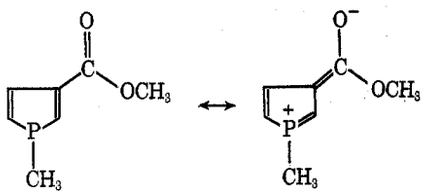
+14.4 ppm[31] 0.0 ppm −7.9 ppm

The results do reveal that both the phospholene and the phosphole possess a considerably more deshielded phosphorus than does the saturated cyclic phosphine, consistent with electron delocalization from phosphorus *via* p_π–p_π conjugation in both unsaturated systems.[24] However, an important influence on ^{31}P values is the bond angles about phosphorus,[32] and insufficient data are presently available to assess thoroughly the importance of this factor in the series above. Furthermore, conformational differences exist between saturated and unsaturated rings,[31] and these steric differences must also be taken into consideration. Nevertheless, that phospholes have the most deshielded phosphorus is, qualitatively, in ac-

(25) A. J. Ashe, III, *J. Amer. Chem. Soc.*, **93**, 3293 (1971).
(26) J. C. J. Bart and J. J. Daly, *J. Chem. Soc. A*, 567 (1970).
(27) L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960).
(28) G. Märkl and R. Potthast, *Angew. Chem., Int. Ed. Engl.*, **6**, 86 (1967).
(29) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969, p 322.
(30) (a) H. Fukui, S. Shimokawa, S. Sohma, T. Iwadare, and N. Esume, *J. Mol. Spectrosc.*, **39**, 521 (1971); (b) R. A. Jones, T. M. Spotswood, and P. Cheuychit, *Tetrahedron*, **23**, 4469 (1967).
(31) J. J. Breen, J. F. Engel, D. K. Myers, and L. D. Quin, *Phosphorus*, **2**, 55 (1972).
(32) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, and J. R. Van Wazer, "Topics in Phosphorus Chemistry," Vol. 5, E. J. Griffith and M. Grayson, Ed., Wiley, New York, N. Y., 1967, Chapter 3.

cord with the concept of cyclic electron delocalization in this system. A theoretical discussion of this matter has been published recently.[5]

As seen in Table II, ^{31}P signals for other phospholes we have prepared also occur at low field. Three observations of significance can be made from these data. (1) A carbomethoxy group placed on the ring causes pronounced additional deshielding. This is easily interpretable on the basis of resonance involving this group and the ring, with further reduction of electron density on phosphorus. Indeed, this



effect may be taken as evidence supporting the delocalization explanation of deshielding at phosphorus in phospholes, since the deshielding is enhanced by a known conjugating group. (2) As in the phospholane and 3-phospholene series,[31] the phosphole ring appears to make a definite contribution to the ^{31}P value; subtracting the group contribution[33] (+21 ppm for CH_3, +4 ppm for $CH_2C_6H_5$) for the exocyclic substituent from the phosphole value leaves an increment for the ring contribution of −12 ppm in both 1-methyl- and 1-benzylphospholes. Similar constancy occurs for the ring contribution (−14 ppm) among derivatives of the 3-methylphosphole system, as well as for the 3,4-dimethylphosphole ring (−1 ppm). Such additive effects are of value[32,33] in calculating chemical shifts where experimental values are not available. (3) The ring contributions reveal a remarkable effect: one β methyl causes a small additional deshielding of P, but two β-methyl groups result in marked *shielding*[34] of phosphorus. The same effect has been noted for 1-phenyl- and 1-butylphospholes.[5] The upfield shift in the ^{31}P value may be explained on the basis of diminished electron delocalization from phosphorus, as have other manifestations of the 3,4-dimethyl effect. The fact that one β-methyl substituent causes the opposite effect (deshielding), however, makes it seem questionable that an explanation based solely on the electronic properties of methyl can suffice for this phenomenon. That steric effects which moderate conjugation in the system can influence ^{31}P shifts is seen from a consideration of the two phosphole esters **9** and **10**. In **9**, the conjugating carbomethoxy group causes additional deshielding of almost 12 ppm relative to 1-methylphosphole; placement of a methyl adjacent to carbomethoxy nullifies the effect through steric inhibition of conjugation, and even leads to shielding (by 4 ppm) relative to 1-methylphosphole.

We would also note in conclusion that ^{13}C nmr studies of phospholes have revealed the presence of steric interactions between vicinal methyls. It has been observed[36] that the upfield shift seen for substituents suffering steric crowding in benzene derivatives (*e.g.*, the methyls of *o*-ylene are upfield of those of *m*-xylene by 1.9 ppm[37]) occurs among phospholes. Thus, for **7**, the 3-CH_3 group resonates at 18.6 ppm (TMS 0), while the 3,4-dimethyl derivative **8** has a value of 17.8 ppm.

(33) S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, **32**, 781 (1967).

(34) Shielding by carbon γ to phosphorus is consistent with considerations of acyclic compounds,[35] and indeed is observed also in 3,4-dimethyl substitution in 3-phospholenes.[31] The precise nature of the steric effects would be expected to be quite dependent on the particular system involved, particularly where delocalization (as in the phospholes) and anisotropic effects (as in the 3-phospholenes) are also involved.

(35) L. D. Quin and J. J. Breen, *Org. Magn. Resonance*, in press.

Experimental Section

General.—Melting points were taken on a Mel-Temp apparatus and are corrected, while boiling points are uncorrected. Proton nmr spectra were obtained with a Varian A-60 spectrometer or a Bruker HFX-10 spectrometer at 90 MHz. ^{31}P nmr spectra (referenced to external 85% H_3PO_4) were obtained with a Varian V-4300B spectrometer at 19.3 MHz; the Bruker instrument (36.43 MHz) was also used, under conditions of proton decoupling. Mass spectra were obtained on an AEI MS 903 mass spectrometer operated by the Research Triangle Mass Spectrometry Center. Gas chromatography (gc) was performed with a Varian Aerograph 202-1B dual column gas chromatograph using helium carrier gas and a 5 ft × 0.25 in. column packed with 20% SE-30 silicone oil on Chromosorb W. In specified cases, a similar column of 4% OV-17 on Chromosorb G was used. The flow rate was approximately 65–70 ml/min. Analyses were performed by commercial laboratories. All manipulations involving trivalent phosphorus compounds and other oxygen- or moisture-sensitive materials were done under a nitrogen atmosphere. Cycloadditions of dienes and phosphorus dihalides were performed by published procedures.[9] Reagents were commercially available except where noted by a reference to their preparation.

1-Benzyl-3-phospholene Oxide.—The adduct prepared from the benzylphosphonous dibromide[38] and butadiene adduct was hydrolyzed on ice and the aqueous layer was then extracted with four 100-ml portions of chloroform. The chloroform was stripped off and the residue was distilled to give 7.52 g of oxide, bp 151–155° (0.5 mm). Gc indicated only the 3-phospholene isomer to be present; pmr ($CDCl_3$, internal TMS) δ 5.84 (d, $^3J_{PH}$ = 28 Hz, HC=CH), 3.37 (d, $^2J_{PH}$ = 13.8 Hz, benzyl CH_2), 2.44 (d, $^2J_{PH}$ = 11 Hz, ring CH_2); ^{31}P nmr ($CDCl_3$) δ −63.2. Because of its hygroscopicity, analysis was deferred to the dibromo state (*vide infra*).

1-Benzyl-3-phospholene.—Benzylmagnesium chloride, prepared from 3.94 g (0.169 mol) of magnesium and 20.5 g (0.162 mol) of benzyl chloride in 150 ml of dry ether, was added dropwise to a well-stirred mixture of 24.4 g (0.148 mol) of 1-bromo-3-phospholene[7] and 25 ml of dry ether at 5°. A hard solid formed during the reaction. After being stirred for 1 hr at room temperature, the mixture was chilled and 100 ml of a 10% NH_4Cl solution was carefully added. The organic layer was separated and the aqueous layer was extracted three times with 20 ml of ether. The combined ether extracts were dried and distilled to give 21.1 g (81.1%): bp 80–82° (0.6 mm); pmr (neat) δ 5.79 (d, $^3J_{PH}$ = 7 Hz, HC=CH), 2.60 (s, benzyl CH_2), 2.14–2.50 (ABX, m, ring CH_2); ^{31}P nmr (neat) δ 23.4.

The phosphine was also prepared by reduction of 1-benzyl-3-phospholene oxide (7.60 g, 0.040 mol) in 125 ml of benzene (dried by distillation) with a solution of 21.4 g (0.158 mol) of trichlorosilane in 30 ml of benzene at 5°. Some gas evolution occurred. The reaction mixture was stirred for 45 min at room temperature, refluxed for 3 hr, and then cooled for hydrolysis with 125 ml of 25% NaOH solution. The benzene layer was removed and the aqueous layer was extracted twice with 15-ml portions of benzene. After drying the benzene extract, it was distilled to give 3.93 g of oxide [56.5%, bp 70–73° (0.4 mm)]. The spectra were identical with those for the first product. A sample quaternized with methyl bromide gave a salt of mp 185–186° with spectra identical with those of a specimen prepared by another route.[14]

1-Benzyl-2-phospholene Oxide.—A solution of 12.0 g (0.087 mol) of 1-chloro-2-phospholene oxide[7] in 50 ml of dry ether was

(36) L. D. Quin, S. G. Borleske, and J. F. Engel, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 30, 1972, No. ORGN-109.

(37) W. R. Woolfenden and D. M. Grant, *J. Amer. Chem. Soc.*, **88**, 1496 (1966).

(38) R. B. Fox, *ibid.*, **72**, 4147 (1950).

chilled in an ice bath and treated with benzylmagnesium chloride solution [prepared from 2.43 g (0.100 mol) of magnesium and 12.7 g (0.100 mol) of benzyl chloride in 115 ml of dry ether]. After stirring for 30 min at room temperature, the solution was again cooled and 100 ml of 15% NH_4Cl solution was slowly added. The ether layer was then removed and the aqueous layer was extracted four times with 50 ml of chloroform. The combined and dried ether and chloroform extracts were distilled, giving two fractions: (1) 3.23 g, bp 168–178° (0.3 mm); (2) 0.39 g, bp 179–186° (0.3 mm). Gc indicated the following ratios of 3-phospholene to 2-phospholene: (1) 1:99 and (2) 2:98. The yield of 2-phospholene oxide was 3.61 g (21.3%); pmr ($CDCl_3$, internal TMS) δ 5.9–6.65 (m, HC=CH), 3.29 (d, $^3J_{PH}$ = 15 Hz, benzylic CH_2), 1.6–2.7 (m, ring CH_2); ^{31}P nmr ($CDCl_3$) δ −67.7.

1-Benzyl-2-phospholene.—A solution of 3.30 g (0.017 mol) of 1-benzyl-2-phospholene oxide and 100 ml of benzene was dried by distilling off 20 ml of benzene. It was treated with 9.3 g (0.069 mol) of trichlorosilane in 15 ml of benzene, while being cooled with an ice–water bath. The mixture was brought to room temperature and then refluxed for 3 hr. The solution was again cooled and 125 ml of 20% NaOH was added cautiously. The organic layer was removed and the aqueous layer was extracted three times with 20 ml of benzene. The combined benzene portions, after being dried, were distilled, giving 1.40 g (46.2%): bp 80–83° (0.3 mm); pmr (CD_3COCD_3, internal TMS) δ 5.74–6.41 (m, HC=CH), 2.76 (broad s, benzylic CH_2), 1.5–2.6 (m, ring CH_2); ^{31}P nmr (CD_3COCD_3) δ 0.0. The benzyl bromide salt, formed in benzene and recrystallized from methanol–ethyl acetate, had mp 230–231°, ^{31}P nmr ($CDCl_3$) δ −61.8.

Anal. Calcd for $C_{18}H_{25}BrP$: C, 62.26; H, 5.80; Br, 23.01; P, 8.92. Found: C, 62.45; H, 5.53; Br, 23.33; P, 9.21.

1-Benzyl-3,4-dibromophospholane.—A solution of 1-benzyl-3,4-dibromophospholane oxide (17.4 g, 0.0493 mol) and 350 ml of benzene was dried by distilling off 90 ml of benzene. While at 0°, the solution was treated dropwise with 33.2 g (0.246 mol) of trichlorosilane. The ice bath was removed and within 30 min a homogeneous solution resulted. This solution was stirred for 1 hr at room temperature, whereupon slight cloudiness occurred. The solution was cooled to about 0° and 125 ml of 30% NaOH solution was added cautiously. Considerable foaming occurred. The benzene layer was then removed and the aqueous layer was extracted three times with benzene. The combined benzene portions were dried and filtered through glass wool to remove the drying agent. The total volume of benzene solution was 300 ml. A 10.0-ml aliquot required 45.30 ml of a 0.0245 *M* I_2 solution (standardized against As_2O_3), indicating 0.0333 mol (67.5%) of phospholane to be present. Another 10-ml aliquot was treated with an excess of methyl bromide and stirred for 46 hr. The resulting salt (0.05 g, 70.7% based on starting oxide) after recrystallization from methanol–ethyl acetate had mp 167–169°. The pmr and ir spectra were identical with those of the salt (mp 172°) obtained[3] by treating 3,4-dibromo-1-methylphospholane with benzyl bromide.

1-Benzyl-3,4-dibromophospholane Oxide.—To a well-stirred mixture of 21.1 g (0.120 mol) of 1-benzyl-3-phospholene and 100 ml of cyclohexane at 5° was added dropwise a solution of 38.0 g (0.24 mol) of bromine in 50 ml of cyclohexane. A hard, granular orange solid formed. After the addition was complete, the reaction mixture was stirred for 1 hr at room temperature and then filtered; the resulting orange solid was immediately hydrolyzed with ice, giving an orange, gummy substance. This gum was dissolved and removed from the aqueous layer by several extractions with chloroform (total volume about 1.2 l.). Removal of chloroform from the extracts left a solid residue which was recrystallized from isopropyl alcohol, giving 37.0 g (87.8%) of white needles, mp 158–159°.

Anal. Calcd for $C_{11}H_{13}Br_2OP$: C, 37.53; H, 3.72; Br, 45.40; P, 8.79. Found: C, 37.48; H, 3.86; Br, 45.03; P, 8.65.

The oxide was also obtained (89.9% yield) by addition of bromine to the phospholene oxide, following a published procedure.[14]

1-Benzylphosphole (1) by Method A.—A solution of 16.4 g (0.0488 mol) of 1-benzyl-3,4-dibromophospholane in 475 ml of benzene was treated with 22.6 g (0.200 mol) of potassium *tert*-butoxide over a 45-min period at room temperature. The reaction was mildly exothermic and was accompanied by rapid darkening of the solution. After an additional 3 hr, 10 g of ice was added and, after stirring for 45 min, the benzene layer was removed and then washed twice with 25 ml of saturated $NaHCO_3$ solution. Distillation gave 3.89 g at 76–81° (0.3 mm). Gc of this distillate showed two peaks in the ratio of 4:1; the minor peak was 1-benzyl-3-phospholene from its ^{31}P nmr chemical shift and gc retention time. It was removed by washing the crude product (in 10 ml of benzene) with four 10-ml portions of 2 *N* HCl, then with two 10-ml portions of saturated $NaHCO_3$ solution, and finally with 5 ml of water. The solution was dried ($MgSO_4$) and then distilled (71–72°, 0.2 mm) to give 2.22 g (26%) of **1**. This liquid solidified upon standing, mp 34–34.5° (sealed capillary). Gc showed less than 2% of phospholene remaining; nmr, see Table II; uv (95% ethanol) λ_{max} 286 nm (log ϵ 3.56); benzyl bromide salt, see Table I. An attempt to prepare **1** by method C from the benzylphosphonous dibromide–butadiene adduct gave less than 2% of a crude product.

1-(2-Phenylethyl)-3-phospholene.—Using the procedure employed for the preparation of 1-benzyl-3-phospholene, β-phenethylmagnesium bromide [from 3.30 g (0.136 g-atom) of magnesium and 21.0 g (0.114 mol) of freshly distilled β-phenethyl bromide in 150 ml of dry ether] was added to 17.2 g (0.103 mol) of 1-bromo-3-phospholene[7] in 50 ml of dry ether. The product was worked up also as before. Distillation gave 14.3 g (76.4%): bp 85–94° (0.1–0.2 mm); pmr (neat, external TMS) δ 5.93 (d, $^3J_{PH}$ = 7 Hz, HC=CH); ^{31}P nmr (neat) δ +29.9. The salt formed with methyl bromide in benzene had mp 156–158° after two recrystallizations from methanol–ethyl acetate; pmr (CF_3COOH, external TMS) δ 5.97 (d, $^3J_{PH}$ = 28 Hz, HC=CH), 2.35 (d, $^2J_{PH}$ = 15 Hz, PCH_3).

Anal. Calcd for $C_{13}H_{18}BrP$: C, 54.75; H, 6.35; Br, 28.02; P, 10.86. Found: C, 54.36; H, 6.57; Br, 27.88; P, 10.87.

3,4-Dibromo-1-(2-phenylethyl)phospholane Oxide.—Using the procedure for the bromination of 1-benzyl-3-phospholene oxide, 1.3 g (0.068 mol) of 1-(2-phenylethyl)-3-phospholene in 125 ml of cyclohexane was treated with 21.9 g (0.137 mol) of bromine in 25 ml of cyclohexane. The product was recrystallized twice from aqueous methanol to give 20.6 g (82.3%) of a light tan solid, mp 116–117.5°.

Anal. Calcd for $C_{12}H_{15}Br_2OP$: C, 39.38; H, 4.13; Br, 43.66; P, 8.46. Found: C, 39.68; H, 4.33; Br, 43.60; P, 8.54.

3,4-Dibromo-1-(2-phenylethyl)phospholane.—Using the same procedure as employed for the 1-benzyl compound, 18.5 g (0.0508 mol) of 3,4-dibromo-1-(2-phenylethyl)phospholane oxide in 450 ml of dry benzene was reduced with 27.7 g (0.203 mol) of trichlorosilane. The total volume of benzene solution after work-up was 425 ml; a 5.00-ml aliquot required 20.70 ml of 0.0224 *M* I_2 solution, indicating 0.0394 mol (77.6%) of phospholane to have been formed.

The salt formed from another 10-ml aliquot with methyl bromide weighed 0.37 g (69.9%) and after three recrystallizations from methanol–ethyl acetate had mp 140–142°.

Anal. Calcd for $C_{13}H_{18}Br_3P$: C, 35.09; H, 4.08; Br, 53.87; P, 6.96. Found: C, 34.81; H, 4.01; Br, 53.78; P, 7.07.

1-(2-Phenylethyl)phosphole (2).—Using method A as employed for the preparation of **1**, 13.3 g (0.039 mol) of 3,4-dibromo-1-(2-phenylethyl)phospholane in 410 ml of benzene was dehydrobrominated with 11.0 g (0.098 mol) of potassium *tert*-butoxide. Distillation gave 1.70 g of tan liquid, bp 91–93° (0.2 mm). Gc (170°) showed two peaks in a ratio of 3:2. The minor peak was shown to be 1-(2-phenylethyl)-3-phospholene by ^{31}P nmr and gc. After the acid wash, distillation gave 0.74 g (10.1%), bp 91–92° (0.2 mm), free of phospholene (gc): nmr, see Table II; uv (95% ethanol) 284 nm (log ϵ 3.93); benzyl bromide salt, see Table I.

1-(*p*-Chloro-2-phenylethyl)-3-phospholene.—Using the procedure employed for the 1-benzyl compound, *p*-chloro-β-phenethylmagnesium bromide [prepared from 5.84 g (0.240 g-atom) of magnesium and 45.6 g (0.209 ml) of freshly distilled *p*-chloro-β-phenethyl bromide[39] in 275 ml of dry ether] was added to 31.6 g (0.190 mol) of 1-bromo-3-phospholene[7] in 80 ml of dry ether. Distillation gave 22.6 g (53.4%) at 124–131° (1.2 mm): pmr (neat, external TMS) 6.12 (d, $^3J_{PH}$ = 8 Hz, HC=CH); ^{31}P nmr (neat) δ +28.6. The phospholene was used directly in the next step of the phosphole synthesis.

3,4-Dibromo-1-(*p*-chloro-2-phenylethyl)phospholane Oxide.—Using the same procedure as for the 1-benzyl compound, 20.4 g (0.091 mol) of 1-(*p*-chloro-2-phenylethyl)-3-phospholene in 150 ml of cyclohexane was treated with 29.0 g (0.182 mol) of bromine in 30 ml of cyclohexane. The product was recrystallized three times from aqueous methanol, giving 26.9 g (74.5%), mp 124–126°.

(39) R. W. Griffin, J. D. Gass, M. A. Berwick, and R. S. Shulman, *J. Org. Chem.*, **29**, 2109 (1964).

Anal. Calcd for $C_{12}H_{14}Br_2ClOP$: C, 35.99; H, 3.52; P, 7.73. Found: C, 35.78; H, 3.32; P, 7.73.

3,4-Dibromo-1-(*p*-chloro-2-phenylethyl)phospholane.—Using the same procedure as for the 1-benzyl compounds, 25.0 g (0.0628 mol) of 3,4-dibromo-1-(*p*-chloro-2-phenylethyl)phospholane oxide in 450 ml of dry benzene was reduced with 34.0 g (0.251 mol) of trichlorosilane. The total volume of the benzene solution was 470 ml; a 5.00-ml aliquot required 23.40 ml of 0.0232 *M* I_2 solution, indicating 0.0543 mol (81.3%) of phospholane to have been formed. The phospholane was not isolated from the benzene solution, but was used directly in the next step.

1-(*p*-Chloro-2-phenylethyl)phosphole (3).—Using method A as in the preparation of **1**, 18.9 g (0.049 mol) of 3,4-dibromo-1-(*p*-chloro-2-phenylethyl)phospholane in 455 ml of benzene was dehydrobrominated with 14.3 g (0.127 mol) of potassium *tert*-butoxide. Distillation gave 3.91 g of a tan liquid, bp 123–135° (0.85 mm). Gc (170°) indicated two products in a 3:1 ratio, the minor one being 1-(*p*-chloro-2-phenylethyl)-3-phospholene. After the acid wash, distillation gave 1.91 g of **3** (17.3%), bp 118–122° (0.7 mm), containing only 2% of phospholene (gc): nmr, see Table II; uv (95% ethanol) λ_{max} 285 nm (log ϵ 3.85); benzyl bromide salt, see Table I.

Quaternization of 1-Bromo-3,4-dimethyl-3-phospholene. A. With Methyl Bromide.—A mixture consisting of 9.73 g (0.050 mol) of 1-bromo-3,4-dimethyl-3-phospholene, 5 ml (*ca.* 0.10 mol) of methyl bromide, and 25 ml of cyclohexane was placed in a brown, narrow-mouth bottle and the cap was then sealed. After 2 months, the precipitated white solid was collected, washed with *n*-pentane, and dried (5.4 g, 37.4%). A sample on hydrolysis gave the known[14] 1,3,4-trimethylphospholene oxide.

B. With Benzyl Bromide.—A mixture of 34.2 g (0.175 mol) of 1-bromo-3,4-dimethyl-3-phospholene, 30.6 g (0.18 mol) of benzyl bromide, and 80 ml of cyclohexane after standing for 5 weeks gave 37.5 g (58.8%) of salt, used directly in the synthesis of **4**.

1-Benzyl-3,4-dimethylphosphole (4).—To 32.7 g (0.090 mol) of 1-bromo-1-benzyl-3,4-dimethyl-3-phospholenium bromide from above in 250 ml of benzene at room temperature was added dropwise a solution of 29.0 g (0.190 mol) of DBU in 50 ml of benzene. The solution was stirred for 45 min and then refluxed for 3.5 hr. The solution was filtered through a sintered glass funnel and then distilled to give 8.77 g of tan liquid, bp 83–107° (0.3 mm). After an acid wash, a second distillation gave 5.23 g (28.6%), bp 92–94° (0.3 mm). Less than 2% 1-benzyl-3,4-dimethyl-3-phospholene[32] remained (gc): nmr, see Table II; uv (95% ethanol) λ_{max} 280 nm (log ϵ 3.26); benzyl bromide salt, see Table I.

1-Benzyl-3-methylphosphole (5).—Using the same procedure, 22.0 g (0.063 mol) of the benzylphosphonous dibromide–isoprene cycloadduct in 100 ml of benzene was dehydrobrominated with a solution of 21.0 g (0.133 mol) of DBU in 25 ml of benzene. The product was worked up as before. Final distillation gave 0.88 g (7.4%), bp 84–85° (0.3 mm). Gc indicated only the phosphole to be present: nmr, see Table II; uv (95% ethanol) λ_{max} 285 nm (log ϵ 3.58); benzyl bromide salt, see Table I.

1,2-Dimethylphosphole (6).—To 26.8 g (0.145 mol) of the cycloadduct[40] of CH_3PCl_2 and 1,3-pentadiene in 150 ml of petroleum ether (bp 30–60°) and 50 ml of methylene chloride was added 44 g (0.29 mol) of DBU in four portions over 10 min. The reaction was moderated with an ice bath. The mixture was stirred at 25° for 3.5 hr, insoluble material was separated, and then the upper (organic) layer was recovered, washed with water, and dried over $MgSO_4$. Distillation gave 2.2 g (14%) of **6**, bp 98–100° (500 mm). Gc (OV-17 at 100°) showed the presence of 6% of 1,2-dimethyl-3-phospholene.[40] Nmr data (Table II) were collected on the 1,2-dimethylphosphole without purification. The phosphole was analyzed as its methyl iodide salt (Table I).

1,3-Dimethylphosphole (7).—A slurry of 5.2 g (0.03 mol) of the cycloadduct[14] of CH_3PCl_2 and isoprene in 50 ml of petroleum ether and 10 ml of methylene chloride was treated with a solution of 9.35 g (0.06 mol) of DBU and 10 ml of methylene chloride; 30 ml of methylene chloride was then added to thin the slurry. The product was worked up as for **6**, giving 0.4 g (12%) of **7**, bp 110–112° (500 mm). Gc (OV-17 column at 100°) showed the presence of only one component. Nmr data are given in Table II. Analysis of the methiodide, recrystallized from methanol–ether, is given in Table I.

1,3,4-Trimethylphosphole (8).—The adduct[14] of 2,3-dimethylbutadiene and CH_3PCl_2 was placed in a mixture of 150 ml of dry petroleum ether and 40 ml of dry methylene chloride. With gentle stirring, 43 ml (66 g, 0.43 mol) of DBU was added in four portions over a 10-min period. The reaction and work-up were conducted as for **6**. Distillation gave 3.5 g (12.7%) of **8**, bp 135–136° (500 mm) [lit.[5] bp 60° (15 mm)]. Gc (OV-17 at 125°) showed 1% of 1,3,4-trimethyl-3-phospholene[14] to be present. Analysis of the methiodide, recrystallized from methanol–ether, is given in Table I; nmr data for **8** are in Table II.

1-Methyl-3-phospholene 1-Oxide 3-Carboxylic Acid and Its Methyl Ester.—To a solution of 200 ml of anhydrous tetrahydrofuran (THF) and 165 ml of 2.38 *M* *n*-butyllithium (0.39 mol) in hexane at −75° was added dropwise a solution of 41.6 g (0.36 mol) of freshly distilled 1-methyl-3-phospholene 1-oxide. A yellowish-orange color developed. Stirring was continued for 10 min and then the solution was transferred into a vigorously stirred Dry Ice–ether slurry, avoiding contact with the atmosphere. The reaction mixture (a white slurry) was stirred for several hours without temperature control, and then hydrolyzed with 500 ml of water. The aqueous solution was separated and acidified with 250 ml (wet volume) of Dowex 50-WX8 (H^+) ion exchange resin. After CO_2 evolution had ceased, the supernatant liquid was passed through a column (5 × 50 cm) of fresh resin to complete the acidification. The resin was eluted with water until the pH of the eluate was 6.5–7.0. The solution was evaporated *in vacuo;* the gummy yellow residue was dried further over P_2O_5 in a vacuum oven (40°, 1 mm, for 24 hr). The residue was dissolved in 150 ml of hot chloroform and placed in a freezer for 4–8 hr. From this solution 7.0 g of a white solid precipitated; reduction of the filtrate volume to 100 ml gave more solid. By a process of adding benzene and then reducing the solution volume, repeated several times, additional crops of solid were obtained (total 32.3 g, 56%). The product was a mixture of the desired compound (30%) and the isomeric 2-phospholene oxide 3-carboxylic acid (70%). They were not readily separated and the mixture was subjected directly to esterification with methanol containing concentrated sulfuric acid (2 drops to 50 ml for a 2-g sample). After 10 hr reflux, the methanol was stripped off and the residue was dissolved in water. The solution was neutralized with sodium bicarbonate and extracted three times with chloroform. The combined organic extracts were dried (Na_2SO_4) and stripped of solvent on a rotary evaporator. The residual oil was further dried at 1 mm. The isomer separation was then accomplished by placing the residue in benzene and after 7 days adding ether until a yellow oil (a polymer of the 2-phospholene derivative) dropped out of solution. The solution was decanted from the oil, and removal of the solvent gave the desired methyl 1-methyl-3-phospholene 1-oxide 3-carboxylate (80% from the corresponding acid). The isomers were also separable on a silica gel chromatographic column. The compound was not readily purified by distillation because of instability. The crude sample sufficed for spectral identification: pmr ($CDCl_3$, internal TMS) δ 6.96 (d, $^3J_{PH}$ = 31 Hz, C=CH), 3.79 (s, OCH_3), 2.82 (4 H, d, $^2J_{PH}$ = 11 Hz, ring CH_2), 1.73 (d, $^2J_{PH}$ = 13.5 Hz, PCH_3); ir (neat) $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1630, ν_{CO} 1280, 1215, $\nu_{P=O}$ 1175 cm^{-1}.

Methyl 1-Methyl-3-phospholene-3-carboxylate.—A solution of 2.5 g (0.016 mol) of methyl 1-methyl-3-phospholene 1-oxide 3-carboxylate and 100 ml of benzene was first dried by distilling off 20 ml of benzene, and then cooled to 5° for dropwise addition of 6.7 g (0.05 mol) of trichlorosilane in 10 ml of benzene. After the addition was complete, the solution was stirred at 25° for 4 hr. The flask was placed in an ice bath and several pieces of ice were added to destroy excess trichlorosilane. To the white, gelatinous mixture, 50 ml of 40% sodium hydroxide solution was added slowly with stirring. The benzene layer was recovered, washed with 10 ml of water, and dried over sodium sulfate. Distillation gave 0.70 g (32%): bp 41–42° (0.1 mm); pmr ($CDCl_3$, external TMS) δ 7.34–7.58 (m, C=CH), 4.23 (s, OCH_3), 2.4–3.6 (4 H, m, CH_2), 1.45 (d, $^2J_{PH}$ = 3 Hz, PCH_3); ^{31}P nmr ($CDCl_3$) δ +33.5. The methiodide, recrystallized from isopropyl alcohol–ether, had mp 189–191°.

Anal. Calcd for $C_8H_{14}IO_2P$: C, 32.02; H, 4.70; P, 10.32. Found: C, 31.85; H, 4.99; P, 10.40.

Methyl 1-Methylphosphole-3-carboxylate (9).—A solution of 2.1 g (0.013 mol) of methyl 1-methyl-3-phospholene-3-carboxylate in 100 ml of petroleum ether cooled with an ice bath was treated dropwise with 2.1 g (0.013 mol) of bromine in 30 ml of methylene chloride. The precipitated phospholenium bromide (yellow) was allowed to settle and the solvent was decanted. The solid was then washed twice with 50-ml portions of petroleum ether,

(40) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970).

covered with 30 ml of benzene, and while at 0–5° treated with a solution of 4.0 g (0.026 mol) of DBU and 10 ml of benzene, added in three portions over a 10-min period. Slight darkening was observed; 40 ml of methylene chloride was added (10 min), during which time the slurry turned black. Vigorous stirring was continued at 0–5° for 3 hr. The mixture was filtered from a gummy solid and the filtrate was washed twice with 50-ml portions of deoxygenated water. Gc (SE-30, 150°) indicated the presence of one component with a retention time of 5 min; no need was indicated for acid washing. The dried (Na_2SO_4) solution was distilled at 20 mm to remove solvent. The black residue was then rapidly distilled directly into a receiver chilled by a Dry Ice–acetone bath. A total of 0.47 g (23%) of **9** was collected at 40–50° (0.1 mm). The liquid remained colorless in the Dry Ice–acetone bath, but darkened rapidly at 25° and precipitated black solid. The purity of the product (gc, 150°, 5 min retention time) exceeded 95%; the impurity was methyl 1-methyl-3-phospholene-3-carboxylate (4 min retention). The nmr data (Table II) were collected on the sample without further purification. Quaternization with methyl iodide was very slow and gave salt badly contaminated with the decomposition material. It could not be successfully analyzed. The mass spectrum of **9** showed a molecular ion of *m/e* 156.0334 (calcd for $C_7H_9O_2P$, 156.0341) (at 17.5% abundance, it was the base peak); uv (cyclohexane) λ_{max} 307 nm; ir (neat) ν_{CH} 3110, $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1535, ν_{CO} 1250 and 1186; 1075 (s), 1062 (s), 888 (m), 793 (s), 740 (s), and 700 cm^{-1} (s).

1,4-Dimethyl-3-phospholene 1-Oxide 3-Carboxylic Acid and Its Methyl Ester.—A solution of 300 ml of THF, 30 ml of tetramethylethylenediamine, and 73 ml of 2.5 *M* *n*-butyllithium at −75° was treated with a solution of 21.4 g (0.17 mol) of 1,3-dimethyl-3-phospholene 1-oxide in 25 ml of THF. As for the previously prepared acid, the mixture was carbonated, acidified by the ion-exchange procedure, and crystallized from chloroform and benzene. The yield was 8.5 g (30%), consisting of 70% of the desired compound and 30% of the isomeric 1,3-dimethyl-2-phospholene 1-oxide 2-carboxylic acid. The unwanted isomer was readily removed by its greater solubility in chloroform; addition of 8 g of the mixture to about 50 ml of chloroform at room temperature completely removed the 2-phospholene and left the desired acid as a residue. Recrystallization from methanol–ether gave a sample of mp 193–195°: pmr (D_2O, external TMS) δ 3.3–3.6 (4 H m, CH_2), 2.68 (broad s, CCH_3), 2.27 (d, $^2J_{PH}$ = 14 Hz, PCH_3); no C=CH signal was present.

Anal. Calcd for $C_7H_{11}O_3P$: C, 48.26; H, 6.37; P, 17.74. Found: C, 48.06; H, 6.36; P, 17.63.

The methyl ester was prepared by treating a refluxing mixture of 3.0 g (0.017 mol) of the acid in 75 ml of *tert*-butyl alcohol containing 2.62 g (0.019 mol) of potassium carbonate with 2.43 g (0.019 mol) of dimethyl sulfate. After 5 hr of reflux, the mixture was filtered and solvent was stripped from the filtrate. The residue, in 75 ml of chloroform, was extracted with 20 ml of 0.5 *M* hydrochloric acid. The organic solution was dried (Na_2SO_4) and stripped to leave 2.4 g of an oil (76%): pmr ($CDCl_3$, external TMS) δ 4.2 (s, OCH_3), 3.1–3.5 (4 H, broad d, CH_2), 2.7 (s, CCH_3), 2.15 (d, $^2J_{PH}$ = 13.5 Hz); ^{31}P nmr (D_2O) δ −68.9; ir $\nu_{C=O}$ 1722, $\nu_{C=C}$ 1642, ν_{CO} 1300, 1230, $\nu_{P=O}$ 1175 cm^{-1}.

Methyl 1,4-Dimethyl-3-phospholene-3-carboxylate.—A solution of 0.60 g (0.003 mol) of methyl 1,4-dimethyl-3-phospholene 1-oxide 3-carboxylate and 100 ml of benzene was dried by distilling off 20 ml of benzene. A solution of 1.40 g (0.01 mol) of trichlorosilane and 10 ml of benzene was added dropwise over 15 min with ice-bath chilling. The reaction mixture was then stirred at 25° for 3 hr, and again cooled, and the excess trichlorosilane was destroyed by the addition of several pieces of ice and then 25 ml of 20% sodium hydroxide. The benzene layer was isolated, washed with 10 ml of H_2O, and dried over sodium sulfate. Distillation yielded 0.22 g (40%) of a colorless liquid: bp 73–74° (0.5 mm); pmr ($CDCl_3$, internal TMS) δ 3.75 (s, OCH_3), 1.8–3.2 (4 H, m, CH_2), 2.21 (s, CCH_3), 0.93 (d, $^2J_{PH}$ = 3 Hz, PCH_3); ^{31}P nmr (neat) δ +46.1. The methiodide (very hygroscopic), recrystallized from isopropyl alcohol–ether, had mp 144.5–145.5°.

Anal. Calcd for $C_9H_{16}IO_2P$: C, 34.41; H, 5.13; P, 9.86. Found: C, 34.13; H, 5.62; P, 9.67.

Methyl 1,4-Dimethylphosphole-3-carboxylate (10).—A solution of 1.11 g (0.0064 mol) of methyl 1,4-dimethyl-3-phospholene-3-carboxylate,[15] 5 ml of methylene chloride, and 90 ml of petroleum ether was treated with 1.14 g (0.0070 mol) of bromine in 10 ml of methylene chloride as in the synthesis of **9**. The product was treated with a solution of 1.9 g (0.013 mol) of DBU in 20 ml of benzene. After work-up, gc (OV-17 at 150°) indicated the presence of the starting phospholene, the phosphole, and DBU. The solution was therefore washed very rapidly with 20 ml of cold 0.05 *M* HCl. The organic layer was dried over sodium sulfate, and the solvent was stripped off at 20 mm. The black residue was rapidly distilled under high vacuum directly into a receiver chilled by a Dry Ice–acetone bath. Methyl 1,4-dimethylphosphole-3-carboxylate (0.25 g, 23%) was collected at 67° (0.3 mm). The colorless liquid obtained was unstable at 25°, but solidified in, and could be preserved in, a Dry Ice–acetone bath. The purity of the product (gc) exceeded 98%, with an impurity of methyl 1,4-dimethyl-3-phospholene-3-carboxylate. The base peak in the mass spectrum was the molecular ion of *m/e* 170.0502 (calcd for $C_8H_{11}O_2P$, 170.0479) in 20.0% abundance; uv (cyclohexane) λ_{max} 300 nm; ir (neat) ν_{CH} 3110, $\nu_{C=O}$ 1725, $\nu_{C=C}$ 1560, ν_{CO} 1250 and 1190, 1035 (s), 886 (m), 774 cm^{-1} (m).

Registry No.—**1,** 29853-74-5; **1** benzyl bromo salt dimer, 38863-80-8; **2,** 38864-26-5; **2** benzyl bromo salt, 38864-27-6; **3,** 38864-28-7; **3** MeI, 38864-29-8; **4,** 38864-30-1; **4** benzyl bromo salt, 38864-31-2; **5,** 38864-32-3; **5** benzyl bromo salt, 38857-58-8; **6,** 38864-34-5; **6** MeI dimer, 38884-24-1; **7,** 38864-35-6; **7** MeI dimer, 38884-25-2; **8,** 37739-99-4; **9,** 36163-75-4; **10,** 38864-38-9; benzylphosphonous dibromide–butadiene adduct, 38864-39-0; 1-benzyl-3-phospholene oxide, 38864-40-3; benzyl chloride, 100-44-7; 1-bromo-3-phospholene, 28273-34-9; 1-benzyl-3-phospholene, 28278-53-7; 1-benzyl-3-phospholene methyl bromide salt, 1130-42-3; 1-chloro-2-phospholene oxide, 1003-18-5; 1-benzyl-2-phospholene oxide, 38864-45-8; 1-benzyl-2-phospholene, 28278-52-6; 1-benzyl-2-phospholene benzyl bromide salt, 38864-47-0; 1-benzyl-3,4-dibromophospholane oxide, 38864-48-1; 1-benzyl-3,4-dibromophospholane, 38864-49-2; 1-benzyl-3,4-dibromophospholane methyl bromide salt, 1130-42-3; β-phenethyl bromide, 103-63-9; 1-(2-phenylethyl)-3-phospholene, 38864-51-6; 1-(2-phenylethyl)-3-phospholene methyl bromide salt, 38864-52-7; 3,4-dibromo-1-(2-phenylethyl)phospholane oxide, 38864-53-8; 3,4-dibromo-1-(2-phenylethyl)phospholane, 38864-54-9; 3,4-dibromo-1-(2-phenylethyl)-phospholane methyl bromide salt, 38864-55-0; *p*-chloro-β-phenethyl bromide, 6529-53-9; 1-(*p*-chloro-2-phenyl; ethyl)-3-phospholene, 38864-56-1; 3,4-dibromo-1-(*p*-chloro-2-phenylethyl)phospholane oxide, 38864-57-2-3,4-dibromo-1-(*p*-chloro-2-phenylethyl)phospholane, 38864-58-3; 1-bromo-3,4-dimethyl-3-phospholene, 28273-33-8; 1-bromo-1-benzyl-3,4-dimethyl-3-phospholene bromide, 38906-68-2; benzyl phosphonous dibromide–isoprene adduct, 38864-60-7; cycloadduct of CH_3PCl_2 and 1,3-pentadiene, 38864-61-8; cycloadduct of CH_3PCl_2 and isoprene, 36044-15-2; cycloadduct of CH_3PCl_2 and 2,3-dimethylbutadiene, 38864-63-0; 1-methyl-3-phospholene 1-oxide 930-38-1; 1-methyl-3-phospholene 1-oxide 3-carboxylic acid, 38864-65-2; methyl 1-methyl-3-phospholene 1-oxide 3-carboxylate, 38864-66-3; methyl 1-methyl-3-phospholene-3-carboxylate, 36163-72-1; methyl 1-methyl-3-phospholene-3-carboxylate methyl iodide salt, 36163-73-2; 1,3-dimethyl-3-phospholene 1-oxide, 15450-79-0; 1,4-dimethyl-3-phospholene 1-oxide 3-carboxylic acid, 38864-70-9; 1,4-dimethyl-3-phospholene 1-oxide 3-carboxylic acid methyl ester, 38864-71-0; methyl 1,4-dimethyl-3-phospholene-3-carboxylate 38864-72-1; methyl 1,4-dimethyl-3-phospholene-3-carboxylate methyl iodide salt, 38864-73-2.