11-(Methylsulfonyl)-9α-tricyclo[7.3.0.0^{1,6}]dodecane-3,7,10-trione (**33**).—A sample of **32** (95 mg, 0.3 mmol) in dry glyme (20 ml) was added to a suspension of oil-free sodium hydride (0.144 g, 0.60 mmol) in glyme (40 ml), and the mixture was refluxed for 8 hr. The cooled reaction mixture was acidified with concentrated hydrochloric acid and evaporated under reduced pressure. The residue was leached with hot ethyl acetate and concentrated to give 0.091 g of light brown foam which was separated on a 20 × 20 silica gel (PF_{254}) thin layer plate eluted with ethyl acetate. Collection of two components (R_f 0.48 and 0.54) gave an isomeric mixture of **33** (47 mg, 45%) which crystallized from ethyl acetate: mp 166–169°; ir $\tilde{\nu}_{max}^{CH_3CN}$ 3700–3400 (broad, partly as enol form), 1745, 1720, 1310, and 1145 cm^{-1}; pmr (CD_3CN) δ 1.7–2.9 (complex multiplets, 12 H), 3.08, 3.16 (two singlets because of the two isomeric forms, 3 H), and 4.3 (complex multiplet, 1 H); mass spectrum molecular ion peak at *m/e* 284. The exact molecular weight determined by high resolution mass spectrometry was 284.078 (calcd for $C_{13}H_{16}O_5S$, 284.075) and for M − CH_3SO_2· was 205.092 (calcd for $C_{12}H_{13}O_3$, 205.089).

Registry No.—**4**, 28269-01-4; *cis*-**6**, 28269-02-5; *trans*-**6**, 28269-03-6; **7**, 26269-04-7; *cis*-**8**, 28269-05-8; *trans*-**8**, 28269-06-9; *cis*-**9**, 28269-07-0; *trans*-**9**, 28269-08-1; **10**, 28269-09-2; **11**, 28269-10-5; **12**, 28269-11-6; **14**, 28269-12-7; **16**, 28269-13-8; **17**, 28269-14-9; **18**, 28269-15-0; **19**, 28269-16-1; **20**, 28392-70-3; **21**, 28269-17-2; **24**, 28269-18-3; **25**, 28269-19-4; **26**, 28269-20-7; **27**, 28269-21-8; **28**, 28392-71-4; **29**, 28278-27-5; **30**, 28278-28-6; **31**, 28278-29-7; **32**, 28278-30-0; 11α-**33**, 28278-31-1; 11β-**33**, 28278-32-2; *cis*-2-carbethoxy-3aβ-carbomethoxy-7aβ-hydroxy-3-methyl-3a,4,5,6,7,7a-hexahydroindene, 28278-33-3; *cis*-2,3aβ-dicarboxy-7aβ-hydroxy-3-methyl-3a,4,7,7a-tetrahydroindene, 28278-34-4; *cis*-2,3aβ-dicarboxy-7aβ-hydroxy-3-methyl-3a,4,5,6,7,7a-hexahydroindene, 28278-35-5; *cis*-2,9β-dicarboxy-8β-hydroxy-3-methylhydrindan, 28278-36-6; *cis*-1-methyl-2-carboxyindene, 28278-37-7; *trans*-1-methyl-2-carboxyindan, 28278-38-8; *trans*-3β,3aβ-dicarbomethoxy-1-hydroxy-3a,4,7,7aα-tetrahydroindan, 28278-39-9; 3β,3aβ-dicarbomethoxy-1-hydroxy-3a,4,7,7a-tetrahydroindan, 28278-40-2; *cis*-3β,3aβ-dicarbomethoxy-1-hydroxy-3a,4,7,7aβ-tetrahydroindan, 28278-41-3.

Synthesis and Properties of Some 1-Halophospholenes[1]

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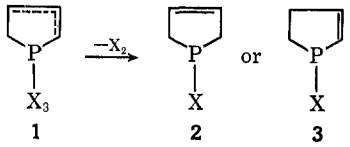
Two methods have been devised for preparing the previously unknown 1-halophospholenes. These compounds, which are formally cyclic phosphinous halides, resulted from reduction (dehalogenation) of diene–phosphorus trihalide cycloadducts with triphenylphosphine, as well as from reduction with hexachlorodisilane of 1-halophospholene oxides. Examples of both 2- and 3-phospholene derivatives were prepared. Structures were assigned from nmr spectral data. Of particular value was the exceptionally large (over 40 Hz) value for coupling of ^{31}P with the vinyl proton at the 2 position of the 2-phospholene derivatives. The halophospholenes were hydrolyzed to give cyclic secondary phosphine oxides (characterized as their chloral adducts). Successful displacement of halogen with a secondary amine as well as with a Grignard reagent demonstrates further the synthetic utility of these substances in phospholene chemistry.

The discovery of the cycloaddition of dienes with phosphonous dihalides[2] has made possible the synthesis of a number of derivatives of the phospholene ring system and stimulated a considerable amount of work on this family of compounds.[3] To date no 1-halophospholenes, where phosphorus is trivalent, have been prepared; yet these compounds, which may be classed as cyclic phosphinous halides, should be particularly valuable as synthetic intermediates in this family. We report in this paper two methods which have made these compounds available, and describe several reactions leading to new phospholene derivatives.

Reduction of Diene–Phosphorus Trihalide Cycloadducts.—We have previously shown that the diene–phosphonous dihalide cycloadducts may be reduced (dehalogenated) with magnesium in tetrahydrofuran to form 1-alkyl- or arylphospholenes.[4] Application of this reaction to cycloadducts from phosphorus trihalides[5] (**1**; the position of the double bond is uncertain) should provide the desired 1-halophospholenes (**2** or **3**).



1 **2** **3**

However, the magnesium–THF system, when applied to isoprene–PCl_3 or PBr_3 cycloadducts, provided none of the desired product; the only material isolated was the 1,4-dihalobutane from cleavage of the solvent.[6] It was then found that the dehalogenation could be successfully accomplished with triphenylphosphine in methylene chloride as solvent. The other product of the reaction, presumably the dihalotriphenylphosphorane, is partially soluble in the reaction medium, but is precipitated with pentane. Its removal from the reaction medium was considered desirable as the halogen exchange process is probably reversible. Unreacted cycloadduct is also precipitated in this step. The halophospholenes are then recovered by distillation. Products and yields are included in Table I. The halides are highly reactive substances, sensitive to air and to water; even protected from these, some products proved to be unstable, precipitating orange solids on standing. The most unstable was compound **3a** which began to decompose in the receiver even before distillation was complete, and was obtained in only 5% yield. On the other hand, compound **2a** remained unchanged on standing for several weeks; it was obtained in 79%

(1) Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute.

(2) W. B. McCormack, U. S. Patents, 2,663,736 and 2,663,737 (Dec 22, 1953).

(3) For a review, see L. D. Quin in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

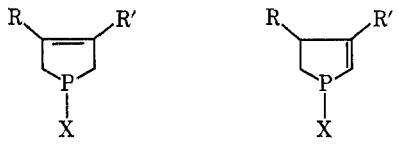
(4) L. D. Quin and D. A. Mathewes, *J. Org. Chem.*, **29**, 836 (1964).

(5) U. Hasserodt, K. Hunger, and F. Korte, *Tetrahedron*, **19**, 1563 (1963).

(6) A. G. Anderson and F. J. Freenor, *J. Amer. Chem. Soc.*, **86**, 5037 (1964), have reported a similar cleavage of THF by dibromotriphenylphosphorane.

TABLE I

1-HALOPHOSPHOLENES SYNTHESIZED



2 3

	Compound R	R′	X	Method[a]	Yield	Bp, °C (mm)
2a	CH_3	CH_3	Br	A	79[b]	99–102 (27)
2b	H	H	Br	A	23	77–80 (32)
2c	H	CH_3	Cl	B	26	61–63 (17)
3a	H	H	Cl	A	5[c]	67–68 (32)
3b	H	CH_3	Cl	B	58[d]	67–70 (18)
3c	H	CH_3	Br	A	42[e]	94–98 (30)

[a] A, cycloadduct with triphenylphosphine; B, oxide of the 1-halophospholene with hexachlorodisilane. [b] Product from one reduction contained as much as 10% 2 isomer while other reductions gave pure 3 isomer. [c] Method B gave 1% yield. [d] Method A gave 21% yield containing 30% **2c**. [e] Product contained 30% of 3-phospholene isomer.

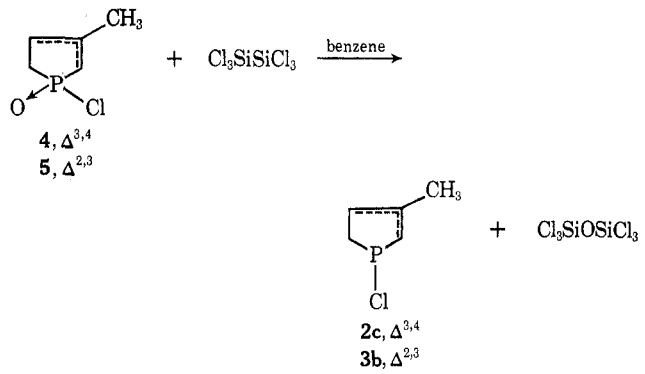
yield. The low yields are therefore more a reflection of product instability than of process inefficiency.

A possible yield-reducing complication in this process is the further reaction of the 1-halophospholenes with triphenylphosphine. Tributylphosphine has been reported to react with halophosphines to form products containing the P–P bond,[7] and indeed, when a methylene chloride solution of **2a** and **2b** was treated with triphenylphosphine, an immediate exothermic reaction occurred, precipitating yellow solid. The products have not been examined. To minimize the occurrence of this side reaction in the reduction process, the triphenylphosphine was slowly added to the cycloadduct, which was used in excess (20%).

The location of the double bond in phospholene derivatives obtained from cycloadducts has been a troublesome matter.[3] Originally, all cycloadducts formed from phosphonous dihalides were assumed to contain the 3-phospholene ring; if on subsequent reaction a product was obtained with the 2-phospholene ring, this was thought to be the result of rearrangement during the particular reaction. It is now known, however, that for cycloadducts formed from phosphonous dihalides the position of the double bond is already established in the cycloadduct itself.[8] Thus, cycloadducts from methylphosphonous dichloride and phenylphosphonous dibromide are 3-phospholene derivatives, while those from phenylphosphonous dichloride are 2-phospholenes (except where the diene is 2,3-dimethylbutadiene). Such a study on the cycloadducts from phosphorus trihalides has not yet been carried out, although it is known that adducts from the tribromide lead on alcoholysis or hydrolysis to 3-phospholenes while those from the trichloride generally lead to 2-phospholenes.[5,9] As will be discussed later in this paper, spectral properties of the 1-halophospholenes establish clearly the location of the double bond and reveal that to some extent the same trend is followed, the bromides being 3-phospholenes, while the chlorides are 2-phospholenes. However, some products proved to be mixtures of isomers (see Table I), and one bromide (**3c**) proved to be largely (70%) the 2 isomer rather than the expected 3 isomer. To account for these cases, it has to be assumed either that the cycloadducts are rearranged in the reaction medium during the reduction process (*e.g.*, by the base triphenylphosphine) or that the halophospholene products rearrange after their formation, perhaps during distillation. Certainly the former explanation is a possibility, for we have found that the isoprene–phosphorus tribromide adduct can under certain conditions of hydrolysis give 1-hydroxy-3-methyl-2-phospholene oxide as the main product, just as the trichloride adduct does, whereas earlier reports describe reactions of this adduct in which only 3 isomers are obtained.[9] On the other hand, evidence has also been obtained for thermal rearrangement of the halophospholenes; a sample of pure **2a** after heating at 100° for 2 hr was found to contain about 10–15% of the 2-phospholene isomer. Distillation of the products should therefore be conducted rapidly, with the lowest practical temperatures, to minimize the formation of unwanted isomer.

This synthesis has been most useful in obtaining 1-bromo-3-phospholene (**2b**) and its 3,4-dimethyl derivative (**2a**). The latter is formed in particularly high yield, and both are obtained relatively free of isomer. Some reactions of the halides are described later in this paper.

Reduction of 1-Halophospholene Oxides.—The effectiveness of silicon hydrides for reduction of phosphoryl compounds was first announced in 1965,[10] and more recently hexachlorodisilane has been employed for this purpose.[11] We have found that the latter reagent may be used to reduce 1-halophospholene oxides, which are cyclic phosphinic halides, to the corresponding halophospholenes. Two reactions of this type were successfully conducted on oxides **4** and **5**; data are given in Table I. The products, however, showed some contamination from silicon-containing material, as evi-



denced by a Si–O–Si stretching band in their infrared spectra. In one case the halophospholene (**3b**) was obtained in more than twice the yield as from cycloadduct reduction. The synthesis of 1-chloro-3-methyl-3-phospholene (**2c**) is of note; this compound could not have been obtained from the cycloadduct, which leads mainly to the 2-phospholene isomer (**3b**). This is, therefore, a particular advantage of the phosphinic chloride ap-

(7) S. E. Frazier, R. P. Nielsen, and H. H. Sisler, *Inorg. Chem.*, **3**, 292 (1964).

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

(9) K. Hunger, U. Hasserodt, and F. Korte, *Tetrahedron*, **20**, 1593 (1964).

(10) H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **98**, 171 (1965).

(11) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788 (1969).

proach to the halophospholenes, although more steps are involved in the over-all process.

Since cycloadduct reduction had given only a 5% yield of 1-chloro-2-phospholene (**3a**), an attempt to improve the yield by the phosphinic chloride reduction method was made. However, this was even less successful (1% yield). As noted, the poor yield in this case is attributable to the instability of the product.

The phosphinic chlorides (**4** and **5**) used in this study have been previously prepared[5,9] from the reaction of thionyl chloride with the acids, or phosgene with the methyl esters. The location of the double bond in these compounds has been established.[12] The reported synthetic procedures were used, except that oxalyl chloride was substituted for phosgene in the synthesis of **4**. While this reagent was easier to handle and the over-all yield was better, the product contained a significant amount (30%) of the 2 isomer (**5**). It is not known if the rearrangement occurred in the chlorination medium or on distillation of the product. The undesired 2 isomer, which is not noted to form in the phosgene reaction, was removed readily by fractional distillation.

Spectral Properties of 1-Halophospholenes.—The proton nmr spectra of the six 1-halophospholenes prepared in this study are summarized in Table II. The

TABLE II

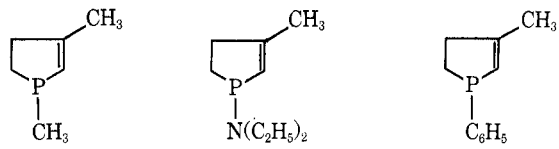
SPECTRAL PROPERTIES OF 1-HALOPHOSPHOLENES

Compd[h]	$\nu_{C=C}^{neat}$, cm^{-1}	^{1}H nmr, δ, ppm (J, Hz)[a] =CH	-CH$_2$-	C-CH$_3$	^{31}P nmr, ppm[d]
2a	1676[b]	...	3.52 (20.0)[c]	2.28	−104.8
2b	1627	6.60 (6.5)[c]	3.66 (2.05)[c]	...	−111.4
2c	1655	5.92[e]	2.97, 3.30[f]	2.27	−127.5
3a	...[f]	6.30–7.80[e]	2.20–3.50[e]	...	...[g]
3b	1601	6.52 (46.5)[c]	2.50–3.46[e]	2.46 (3.5)[c]	−132.5
3c	1601	6.75 (46.5)[c]	2.80–3.90[e]	2.62 (3.5)[c]	−130.6

[a] Neat with external TMS. [b] Weak. [c] Doublet. [d] Neat; relative to 85% H_3PO_4. [e] Multiplet. [f] Unsymmetrical doublet, peak separation 20 Hz. [g] Not determined. [h] Structures can be found in Table I.

spectra permitted conclusive assignment of the position of the double bond in these compounds. Structure **2a** was obvious from the absence of a vinyl proton signal, as well as from the simplicity of the spectrum, which consisted only of two signals. The methyl groups gave a singlet, while the ring methylenes appeared as a doublet (J = 20 Hz) with additional small splitting, apparently from the methyl protons. The doublet was due to coupling with ^{31}P, as revealed by double irradiation experiments. Structure **2b** is also symmetrical; it gave a sharp doublet (J = 20.5 Hz) for the ring methylenes, as well as a doublet for the vinyl protons. The coupling constant (6.5 Hz) of the latter is in accord with that of 1-alkyl-3-phospholenes.[8]

Structures with the double bond in the 2,3 position were evident particularly from the totally different characteristic of the vinyl proton signals. When a substituent was present at the 3 position (**3b**, **3c**), the 2 proton was again a doublet but with an enormous coupling constant (46.5 Hz) with ^{31}P. This same feature is found in several other related structures with trivalent phosphorus and is an obvious characteristic of the system. Thus, structures **6** and **7**, prepared in this study, had J_{PCH} = 42 and 40 Hz, respectively, while in earlier work[8] structure **8** was found to have J_{PCH} = 42.[13] Few data are available for phosphines with sp^2 carbon;



6 **7** **8**

a value of 11.74 for J_{PCH} has been reported for trivinylphosphine.[14] It thus appears that the fixed geometry of the 2-phospholenes may be associated with the large J_{PCH}. A similar situation prevails for J_{PCH} in saturated cyclic phosphines, where an apparent relation between J_{PCH} and the dihedral angle formed by the orbital of the lone electron pair on phosphorus and the α-CH has been noted.[15] Maximum values are observed where the dihedral angle is small. It may be that the orientation of the lone pair on phosphorus is also important in establishing J_{PCH} for the proton on sp^2 carbon; implication of the electron pair in the effect is evident from the observation that the corresponding oxides have normal values (*e.g.*, J_{PCH} = 25.7 Hz for the oxide of **6**[8]). A more direct explanation of the influence of the electron pair on J_{PCH} might involve modification of the structure about the P—C=C unit through p_π–p_π conjugation, a point to be brought up later in this paper. This would give the P–C bond partial double-bond character. Suitable phosphine models with definite P–C double-bond character are not presently available to explore this correlation further; phosphorins (phosphabenzenes) are potentially useful in this sense, but up to the present none have been reported in the literature where a proton is present at the 2 position.

Compound **2c** is isomeric with **3b**, and its spectrum differed considerably in the methylene region. The signal of **2c** was a distorted doublet, having a peak separation of the same size (20 Hz) as observed for the symmetrical 3-phospholenes **2a** and **2b**. The signal of **3b**, wherein structural differences between the two methylene groups are more pronounced, was a complex multiplet. Differences also occurred in the vinyl proton signals (Table II).

Finally, the structure **3a** is characterized in particular by the extreme complexity of the vinyl signals, where, in keeping with other 2-phospholene derivatives bearing no substituents on positions 2 and 3,[12] cross-ring coupling occurs. Had this compound possessed the 3-phospholene ring, a simple spectrum such as that of **2b** would have been observed.

The methylene signals of the symmetrical compounds **2a** and **2b** warrant further comment. In the first place, the signals would seem to be at unusually low field (δ 3.5–3.6 ppm). Few data are available for proton nmr spectra of phosphinous halides, and we are aware of none for cyclic forms. Dimethylphosphinous chloride is reported to have δ 1.54 ppm;[16] replacement of chlo-

(12) H. Weitkamp and F. Korte, *Z. Anal. Chem.*, **204**, 245 (1964).

(13) Unusually large coupling has also been observed for the α protons of 1-methylphosphole [J_{PCH} = 38.5 Hz: L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, **91**, 3308 (1969)] and 1,3,4-trimethylphosphole (J_{PCH} = 41 Hz: L. D. Quin and S. G. Borleske, unpublished results).

(14) W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963).

(15) J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.*, 40 (1969).

(16) J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, **22**, 565 (1966).

rine by bromine should, if anything, cause a slight upfield shift because of its lower electronegativity. While the methylene group is allylic in **2a** and **2b**, it is not reasonable to expect a downfield shift relative to the saturated model of the magnitude seen. In the second place, the methylene signal is a doublet. In 1-alkyl-3-phospholenes, the methylene protons are nonequivalent; they couple with each other and ^{31}P to give an ABX pattern.[8] The nonequivalency is due to the stable, pyramidal geometry about trivalent phosphorus, fixing one proton cis to the P substituent, the other trans. The absence of this nonequivalency in the 1-halo-3-phospholenes is therefore suggestive of a loss of configurational integrity about phosphorus. Both of these characteristics can be explained if the halogen is undergoing rapid intermolecular exchange.[17] This process accomplishes inversion at phosphorus and has already been invoked to account for the identity of the methyl groups in 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane when measured neat at room temperature.[18] At lower temperatures, or in inert solvents, the exchange is retarded and two distinct signals appear for the methyls cis and trans to the chlorine on phosphorus. Furthermore, the methyls absorbed at lower field in a neat sample when exchange was occurring than in dilute solution. Exchange was also postulated for ethylene chlorophosphite,[19,20] and more recently an example of exchange in an acyclic compound [$(Me)_2CHPClNMe_2$] was reported.[21]

To test for the possible occurrence of the exchange in the halophospholenes, compound **2a** was subjected to a dilution study with hexane. The results are given in Table III, where it can be seen that upfield shifts expected for retardation of exchange did occur. Although the peaks were slightly broadened, the doublet character of the CH_2 signal remained intact, and, if exchange is indeed involved in this halide, it apparently is still proceeding even in the dilute solutions used at a rate sufficient to cause equivalency of the methylene protons. Attempts to study the halide at low temperatures were thwarted by freezing of the neat sample at about $-10°$ or precipitation of solid from the hexane solutions. However, a hexane solution of **2b** proved more satisfactory to employ in a low-temperature study. A solution 0.0835 mole fraction in **2b** had the expected doublet (J = 20 Hz) at probe temperature. At $-20°$, both peaks were broadened and showed fine structure; at $-40°$, the doublet had disappeared and a multiplet of several peaks was present. The multiplet has not been analyzed, but its appearance is typical of the AB signal of an ABX system. This experiment therefore strongly indicates the occurrence of the exchange process in the 1-bromo-3-phospholenes. The process may also occur in the 2-phospholenes, but these compounds have not been examined. Table III also contains ^{31}P nmr data for the hexane solutions of **2a**, where a pronounced upfield shift on dilution may be noted. This is the shift expected if one considers that an exchanging P–Br bond has more ionic character with increased positivity at phosphorus than does a static bond. The effect correlates with the upfield shift in the proton signals on dilution, for it is to be expected that diminished positivity at phosphorus will be associated with greater shielding at C–H bonds.

TABLE III

EFFECT OF DILUTION ON NMR CHARACTERISTICS OF 1-BROMO-3,4-DIMETHYL-3-PHOSPHOLENE (**2a**)

Mole fraction of **2a**[a]	$\delta(CH_2)$, ppm	$\delta(CH_3)$, ppm	$\delta(^{31}P)$, ppm[b]
1.00	3.50	2.25	−104
0.495	3.28	2.03	...
0.311	3.17	1.95	−97.4
0.192	3.12	1.89	...
0.137	3.10	1.86	−94.9

[a] Solvent, *n*-hexane. [b] H_3PO_4 standard.

A difference in the proton spectra for chlorine *vs.* bromine in 1-halo-2-phospholene may be seen from considering the data for **3b** and **3c**. While the spectra are very similar, the bromo compound has its corresponding protons at lower field. This effect cannot be explained by electronegativity differences of the halogens, which should act to produce the opposite effect. The effect can be explained on the exchange basis, however, since it is known that bromides participate more readily in this process than do chlorides,[17] and a possible connection between exchange and deshielding has already been noted.

The ^{31}P chemical shift values for the 1-halophospholenes are in keeping with their phosphinous halide structure; the range covered (−104.8 to −132.5 ppm) surrounds the values for the acyclic models $(C_2H_5)_2PCl$ (−119.0 ppm) and $(C_2H_5)_2PBr$ (−116.2 ppm).[22] As for these models, the bromides absorb at slightly higher field than do the chlorides (*e.g.*, bromide **3c** −130.6, chloride **3b** −132.5 ppm), and the 3-phospholene is at higher field than the 2 isomer (*cf.* **2c**, −127.5 ppm, with **3b**).

Another difference for isomer pair **2c** and **3b** is found in their infrared spectra, where the C=C stretching vibration of the 2 isomer occurs at lower frequency and with greater intensity than the 3 isomer. These effects are well known for oxy derivatives of phospholenes[8,12] and for vinyl *vs.* allyl groups in other phosphoryl compounds,[23] but they do not appear to have been observed for trivalent phosphorus compounds. It is obvious that a conjugative effect is present, and as is discussed elsewhere[24] it is believed that the conjugation is of type p_π–p_π.

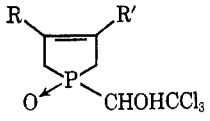
Reactions of 1-Halophospholenes.—Consistent with their phosphinous halide character, the 1-halophospholenes are highly susceptible to nucleophilic displacement reactions. Some reactions of this type were performed in this study.

Hydrolysis occurs rapidly on addition to water (or to ether saturated with water), but the process is preferably conducted in concentrated hydrochloric acid to suppress disproportionation to the phosphine and

(17) J. C. Lockhard, *Chem. Rev.*, **65**, 131 (1965).
(18) B. Fontal and H. Goldwhite, *Tetrahedron*, **22**, 3275 (1966).
(19) P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Amer. Chem. Soc.*, **90**, 715 (1968).
(20) D. Gagnaire, J. B. Robert, J. Verrier, and R. Wolf, *Bull. Soc. Chim. Fr.*, 3719 (1966).
(21) J. E. Bissey, H. Goldwhite, and D. G. Rowsell, *Org. Magn. Resonance*, **2**, 81 (1970).
(22) K. Moedritzer, L. Maier, and L. C. D. Groeneweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).
(23) R. G. Gillis, J. F. Horwood, and G. L. White, *J. Amer. Chem. Soc.*, **80**, 2999 (1958).
(24) L. D. Quin, J. J. Breen, and D. K. Myers ,*J. Org. Chem.*, **36**, 1297 (1971).

TABLE IV

CHLORAL ADDUCTS OF PHOSPHOLENE OXIDES



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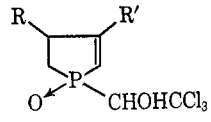
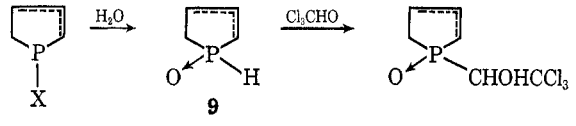


11

Compound							Carbon, %		Hydrogen, %		Phosphorus, %		Chlorine, %	
No.	R	R′	Source	Mp, °C	$\nu_{C=C}^{Nujol}$, cm^{-1}	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
10a	CH_3	CH_3	2a	166.5–168.5	...[a]	$C_8H_{10}Cl_3O_2P$	34.37	34.49	5.06	4.86	11.08	11.06	38.04	38.21
10b	H	H	2b	172.5–173	1616	$C_6H_8Cl_3O_2P$	28.89	29.02	3.24	3.45	12.41	12.62	42.63	42.33
10c	H	CH_3	2c	162.5–163.5	1650	$C_7H_{10}Cl_3O_2P$	31.90	31.77	3.83	3.84	11.75	11.80	40.37	40.40
11a	H	H	3a	160.5–161	1588	$C_6H_8Cl_3O_2P$	28.89	28.71	3.24	3.17	12.41	12.48	42.63	42.62
11b	H	CH_3	3b or 3c	159.0–160.5	1614	$C_7H_{10}Cl_3O_2P$	31.90	31.67	3.83	3.89	11.75	11.75	40.37	40.31

[a] Not observed.

phosphinic acid.[25] From this reaction, the secondary phosphine oxides (**9**) can be obtained. This is the first

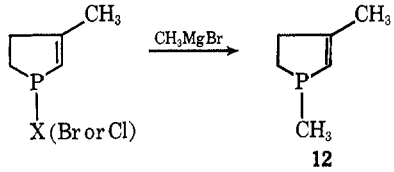


9

report on the synthesis of such oxides in the phospholene family and demonstrates one aspect of the synthetic value of the halophospholenes. These oxides proved to be oils or low-melting, hygroscopic solids, difficult to purify, and were more conveniently handled as their adducts with chloral. These derivatives were in fact used for analytical purposes in this series of compounds (Table IV). The infrared properties of the adducts were useful in showing that the double bond had not migrated during the reactions. Thus, those adducts expected to be 3-phospholene derivatives (**10b** and **10c**) from the assignment of the starting halophospholene had $\nu_{C=C}$ at higher frequency[8,12] than did those expected to be 2 isomers (**11a** and **11b**).

An example of nucleophilic displacement with an amine consisted of the reaction of halide **3c** (containing about 10% of 3 isomer) with diethylamine. The product (**7**), a distillable liquid, was easily characterized from its nmr spectrum; the vinyl proton doublet at δ 5.87 had the expected large coupling (J = 40.0 Hz).

A particularly valuable property of the halophospholenes is their reaction with Grignard reagents. This provides an alternative route to the tertiary phosphines of this family, which have previously been prepared only from reduction of the diene–phosphonous dihalide cycloadducts[4] or of the phospholene oxides derived from the adducts by hydrolysis.[4,26] The phosphonous dihalides required as starting materials are of limited availability or prepared only by tedious processes.[27] Furthermore, the use of alkylphosphonous dichlorides as exemplified by the methyl derivative[8] leads only to the 3-phospholene series, and no 1-alkyl-2-phospholenes are reported in the literature. We have demonstrated the utility of the halophospholenes as precursors to the tertiary phosphines by preparing 1,3-dimethyl-2-phospholene (**12**) from either **3b** or **3c** in good yield. Com-



12

pound **12** possessed the expected nmr spectral feature of large (42.0 Hz) coupling of the vinyl proton with phosphorus. Other spectral differences with regard to the previously prepared 3 isomer[8] are discussed elsewhere.[24]

Experimental Section

Melting and boiling points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Proton nmr spectra were run on a Varian A-60 spectrometer; ^{31}P nmr spectra were obtained on a Varian V-4300B spectrometer at 19.3 MHz. Infrared spectra were recorded on Perkin-Elmer Models 137 and 237 spectrometers. Dienes were purchased from commercial sources and were used as received. Hexachlorodisilane was obtained from Peninsular ChemResearch, Inc. Oxalyl chloride[28] and 1-methoxy-3-methyl-3-phospholene oxide[8] were prepared according to published procedures. All operations involving trivalent phosphorus were conducted in a nitrogen atmosphere.

Formation of Diene–Phosphorus Trihalide Adducts.—An equimolar amount of phosphorus trihalide was added to the diene containing 2–4% of cupric stearate. A fourfold excess by volume of hexane was used as a solvent, and a brown bottle with a Teflon cap was used as a reaction vessel. The bottle was sealed with tape and allowed to stand for a 4-week period before using.[29] The adduct, usually crystalline, was then filtered in a drybox, washed with pentane, and thoroughly dried under vacuum to remove all solvents and unreacted starting material. Yields were not calculated.

Synthesis of 1-Halophospholenes. A. Triphenylphosphine Reduction.—The adduct (20% excess) was suspended in methylene chloride in a ratio of 50 g to 100 ml, and triphenylphosphine in an equal volume of methylene chloride was slowly added in 25- to 50-ml increments. The flask was shaken after each addition and allowed to stand for several minutes before more triphenylphosphine was added. After the final addition, sufficient pentane was added to precipitate any solids in solution. The solids were removed by filtration and washed with pentane. The filtrate and washings were combined and the solvents removed at atmospheric pressure; the resulting product was then distilled.

(25) R. S. Marmar and D. Seyferth, *J. Org. Chem.*, **34**, 748 (1969).

(26) H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964).

(27) In connection with another program, we have prepared 1-benzyl-3-phospholene from benzylmagnesium chloride and halide **2b** and have found this to be the preferred route to this phosphine: P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, **92**, 5779 (1970).

(28) H. Staudinger, *Ber.*, **41**, 3563 (1908).

(29) Butadiene can be collected at Dry Ice–acetone temperature and added directly to the hexane solution of phosphorus trihalide. In all cases precaution should be taken against possible excessive pressure buildup during early stages of adduct formation.

Yields and boiling point values are reported in Table I and spectral data in Table II.

B. Hexachlorodisilane Reduction.—Hexachlorodisilane in benzene (1:2 v/v) was added to the appropriate 1-chlorophospholene oxide dissolved in an equal volume of benzene. A mild exothermic reaction occurred; the mixture was stirred overnight at room temperature, filtered if necessary to remove any solid, and stripped of solvent at atmospheric pressure. The product was then distilled under vacuum. Yields are recorded in Table I and spectral data in Table II.

Synthesis of 1-Chloro-3-methyl-3-phospholene Oxide (4).—To 10.0 g (0.068 mol) of 1-methoxy-3-methyl-3-phospholene oxide in 25 ml of benzene was added 10.1 g (0.080 mol) of oxalyl chloride in 25 ml of benzene. The reaction flask was cooled in an ice bath during addition; a vigorous evolution of gas occurred. When addition was complete the mixture was allowed to warm to room temperature and then stirred at room temperature overnight. The benzene was removed and the product distilled, bp 94–120° (1.8 mm). Comparison of the proton nmr spectrum of the product with spectra of authentic samples[8] indicated a mixture of $\Delta^{2,3}$ and $\Delta^{3,4}$ isomers (about 3:7). Fractional distillation gave 4.3 g (41.7%) of **4** containing only a trace of 2 isomer, bp 97–100° (1.8 mm); bp 77° (0.5 mm) has been reported.[8]

Synthesis of 1-Hydroxy-3-methyl-2-phospholene Oxide.—The cycloadduct (114 g, 0.55 mol) obtained from isoprene and PCl_3 was added to 200 g of ice. The resulting red solution was extracted continuously with methylene chloride. Removal of the solvent yielded 25.6 g (39.8%) of crude product. Recrystallization from ether–methylene chloride gave a white solid: mp 120.5–121.5° (lit.[30] mp 116–117°); nmr ($CDCl_3$ external TMS) δ 2.48 (singlet, CH_3), 2.22–3.40 (complex multiplet, $-CH_2-$), 6.40 (doublet, J = 23.0 Hz, C=CH), 13.1 ppm (singlet, OH).

Hydrolysis of the cycloadduct from isoprene and phosphorus tribromide followed by extraction with methylene chloride yielded 42.8% of crude product which on recrystallization gave a white solid, mp 120.5–121.5°. A mixture melting point of the products from the two reactions showed no depression and the nmr spectra were identical.

Synthesis of 1-Chloro-3-methyl-2-phospholene Oxide (5).—Thionyl chloride (59.5 g, 0.05 mol) in 50 ml of benzene was added dropwise to 28.9 g (0.25 mol) of 1-hydroxy-3-methyl-2-phospholene oxide slurried in 100 ml of benzene. After addition the mixture was refluxed for 2 hr; the benzene and excess thionyl chloride were removed at atmospheric pressure and the product was distilled. The yield was 30.5 g (80.4%), bp 116–117° (2 mm), lit.[8] bp 91° (0.07 mm).

Synthesis of 1-Chloro-2-phospholene Oxide.—Crude 1-hydroxy-2-phospholene oxide (18.5 g, 0.15 mol) obtained by the hydrolysis of the cycloadduct from phosphorus trichloride and butadiene was slurried in 100 ml of benzene, and 35.8 (0.30 mol) of thionyl chloride in 50 ml of benzene was added dropwise over a 30-min period. The mixture was refluxed for 1 hr and then distilled. The yield was 18.5 g (89.4%), bp 107–109.5° (2.2 mm), lit.[5] bp 105–110° (0.20 mm).

Conversion of Phosphinous Halides to Secondary Phosphine Oxides.—The following general procedure was used. The phosphinous halide (5–10 g) was slowly added to chilled concentrated HCl (10–50 ml). The mixture was allowed to warm to room temperature and then stirred overnight at that temperature. The solution was extracted continuously for at least 24 hr with methylene chloride. The organic layer was separated and dried. Removal of the solvent left an oil or low-melting solid. The phosphine oxides were characterized by conversion to chloral adducts as described in the next section.

An alternate procedure for hydrolysis when only a small amount of phosphinous halide was available was to add wet ether to the halide. The oil which formed could be used directly in the conversion to chloral adducts.

Chloral Adducts of 1-Halophospholenes.—The following general procedure was used. The crude phosphine oxide (1–2 g) was dissolved in 10 ml of isopropyl alcohol, and 2 g of chloral hydrate in 10 ml of isopropyl alcohol was added. A few drops of sodium methoxide in methanol were added and the mixture allowed to stand overnight. Alternatively, the mixture can be heated for several hours on a steam bath without the addition of sodium methoxide. In either case removal of the solvent gave a crude product that could be recrystallized from ethanol–water. Analytical and spectral data are given in Table IV.

Synthesis of 1,3-Dimethyl-2-phospholene (12).—1-Chloro-3-methyl-2-phospholene (10.4 g, 0.085 mol) in an equal volume of ether was added dropwise to an ice-cooled flask containing methylmagnesium iodide (prepared from 2.92 g-atoms of magnesium and 17.0 g of methyl iodide). The mixture was allowed to warm to room temperature and refluxed for 3 hr. After cooling, the mixture was hydrolyzed with 75 ml of 10% NH_4Cl and stirred for 1 hr. The organic layer was separated and the water layer extracted with 250 ml of ether. After removal of ether, the product was distilled and yielded 5.40 g (55.6%) of 1,3-dimethyl-2-phospholene: bp 139.5–141.5°; nmr (neat, external TMS) δ 1.23 (doublet, J = 2.8 Hz, P-CH_3), 2.13 (doublet, J = 1.0 Hz, C-CH_3), 1.54–3.16 (complex, $-CH_2CH_2-$), 5.90 ppm (doublet, J = 42.0 Hz, C=CH); ir $\nu_{C=C}^{neat}$ 1613 cm^{-1}. A sample (in benzene) was converted into the benzyl bromide salt which was recrystallized from chloroform–ethyl acetate: mp 133.5–134.5°; nmr ($CDCl_3$, internal TMS) δ 1.92 (singlet, C-CH_3), 2.45 (doublet, J = 14.5 Hz, P-CH_3), 2.60–3.25 (complex, $-CH_2CH_2-$), 4.55 (doublet, J = 16.5 Hz, benzyl $-CH_2-$), 6.33 ppm (J = 29.0 Hz, C=CH).

Anal. Calcd for $C_{13}H_{18}BrP\cdot H_2O$: C, 51.45; H, 6.65; P, 10.21. Found: C, 51.13; H, 6.59; P, 10.36.

Synthesis of 1-(*N*,*N*-Diethylamino)-3-methyl-2-phospholene (7).—A solution of 4.4 g (0.060 mol) of diethylamine in 10 ml of dry ether was cooled to 0°. 1-Bromo-3-methyl-2-phospholene (5.3 g, 0.030 mol), containing about 10% of the 3 isomer, was added to the cold solution with vigorous stirring over 45 min. After the addition was complete, the mixture was allowed to warm to room temperature and stirred 1 hr. The white solid was removed by filtration and the liquid distilled, bp 98–102° (19 mm), yield 39.5%. Gas chromatography showed the product to contain about 90% **7** and 10% 3 isomer. Spectra follow: nmr (neat, external TMS) δ 1.25 (triplet, J = 7 Hz, CH_3CH_2-) 3.08 (quartet, J = 7 Hz, N-CH_2), 1.75–3.42 (complex, $-CH_2-CH_2-$), 2.14 (singlet with fine splitting, ring CH_3), 5.87 ppm (doublet, J = 40 Hz, C=CH); ir $\nu_{C=C}^{neat}$ 1604 cm^{-1}.

Anal. Calcd for $C_9H_{18}NP$: N, 8.18; P, 18.09. Found: N, 8.20; P, 17.90.

Registry No.—**2a**, 28273-33-8; **2b**, 28273-34-9; **2c**, 28273-35-0; **3a**, 28273-36-1; **3b**, 28273-37-2; **3c**, 28273-38-3; **7**, 28273-39-4; **10a**, 28273-40-7; **10b**, 28273-41-8; **10c**, 28273-42-9; **11a**, 28273-43-0; **11b**, 28273-44-1; **12**, 28273-45-2; 1-hydroxy-3-methyl-2-phospholene oxide, 3858-24-0.

Acknowledgment.—We thank Mr. Ronald C. Stocks for preparing compound **7**, and Mr. Joseph J. Breen for obtaining ^{31}P nmr spectra.

(30) A. O. Vizel, M. A. Zuereva, K. M. Ivanovskaya, I. A. Studentsova, V. G. Dunaev, and M. G. Berim, *Dokl. Akad. Nauk SSSR*, 826 (1965).