TABLE VII

COMPETITIVE REDUCTION OF ORGANIC HALIDES WITH $Cr^{II}en$

Substrate (A)	M^b	Substrate (B)	M	Av k_A/k_B
$CH_3CH_2CH_2CH_2Br$	0.0135	$BrCH_2CH_2CH_2Br$	0.0135	0.014
	0.0541		0.0135	0.013
	0.135		0.0135	0.017
$CH_3CH_2CH_2CH_2I$	0.00982	$ICH_2CH_2CH_2I$	0.0123	0.014
	0.0393		0.0123	0.020
	0.0982		0.0123	0.018
$BrCH_2CH_2CH_2Br$	0.0135	$BrCH_2CH_2Br$	0.0186	0.065
	0.0405		0.0186	0.066
$ICH_2CH_2CH_2I$	0.0123	$BrCH_2CH_2Br$	0.0186	1.47
	0.0221		0.0186	1.81
$ClCH_2CH_2CH_2I$	0.0177	$CH_3CH_2CH_2CH_2I$	0.0491	6.3[c]
	0.0089		0.0491	7.4[c]
	0.0089		0.0786	5.4[c]
$ClCH_2CH_2CH_2Br$	0.0185	$CH_3CH_2CH_2CH_2Br$	0.0676	13.9[c]
	0.0093		0.0676	16.4[c]
	0.0093		0.108	13.2[c]
$BrCH_2CH_2CH_2OTs$	0.00332	$CH_3CH_2CH_2CH_2I$	0.0098	1.2
	0.00133		0.0196	1.1
	0.00067		0.0491	0.98

[a] Chromous solution added rapidly by syringe to solution of halides and ethylenediamine in DMF at room temperature. [b] $[Cr(ClO_4)_2]$ 0.00518 M, ethylenediamine 0.0202 M. [c] Correction factor of 1.21 included to account for competitive reduction.

was degassed, then the requisite amount of ethylenediamine was added to the rapidly stirred mixture, followed *immediately* by the chromous solution. Various ratios of reactants were employed and relative rates determined in the usual manner. Typical data are included in Table VII.

Gas Chromatographic Data.—Ethylene, propylene, and cyclopropane were measured on a 15-ft Dowtherm A column against *n*-butane as marker (standard). A 6-ft QFI column was used to measure *n*-propyl chloride *vs.* isopropyl chloride marker.

The gases were examined using a Case-constructed instrument having a thermal conductivity detector; liquids, in solution, were measured on a Varian Aerograph A-200 equipped with flame-ionization detectors.

Registry No.—Ethylenediaminechromium(II), 15525-39-0.

Acknowledgment.—We wish to thank the National Science Foundation for a generous grant which supported this study and Mr. John Powers for the preparation of *meso-* and *dl*-2,4-pentanediols.

Structure of Diene–Phosphonous Dihalide Addition Products and of Derived Phospholenes and Phospholene Oxides[1]

LOUIS D. QUIN, JOAN PETERS GRATZ, AND THOMAS P. BARKET

Department of Chemistry, Duke University, Durham, North Carolina 27706

Received September 28, 1967

It has been shown that the cycloadducts of methylphosphonous dichloride and butadiene, isoprene, 3,4-dimethylbutadiene, or piperylene give rise to 3-phospholene oxides on hydrolysis and 3-phospholenes on reduction with magnesium. The cycloadduct from butadiene was also shown to contain the 3-phospholene ring. The 3-phospholene oxides may be caused to rearrange to 2-phospholene oxides either thermally or by refluxing aqueous base. Acid treatment was effective only for rearranging the 3-methyl derivative. The 3,4-dimethyl derivative resisted rearrangement conditions. Phenylphosphonous dibromide (synthesized by a new method from phenylphosphinic acid and phosphorus tribromide) also gave an adduct with isoprene shown by nmr studies to contain the 3-phospholene ring, which was preserved in the oxide and phospholene. However, the isoprene–phenylphosphonous dichloride adduct contained the 2-phospholene ring; the derived oxide and phospholene were also the 2 isomers. Independent syntheses of the isomeric 1-phenyl-3-methylphospholene oxides confirmed the assignments. The adduct from piperylene and phenylphosphonous dibromide also gave on hydrolysis the 3-phospholene oxide, while that from phenylphosphonous dichloride gave the 2 isomer.

The cycloaddition of conjugated dienes and phosphonous dihalides was first reported by McCormack in 1953.[2,3] The halophosphorane adducts and derived products were assumed to contain the 3-phospholene ring. It was not until 1963 that it became evident that the double bond in products derived from the adducts could appear in the 2,3 position. This behavior was first encountered among adducts from the related reaction of dienes and phosphorus trihalides,[4,5] where it was found that the trichloride gave 2-phospholene derivatives while the tribromide gave the 3 isomer. It was later stated that adducts of phenylphosphonous dichloride with isoprene or butadiene gave on hydrolysis the 2-phospholene oxides rather than the

---

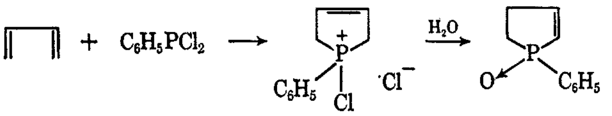
[1] Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute.

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

[3] The literature on this reaction has been reviewed recently: L. D. Quin, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967, Chapter 3.

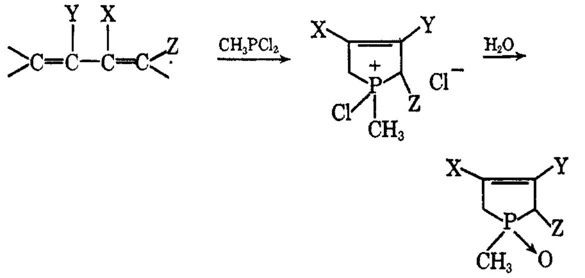
[4] U. Hasserodt, K. Hunger, and F. Korte, *Tetrahedron*, **19**, 1563 (1963).

[5] B. A. Arbuzov, A. O. Vizel, Y. Y. Sametov, and K. M. Ivanovskaya, *Dokl. Akad. Nauk SSSR*, **159**, 582 (1964).


(1)

expected 3 isomers[6] (eq 1), and proton magnetic resonance (pmr) spectral studies[7] supported this contention. This observation has placed considerable doubt[3] on the exact structure of many compounds arising from phosphonous dichloride–diene adducts. We have resolved some of the uncertainty by studying the phospholenes and their oxides resulting from reduction and hydrolysis, respectively, of adducts derived from an alkyl (methyl[8a]) and an aryl (phenyl[8b]) phosphonous dichloride. The study has revealed that the structure of the adduct, and therefore also of derived products, is controlled by the nature of the substituent on the phosphonous dichloride, a methyl substituent leading to 3-phospholene derivatives and phenyl to 2-phospholenes. For the latter substituent, we shall show that replacing chlorine by bromine in the phosphonous dihalide leads to the 3-phospholene system, in parallel to the behavior of the phosphorus trihalides.[4,5] The specificity of the various reactions is remarkably high.

P-Methylphospholene Oxides.—A group of four new P-methyl oxides (**1a–d**) was prepared by addition to cold water of the adducts of methylphosphonous dichloride with dienes (eq 2). The oxides were hygroscopic and difficult to obtain in pure form. For analysis, they were converted to the dibromides, although in two cases (those of **1b** and **c**) instability was encountered. Pmr spectra[9,10] (Table I) of these compounds provide convincing evidence for the assignment of the double bond to the 3,4 position. Compound **1a** had a simple spectrum reflecting the symmetry of the molecule, and consisted of doublets (due to coupling with P^{31}) for the methyl protons at δ 1.60 (J = 13 cps), methylene protons at 2.43 (J = 11 cps), and vinyl protons at 5.87 (J = 28 cps). The spectrum of compound **1b** was quite similar; the two sets of methylene protons, although in slightly different environments because of the 3-methyl substituent, nevertheless were indistinguishable and appeared as a doublet with broad peaks. Compound **1c** showed no vinyl proton signals; compound **1d**, obtained as a separable mixture of *cis* and *trans* isomers,[11] showed two vinyl protons. The latter observation could also indicate the double bond to be in the 4,5 position. However, it will be seen shortly that such a 2-phospholene oxide bearing no substituents on the double bond had a characteristic complicated spectrum not observed for this sample. It is of interest that the protons within the methylene groups of oxides **1a**, **1b**, and **1c** fail to show nonequivalence due to disposition of one proton *cis* to P–CH_3 and the other *cis* to P → O. The protons are equivalent also in the benzyl bromide salts of the corresponding phospholenes (*vide infra*). It will be noted later in this paper, however, that the phospholenes *do* possess nonequivalent protons.


(2)

1a, X = Y = Z = H
b, X = Z = H; Y = CH_3
c, X = Y = CH_3; Z = H
d, X = Y = H; Z = CH_3

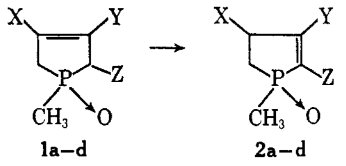
Table I

Spectral Properties of P-Methylphospholenes and Oxides[a]

Compd	$\gamma_{C=C}^{neat}$, cm^{-1}	δ (J, cps)[b] P–CH_3	=CH	CH_2	C–CH_3
		A. 3-Phospholene Oxides[c]			
1a	1620	1.60 (13.0)	5.87 (28.0)	2.43 (11.0)	
1b	1655	1.61 (13.0)	5.48 (29.0)	2.23–2.72[d]	1.79[e]
1c	[f]	1.56 (13.5)[g]		2.47[h]	1.68[e]
		B. 2-Phospholene Oxides[i]			
2a	1585	1.93 (13.5)	6.1–7.8[j]	2.2–3.3[j]	
2b	1615	1.87 (13.5)	6.29 (25.7)	2.1–3.2[j]	2.29[e]
2d	1634	1.82 (13.0)	6.77 (40.0)[k]	1.6–3.1[j]	2.20 (11.0)[l]
		C. 3-Phospholenes[i]			
3a	1626	0.82 (3.5)	5.80 (7.0)	1.7–2.95[m]	
3b	1658	0.87 (3.5)	5.38 (5.5)	2.0–2.9[m]	1.78[e]
3c	[f]	0.82 (3.5)		1.9–2.95[m]	1.65[e]
		D. Benzyl Bromide Salts of 3-Phospholenes[n]			
4a[c]		2.98 (15.0)	6.43 (28.5)	3.92 (10)	
4b[o]		2.37 (14.5)	5.38 (30)	3.24 (10)	1.72[e]
4c[o]		2.38 (14.5)		3.22 (10)	1.60[e]

[a] The spectra of the 2-methyl derivatives **1d** and **3d**, which exist in *cis* and *trans* forms, have been described elsewhere.[11] [b] Doublets from coupling with P^{31}. [c] Pmr run in $CDCl_3$ solution with external standard. [d] Broad, partly resolved doublet; peak separation, 11 cps. [e] Singlet. [f] Not observed. [g] Downfield peak overlapped by C—CH_3 signal. [h] Unsymmetrical, broad doublet; peak separation, 11 cps. [i] Pmr run neat with external TMS. [j] Complex multiplet. [k] Each peak shows additional small splitting. [l] Each peak additionally split 1.7 cps, presumably by vinyl proton. [m] AB multiplet of ABX system. [n] Benzyl CH_2 signals: **4a**, 5.24 (16.7); **4b**, 4.58 (17.2); **4c**, 4.58 (17). [o] Pmr run in $CDCl_3$ with internal standard.

Hunger, *et al.*,[6] found that thermal treatment or exposure to refluxing aqueous base caused rearrangement of the double bond in certain 1-hydroxy-3-phospholene oxides to the 2,3 position, and we have made a similar observation for the 1-methyl-3-phospholene oxides. The observation is of synthetic value as the 2-phospholene oxides so obtained are not available at present by any other method. Refluxing aqueous acid was also used for the first time for such a rearrangement; it was effective for rearranging only one of the


1a–d **2a–d**

---

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

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

(8) Preliminary communications: (a) L. D. Quin, J. A. Peters, C. E. Griffin, and M. Gordon, *Tetrahedron Letters*, 3689 (1964); (b) L. D. Quin and T. P. Barket, *Chem. Commun.*, 914 (1967).

(9) The pmr spectral properties of the 3-phospholene ring as incorporated in phosphinic derivatives have been described by others.[7] Very large coupling constants for the vinyl protons β to phosphorus (J_{PCCH}) are characteristic of the system. The values exceed J_{PCH}. A valuable and extensive discussion of the pmr spectra of organophosphorus compounds, including some of those described in this paper, may be found in the Ph.D. dissertation of M. Gordon, University of Pittsburgh, Pittsburgh, Pa., 1965.

(10) B. A. Arbuzov, Y. Y. Sametov, A. O. Vizel, and T. B. Zykova, *Dokl. Akad. Nauk SSSR*, **159**, 1062 (1964).

(11) L. D. Quin, J. P. Gratz, and R. E. Montgomery, *Tetrahedron Letters*, 2187 (1965).

TABLE II

REARRANGEMENTS OF 1-METHYL-3-PHOSPHOLENE OXIDES

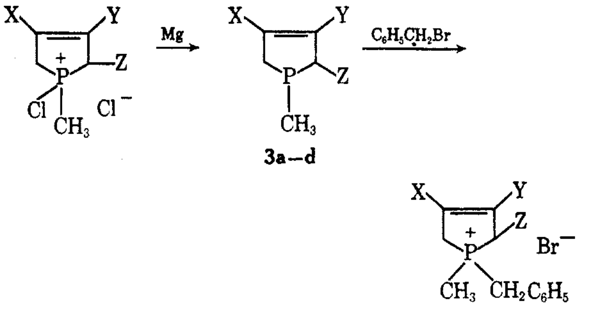
Oxide used	Composition[a] of recovered oxide: Thermal[b]	Base[c]	Acid[d]
1a	1:1 (12 or 20 hr)	2:3 (24 or 48 hr)	*e*
1b	1:1 (6.5 or 12 hr)	1:2 (27 hr)	1:9 (96 hr)
1c	9:1[f] (13.5 hr)	9:1[f] (46 hr)	9:1[f] (52 hr)
1d	1:9 (53 hr)	>99% **2d** (23 hr)	*e*

[a] Ratio of **1** to **2** as determined by gc. [b] Reflux of neat liquid. [c] Reflux in 3 *N* sodium hydroxide. [d] Reflux in 3 *N* hydrochloric acid. [e] No detectable rearrangement. [f] The amount of **2c** was calculated from two peaks on the chromatogram presumed to be *cis* and *trans* forms.

oxides (**1b**). From the results summarized in Table II, one arrives at the following conclusions. (1) The 3 isomer is stabilized to all rearranging conditions by the presence of two methyl substituents on the double bond (**1c**), as has been noted for some other phospholene derivatives.[6] (2) Acid treatment effects extensive rearrangement if the starting 3-phospholene bears one methyl substituent on the double bond (**1b**), but causes little or no rearrangement if the double bond is unsubstituted (**1a**, **d**). This is suggestive of a carbonium ion mechanism for the rearrangement; the former case would involve creation of a tertiary ion by electrophilic attack of a proton on the double bond, followed by proton loss, whereas in the latter case a less stable secondary ion would have to be created. (3) A particular preference for the 2 isomer appears if the double bond moves from an unsubstituted to a substituted situation, as seen by the greater tendency of **1d** to rearrange to **2d** than of **1a** to rearrange to **2a**.

Each of the 2-phospholene oxides **2a**, **b**, and **d** was isolated by distillation in pure form. No attempt was made to isolate **2c**, which was formed in only small amount. The infrared and pmr spectra (Table I) showed distinct differences from those of the 3-phospholene oxides. In the infrared, a difference directly associated with the position of the double bond was noted for two isomer pairs (**1a**–**2a**, **1b**–**2b**). The C=C stretching vibration occurred at lower frequency and significantly greater intensity for the 2 isomers. Both effects have been noted for other phospholene derivatives[7], and the appearance of the band at lower frequency (by 24 cm^{-1}) for a vinylphosphonate than for an allylphosphonate has also been observed.[12] The frequency difference was not observed for **1d**–**2d**, presumably because of a counter effect in the creation of the trisubstituted double bond in **2d** from a disubstituted one in **1d**. The pmr spectra were in accord with the assigned structures. For **2a**, the vinyl proton signals were a complex multiplet spread over the range δ 6.3–7.8. Another 2-phospholene oxide derivative (1-hydroxy) bearing no substituents on the double bond has been found to exhibit a similar complex spectrum, which has been analyzed in terms of cross-ring coupling.[7] The methylene region (δ 2.1–3.2) of **2a** also was considerably more complex than that of the symmetrical 3 isomer since there are two methylenes experiencing different shielding in **2a**. Oxide **2b** had its vinyl signal as a doublet (J_{PCH} = 25.7 cps) at δ 6.29, each peak of which showed slight additional splitting. The more downfield position of the vinyl proton relative to **1b** is in keeping with its location α or β to phosphorus, respectively. As additional proof of structure, the C-methyl substituent was indicated to be on the double bond from its singlet at δ 2.29. Finally, compound **2d** had a single vinyl proton (doublet at δ 6.77, J_{PCCH} = 40 cps with further splitting) and a methyl group on the double bond. Its signal at δ 2.20 was split by phosphorus (J_{PCCH} = 11.0 cps) and by the vinyl proton (1.7 cps). Comparison of δ for the vinyl proton in **2b** and **2d** reveals the proton of the latter (β) to be more deshielded (about 0.5 ppm) than the former (α). The situation is thus similar to that in α,β-carbonyl compounds, where it is well known that a β proton is more deshielded than an α proton. The same relation is evident in the 2- and 3-methyl derivatives of 1-phenyl-2-phospholene oxide (**7a** and **7b**, Table III).

P-Methylphospholenes.—With the magnesium–tetrahydrofuran system described previously,[13] the 3-phospholenes **3a–d** were prepared (eq 3) from the



(3)

4a–c

corresponding adducts. Only **3b**[13] and **d**[11] have been previously reported. The new phospholenes were analyzed as the benzyl bromide salts.

The pmr spectra (Table I) of the phosphines were predictably different from those of the corresponding oxides, since trivalent phosphorus generally produces a much smaller chemical shift and coupling constant than does tetracovalent phosphorus as in phosphoryl or phosphonium compounds.[14] For example, in **3a**, the P-CH_3 doublet appears at δ 0.82 with J = 3.5 cps, and the vinyl protons appear at 5.80 (J = 7.0 cps). In contrast to the oxides and benzyl bromide salts corresponding to these phospholenes, the protons within the methylene groups of **3a**, **b**, and **c** are nonequivalent, and lead to ABX spectra (where X is P^{31}). The same is true of P-phenylphospholenes (*vide infra*). A separate study of this phenomenon is being made in collaboration with Dr. C. E. Griffin, University of Pittsburgh, and will be reported later. Phospholene **3d** shows another property of interest; it exists as *cis* and *trans* isomers owing to the configurational stability of trivalent phosphorus. The separation and properties of these isomers have been reported elsewhere.[11]

The pmr spectra (Table I) of the phospholenes confirm the assignment of the double bond to the 3 position. Phospholene **3c** has no vinyl protons and is necessarily the 3 isomer; the characteristic ABX pattern for its methylene protons is reproduced in the spectra of **3a** and **b**, which could not be the case if each methylene group were differently shielded as in the 2 isomer.

---

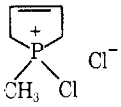
(12) R. G. Gillis, J. F. Horwood, and G. L. White, *J. Amer. Chem. Soc.*, **80**, 2999 (1958).

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

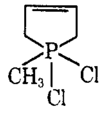
(14) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

Furthermore, the benzyl bromide salts show each ring methylene group to be equivalent, giving a sharp doublet due to P^{31} coupling.

P-Methyl Cycloadducts.—The adducts are highly reactive to water and are not readily characterized directly. We have, however, succeeded in obtaining the pmr spectrum of the butadiene–methylphosphonous dichloride adduct in deuteriochloroform. The spectrum is entirely consistent with the symmetrical 3-phospholene ring system; the spectrum consists only of three doublets, P–CH$_3$ at δ 3.87 (J = 14 cps), the two methylenes at δ 4.47 (J = 8 cps), and vinyl H at δ 6.82 (J = 36 cps). The large downfield shifts resemble those of the benzyl bromide salt (see Table I), and suggest that, at least in solution, phosphorus is ionic (**5**) in these adducts rather than covalent (**6**).



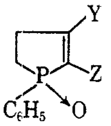
5



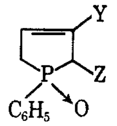
6

Support for this assignment has come from the P^{31} spectrum of the deuteriochloroform solution; a signal at −112 ppm from 85% phosphoric acid was obtained. This value is in line with those reported for tri(*n*-butyl)dichlorophosphorane (−106 ppm in acetonitrile, −104 ppm in nitrobenzene), which has been established to be ionic.[15] Were phosphorus pentacovalent, a signal at much higher field would have been observed.

P-Phenylphospholene Oxides.—The appearance of the double bond in the 3 position of the oxides from hydrolysis to methylphosphonous dichloride adducts was in opposition to results[6] with P-phenyl compounds, where adduct hydrolysis had apparently given the 2-phospholene oxides. However, this observation has now been confirmed with the preparation of two oxides, **7a** and **b**, from the adducts with piperylene and isoprene, respectively. Oxide **7a** was obtained by addition of the adduct to water, and was recovered by chloroform extraction after basification of the mixture. It was readily seen to have the 2-phospholene system by its pmr spectrum (Table III). The methyl group was located on the double bond (δ 1.79); it was coupled with phosphorus (J = 11.5 cps) and lacked the additional coupling to be expected if there were a methine proton as in the 3 isomer **8a**. This coupling has been observed in 1,2-dimethyl-3-phospholene oxide (**1d**).[11] Furthermore, there were two distinct methylene signals. Oxide **7b** was obtained from the procedure of McCormack[16] which is said to provide the 3 isomer. The product was predominantly the 2-phospholene oxide; gas chromatography revealed the presence of only about 4.5% of the 3 isomer (**8b**, *vide infra*) in the extracted oxide. The pmr spectrum (Table III) of the product after distillation resembled that already reported for **7b** by Weitkamp and Korte,[7] although traces of **8b** were evident in our spectrum as in the gas chromatogram. That this product indeed had structure **7b** was proved by preparing authentic specimens of the isomeric pair of 2- and 3-phospholene oxides. It is well established[6,7] that the cycloadduct from isoprene and phosphorus trichloride on alcoholysis gives a 2-phospholene derivative (*e.g.*, **9**) whereas the phosphorus tribromide adduct leads to a 3-phospholene derivative (*e.g.*, **11**). These derivatives from methanolysis were subjected to the reaction sequence shown in Scheme I previously employed in the synthesis of P-alkyl phospholene oxide.[6] Oxide **7b**, a low melting solid, was identical in physical and spectral properties with the oxide obtained by hydrolysis of the isoprene–phenylphosphonous dichloride adduct. Oxide **8b**, a liquid, was quite different from **7b** in its spectral properties. In the infrared, **8b** had a weak C=C stretching band at 1646 cm^{-1}; **7b** would be expected to have this band at lower frequency, and indeed a strong band was present at 1612 cm^{-1} (possibly associated with a phenyl absorption). The pmr spectrum of **8b** contained the vinyl doublet at higher field (δ 5.62) and with a larger coupling constant (31.5 cps) than for **7b** (δ 5.97, J_{PCH} = 25.5 cps). Furthermore,



7a, Y = H; Z = CH$_3$
b, Y = CH$_3$; Z = H



8a, Y = H; Z = CH$_3$
b, Y = CH$_3$; Z = H

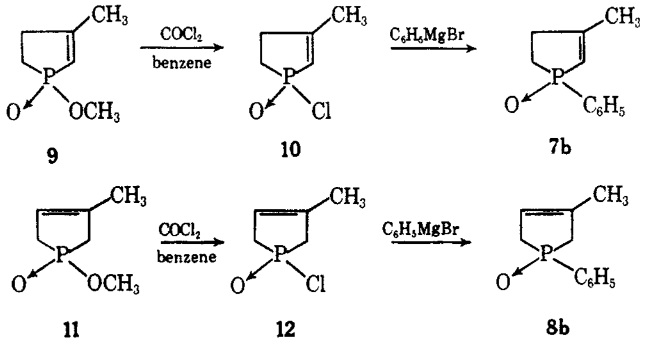
TABLE III

PMR SPECTRA OF P-PHENYLPHOSPHOLENES AND OXIDES

	δ (J,[a] cps)		
	=CH	CH$_2$	C—CH$_3$
2-Phospholene oxides[b]			
7a	6.67 (41)[c]	1.8–3.1[d]	1.79 (11.5)[e]
7b	5.97 (25.5)[f]	1.8–3.1[d]	2.08[g]
3-Phospholene oxides[b]			
8a[h]	5.38–6.45	2.3–3.4[i]	0.62–1.6
8b	5.62 (31.5)	2.4–2.9[j]	1.83[g]
Phospholenes[k]			
14	5.40 (8.0)	1.95–3.15[k]	1.70[g]
17	5.68 (42)[c]	1.5–2.8[d]	1.80[l,m]
Benzyl Bromide Salts[b,n]			
15[o]	5.43 (31.5)	3.0–4.3[d]	1.73[g]
18[p]	6.60 (28.7)	2.1–3.5[d]	2.0[g]

[a] Doublets from coupling with P^{31}. [b] CDCl$_3$ solution with internal standard. [c] Each peak shows small additional coupling. [d] Complex multiplet. [e] Each peak split 2 cps, presumably by vinyl proton. [f] Lit.[7] 5.83 (25.8). [g] Singlet. [h] Mixture of *cis* and *trans* forms giving superimposed spectra. [i] Includes methine proton. [j] Unsymmetrical doublet with broad peaks of 11 cps separation. [k] Neat with internal standard. [l] AB multiplet of ABX system. [m] Doublet from coupling with vinyl proton of 2 cps. [n] Benzyl CH$_2$ signals: **15**, 4.89 (16.0); **18**, 4.68 (15.7). [o] 49 mg in 0.3 ml of CDCl$_3$. [p] 110 mg in 0.3 ml of CDCl$_3$.

SCHEME I



---

(15) G. A. Wiley and W. R. Stine, *Tetrahedron Letters*, 2321 (1967).

(16) W. B. McCormack, *Org. Syn.*, **43**, 73 (1963).

the two methylenes of **7b**, being differently shielded, gave a complex multiplet (δ 1.8–3.1) rather than a doublet as in **8b**.

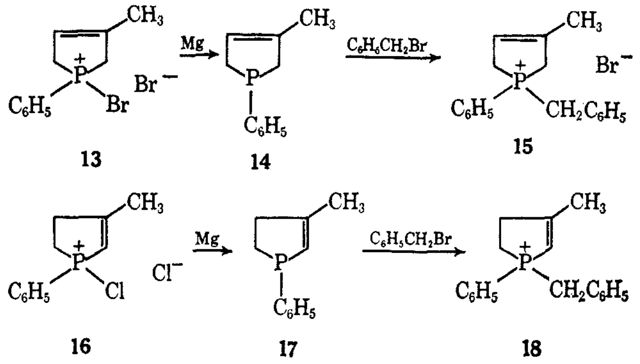
We have furthermore found that cycloadducts from phenylphosphonous **dibromide** provide the 3-phospholene oxides on hydrolysis, a result analogous to the use of phosphorus tribromide *vs.* phosphorus trichloride. Thus, the isoprene–phenylphosphonous dibromide adduct yielded oxide **8b** on hydrolysis, with only about 0.5% of isomer **7b**, and the piperylene adduct gave the new oxide **8a**[17,18] as a mixture of *cis* and *trans* isomers. This isomerism, which will be the subject of further study, was evident from the presence of two C–CH_3 signals, each a four-line pattern from coupling with P^{31} and the methine proton at C_2. Although arylphosphonous dibromides have been used previously in cycloadditions,[3] it has been assumed that the oxide from hydrolysis is the same as that from hydrolysis of arylphosphonous dichloride adducts.

A brief study of the rearrangement of oxides **7b** and **8b** was made. No change took place with either oxide when separately exposed overnight to 3 *N* sodium hydroxide or to 3 *N* hydrochloric acid at room temperature. However, reflux of either mixture containing **8b** caused extensive rearrangement to the 2-phospholene derivative **7b**. The efficacy of acid for the rearrangement of the related 1,3-dimethyl-3-phospholene oxide (**1b**) has already been noted. The mixtures starting with the pure 2-phospholene oxide (**7b**) showed a small amount of **8b** to be formed, suggesting that the rearrangements are reversible.

The formation of the 2-phospholene oxide system from phenylphosphonous dichloride adducts is not entirely general; it has been established elsewhere[6] that the adduct with 2,3-dimethylbutadiene gives mainly the 3-oxide.

P-Phenylphospholenes.—The position of the double bond in the phospholenes from magnesium reduction of the adducts has been found to be the same as in the phospholene oxides from hydrolysis. Thus, the isoprene–phenylphosphonous **dibromide** adduct gave a 45% yield of 1-phenyl-3-methyl-3-phospholene (**14**), as determined by its pmr spectrum and that of its benzyl bromide salt (**15**). Both spectra (Table III) resembled those of the corresponding P-methyl derivatives, the former showing the ABX multiplet. Also on oxidation **14** gave the 3-phospholene oxide **8b**. The isoprene–phenylphosphonous **dichloride** adduct had previously[13] been reduced in this laboratory, and the product assigned structure **14**. This product is in fact the 2-phospholene isomer (**17**) (Scheme II). On oxidation it is converted into 2-phospholene oxide **7b**. Furthermore, its pmr spectrum differed considerably from that of **14** (Table III). Most notable was the extraordinary size of the P^{31}–vinyl H coupling (J_{PCH} = 42 cps). Phosphorus in trialkyl phosphines normally has a small geminal coupling constant (*e.g.*, 3.5 cps for P–CH_3 in **3a–c**) when attached to sp^3 carbons. Few data are available for an attachment to sp^2 carbon; trivinylphosphine is, however, reported[19] to have a somewhat larger than normal value (11.74 cps) for coupling to the α carbon.

SCHEME II



The adduct from 2,3-dimethylbutadiene and phenylphosphonous dichloride had already been demonstrated[13] by pmr spectroscopy to be reduced to 1-phenyl-3,4-dimethyl-3-phospholene. This is consistent with hydrolysis to the 3-phospholene oxide.[6] As for the phosphorus trichloride adducts, the presence of two methyl groups tends to stabilize the double bond in the 3 position. Similar stability in 1,3,4-trimethylphospholene oxide (**1c**) to various rearranging conditions has already been noted.

P-Phenyl Cycloadducts.—In their discussion of the formation of 2-phospholene derivatives from cycloadducts of phosphorus trichloride, Hunger, *et al.*,[6] assumed that the cycloadduct itself possessed the 3-phospholene ring and that rearrangement occurred during subsequent reactions. It is mentioned in their paper, without data, that the adducts do have spectra supporting this structure. This explanation did not seem satisfactory to us for the phenylphosphonous dichloride adducts; hydrolysis to the oxide or magnesium reduction in dry THF represent quite dissimilar reactions; yet the product of each is almost entirely the 2 isomer. As an alternative explanation, the phosphonous dichloride **adduct** could be a 2-phospholene derivative, while the dibromide adduct could be the 3 isomer. From a study of the pmr spectra of the adducts with isoprene, we have concluded that this is indeed the case. The spectra (in deuteriochloroform) are distinctly different in the vinyl proton region. The dichloride adduct **16** has a doublet (J = 32.2 cps) at δ 7.0, while the dibromide adduct **13** had a doublet of larger J (37.5 cps) at considerably higher field (δ 5.80). The same difference may be noted in the benzyl bromide salts of the isomeric phospholenes; the salt of the 2 isomer **18** has the signal at δ 6.60 (J_{PCH} = 30 cps), and that of the 3 isomer **15** is at δ 5.43 (J_{PCCH} = 31.5 cps). Confirmation of a structural difference for the adducts may be obtained from examination of the methylene signals. The dibromide adduct has a symmetrical 4 H signal, though broad and unresolved, at δ 4.15; the dichloride has a complex multiplet (δ 3.1–3.9) for two differently shielded methylenes.

The P^{31} spectra of the adducts in deuteriochloroform solution support their description as phosphonium, rather than pentacovalent, derivatives. Adduct **13** has its signal at −89 ppm from 85% H_3PO_4, while that of **16** is at −99 ppm. Such downfield positions speak against the presence of neutral, pentacovalent phosphorus.

---

[17] This structure has previously been given to the oxide from the phenylphosphonous dichloride–piperylene adduct.[2,18] This oxide is now known to have structure **7a**, and **8a** is reported here for the first time.

[18] B. A. Arbuzov, L. A. Shapshinskaya, and V. M. Erokhina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2074 (1962).

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

Conclusions

It has been conclusively shown that the position of the double bond in diene–phosphonous dihalide adducts is controlled by structural features of both participants in the reaction. Methylphosphonous dichloride with butadiene and some of its methyl derivatives provides the 3-phospholene system. However, the replacement of methyl by phenyl on phosphorus generally leads to the 2-phospholene ring. An exception, which constitutes an example of product control by the diene, occurs with 2,3-dimethylbutadiene, where the stabilizing effect of two methyls on a double bond in the 3 position determines the orientation. On replacement of chlorine by bromine in the phenyl system, the 3-phospholene ring results. The specificity of these cycloadditions is quite high, and it has been shown that the double bond once located in the adducts holds its position during subsequent conversions into other derivatives. The range of substituents on phosphorus so far studied is not sufficient to define the factors controlling the orientation of the double bond, and predictions of product structure from other phosphonous dihalides would seem to be difficult to make with confidence at this time. Since nothing is presently known about the mechanism of the cycloaddition, it remains unknown if the proton migration, which must occur to give 2-phospholene derivatives, takes place before or after ring closure. The most attractive possibility is that the cycloaddition proceeds in a normal manner and initially results in the 3-phospholene derivative; it is followed by an allylic shift made possible by activation of the α position by positive phosphorus. An explanation might then be at hand for the fact that the rearrangement has so far been observed only when phosphorus bears particularly electronegative substituents (*e.g.*, phenyl and chlorine, rather than phenyl and bromine or methyl and chlorine) since the electron attracting power of phosphorus on the α carbon will be enhanced by such substituents.

Experimental Section[20,21]

Methylphosphonous Dichloride–Diene Adducts.—Preparations were based on the following proportions: 1 mol of diene, 400 ml of hexane, and 1.2 g of cupric stearate polymerization inhibitor, to which mixture was added 1 mol of phosphonous dichloride. Wide-mouth, screw-cap bottles, sealed with wax, were convenient reaction vessels, even for the butadiene. The adducts began to separate as nicely crystalline solids generally after a day or two at room temperature, but the mixtures were not processed until the adducts were needed. Generally the mixtures stood for several weeks or even months. They were filtered and the adducts washed with pentane in a drybox.

Preparation of 1-Methyl-3-phospholene Oxides and Their Dibromides.—About 10–20 g of the adduct was treated slow with 10–20 ml of water, with ice bath cooling. While cold, the mixture was neutralized with concentrated sodium hydroxide, filtered to remove precipitated sodium chloride, and extracted with chloroform. The extract was dried with magnesium sulfate and then distilled. Yields of oxides from adducts varied from 60 to 80%. Boiling points obtained were 59° (0.16 mm), **1a** (low-melting solid); 82–83° (0.5 mm), **1b**; 58–64° (0.17–0.25 mm), **1d** (isomer mixture[11]). Compound **1c** was purified by sublimation at 100° (5 mm). The compounds were hygroscopic and it was difficult to obtain melting points or analytical data for them. Oxides **1a–c** were converted into the 3,4-dibromides by addition of a chloroform solution containing 1 mol of bromine to a chilled chloroform solution of the oxide. Consumption of the bromine was rapid. After 1 hr, the mixture was washed with dilute sodium thiosulfate solution, dried with magnesium sulfate, and stripped of solvent. The residual solids were somewhat unstable toward hot solvents in recrystallization attempts; they were crystallized by Dry Ice chilling of solutions prepared at room temperature in ether (for **1b** and **c**) or toluene–pentane (for **1a**). Oxide **1d** was separated into *cis* and *trans* isomers as described elsewhere.[11] Spectral data for **1a–c** are given in Table I; analytical data for the dibromides appear in Table IV.

Preparation of 1-Methyl-3-phospholenes and Their Benzyl Bromide Salts.—A slurry of 0.2 mol of the adduct in 400 ml of THF was treated slowly with 0.22 g-atom of activated magnesium in a flame-dried, nitrogen-flushed apparatus. The reaction was generally mildly exothermic, but was allowed to proceed with no temperature control. The reaction was completed by an 8–10 hr reflux period. If the reaction failed to start, the mixture was heated to reflux and held there for 10–12 hr. (On a few occasions, the reaction could not be initiated; an explanation for this behavior is lacking at present.) The mixture was then treated slowly with about 30 ml of concentrated hydrochloric acid; after residual magnesium had dissolved, the mixture was stripped of THF. The residue was taken up in water, made basic with 0.5 *N* sodium hydroxide solution, and steam distilled. The product layer was separated and dried with Drierite prior to distillation. Yields and boiling points were 73%, 114–115° (**3a**); 46%, 138–139.5° (lit.[13] 135–136°) (**3b**); 79%, 160–161° (**3c**); 54%, 130–134° (isomer mixture) (**3d**)[11]. Spectral data are in Table I. Benzyl bromide salts were prepared in ether solution at room temperature, and recrystallized from methanol–ethyl acetate. Analytical data for the salts are given in Table IV; spectroscopic data are in Table I.

Rearrangement of 1-Methyl-3-phospholene Oxide (1a). Thermal.—The oxide (38.8 g) under nitrogen was refluxed by heating in an air bath at 280°. After 12 hr, gas chromatography (gc) was performed with a 1 m by 8 mm column of 15% Dow-Corning silicone oil 710 on 60–80 mesh Chromosorb W at 150°. (These conditions were used in all gc described subsequently for 1-methylphospholene oxides; in general, the ratio of retention times for the 3 isomer to the 2 isomer was about 1:1.5.) Peaks of equal size for unchanged **1a** and for the 2-oxide **2a** were observed. There was no change in the ratio after another 8 hr. Distillation with a 1-ft column of glass helices gave a 5-ml sample containing 94% **1a** and 6% **2a**; fractionation with a spinning-band column then provided pure **2a** (see Table I and IV).

With Base.—A mixture of 1 g of **1a** and 6 ml of 3 *N* sodium hydroxide was refluxed for 24 hr. A portion of the mixture was neutralized and extracted with chloroform. Gc revealed the ratio **1a**:**2a** to be 2:3. The original mixture after an additional 48 hr showed no change in this ratio.

With Acid.—A mixture of 1 g of **1a** and 6 ml of 3 *N* hydrochloric acid was refluxed for 24 hr. After neutralization and extraction into chloroform, the product was shown by gc to contain only a trace of **2a**.

Rearrangement of 1,3-Dimethyl-3-phospholene Oxide (1b). Thermal.—A 8-g sample of **1b** was refluxed in an air bath at 300° for 6.5 hr. The ratio of **1b** to the 2-oxide **2b** was found by gc to be 1:1. The ratio was unchanged after an additional 6 hr.

With Base.—A sample of 1.8 g of **1b** was refluxed for 27 hr with 10 ml of 3 *N* sodium hydroxide. The mixture was neutralized and extracted with chloroform. Gc showed the ratio of **1b** to **2b** to be about 1:2.

With Acid.—The product after 43-hr reflux of 15 ml of 3 *N* hydrochloric acid and 2.5 g of **1b** was found by gc to contain 84% of **2b**. A 33.4-g sample of **1b** was then refluxed for 96 hr in 500 ml of 3 *N* hydrochloric acid. Gc revealed the product to contain 90% **2b**. The mixture was neutralized with solid sodium hydroxide and concentrated *in vacuo* until precipitation of sodium chloride commenced. The mixture was filtered and the filtrate extracted with chloroform. After drying over magnesium sul-

---

(20) All operations involving trivalent phosphorus compounds were conducted in a nitrogen atmosphere. Tetrahydrofuran (THF) was dried by distillation from lithium aluminum hydride. Phenylphosphonous dichloride was obtained from Eastman; a procedure for methylphosphonous dichloride[21] synthesis has been published. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Infrared spectra were run on Perkin-Elmer 137 and 237 spectrophotometers. Proton nmr were run on a Varian A-60 spectrometer; P^{31} nmr were obtained on a Varian V-4300 B nmr spectrometer at 19.3 Mc. P^{31} chemical shifts are expressed in parts per million from 85% H_3PO_4 and were obtained by tube interchange with P_4O_6 as secondary standard.

(21) J. A. Pianfetti and L. D. Quin, *J. Amer. Chem. Soc.*, **84**, 851 (1962).

TABLE IV

PHYSICAL AND ANALYTICAL DATA FOR PHOSPHOLENE DERIVATIVES

Compd	Bp, °C (mm)	Mp, °C	Formula	Carbon, %		Hydrogen, %		Phosphorus, %	
				Calcd	Found	Calcd	Found	Calcd	Found
1a dibromide[a]		145.5–146	$C_5H_9Br_2OP$	21.76	21.93	3.29	3.62		
1b dibromide[b]		103–103.5	$C_6H_{11}Br_2OP$	24.85	24.82	3.82	3.82		
1c dibromide		98–100[c] dec	$C_7H_{13}Br_2OP$	27.66	27.50	4.31	4.80	10.19	10.30
2a	72 (0.08)		C_5H_9OP	51.72	51.70	7.81	7.91	26.68	26.78
2b	81 (0.14)		$C_6H_{11}OP$	55.38	55.53	8.52	8.50	23.80	23.90
2d	67–68.5 (0.18–0.20)		$C_6H_{11}OP$	55.38	55.71	8.52	8.63	23.80	23.63
4a		185–186.5	$C_{12}H_{16}BrP$	53.15	53.31	5.95	6.01	11.42	11.64
4c		185.5–187.5	$C_{14}H_{20}BrP$	56.20	56.14	6.74	6.65	10.35	10.46
7a	131–133 (0.32)[d]		$C_{11}H_{13}OP$	68.74	68.99	6.82	6.87	16.12	16.14
8a	124–132 (0.16)[e]		$C_{11}H_{13}OP$	68.74	68.98	6.82	6.96	16.12	16.36
8b	133–134 (0.24)		$C_{11}H_{13}OP$	68.74	68.55	6.82	6.72	16.12	16.28
15		178–180	$C_{18}H_{20}BrP$	62.26	62.08	5.80	5.87	8.92	9.13
18		184–185	$C_{18}H_{20}BrP$	62.26	62.33	5.80	5.86	8.92	9.09

[a] Calcd for Br: 57.92. Found, 57.68. [b] Calcd for Br: 55.12. Found, 55.07. [c] Approximate only owing to decomposition. [d] The reaction leading to **7a** has been performed elsewhere but claimed to give **8a**. Boiling point values have been reported: 160–180° (1 mm),[2] 158–159° (3.5 mm).[18] [e] A mixture of *cis* and *trans* isomers.

fate, the filtrate was distilled; there was obtained 25.7 g (77%) of mixed oxides. Distillation with a spinning-band column gave 13.7 g of pure **2b** (see Tables I and IV).

Rearrangement of 1,3,4-Trimethyl-3-phospholene Oxide (1c). Thermal.—A 2.3-g sample of **1c** was refluxed in an air bath at 300° for 6 hr. Gc showed the mixture to contain about 80% unchanged **1c** and about 5% each of two other compounds of slightly longer retention time. Refluxing for an additional 7.5 hr caused no change in the composition.

With Base. A similar product composition resulted from refluxing 0.6 g of **1c** with 5 ml of 3 *N* sodium hydroxide.

With Acid. A 0.6-g sample of **1c** was not detectably affected by refluxing with 5 ml of 3 *N* hydrochloric acid for 18 hr. After another 52 hr, the product contained about 10% each of the two new compounds. No isolations were attempted.

Rearrangement of 1,2-Dimethyl-3-phospholene Oxide (1d). Thermal.—A 25-g sample of **1d** (*cis* and *trans*[11]) was refluxed in an air bath at 265° for 53 hr. The 2-oxide (**2d**) comprised 90% of the gas chromatographable product. The mixture was distilled through a 1-ft column of glass helices; there was obtained 6 g of **2d** (Tables I and IV) whose purity was indicated by gc to be about 99%.

With Base.—The volatile product from refluxing 0.6 g of **1d** with 5 ml of 3 *N* sodium hydroxide for 23 hr was shown to be exclusively **2d**.

With Acid.—A mixture of 0.6 g of **1d** was refluxed for 18 hr with 5 ml of 3 *N* hydrochloric acid. Gc showed that no rearrangement to **2d** had occurred. After an additional 52 hr, only a trace of **2d** was detected.

Synthesis of Phosphorus Trihalide–Isoprene Adducts.—To a widemouth bottle was added 1 g of copper stearate and 38.3 g (0.562 mol) of isoprene, and then 58.5 g (0.426 mol) of phosphorus trichloride. The bottle was tightly sealed and put aside for 1 month. The mixture had become solid and reaction was presumed complete. The phosphorus tribromide–isoprene adduct was prepared similarly. The adducts were used directly in alcoholysis reactions.

Synthesis of 1-Methoxy-3-methyl-2-phospholene Oxide (9).—To 400 ml of methylene chloride was added 85 g (0.426 mol) of phosphorus trichloride–isoprene adduct. The mixture was held at −10° while 37 ml of methanol (dried over sodium sulfate) was slowly added. The solution was then allowed to come to room temperature. It was flushed with nitrogen for 1 hr, cooled to 0°, and then neutralized with saturated sodium bicarbonate solution to pH 7 (Hydrion paper). The methylene chloride layer was separated and the aqueous layer extracted with methylene chloride. The organic layers were combined and the solvent removed. The residue was distilled; after a forerun at 40° (0.6 mm), the product was received at 83–90° (0.6 mm). This fraction was redistilled with a spinning-band column to give 11.3 g of **9**,[7] bp 79° (0.4 mm), in 18.5% yield. Its pmr spectrum ($CDCl_3$, internal standard) contained a vinyl proton doublet (J = 24.0) at δ 6.3 (lit.[7] for ethyl ester, J = 23.75 cps).

Synthesis of 1-Methoxy-3-methyl-3-phospholene Oxide (11).—The procedure for the synthesis of **9** was followed, and employed 200 ml of methylene chloride, 199.5 g (0.351 mol) of phosphorus tribromide–isoprene adduct, and 40 ml of methanol. On distillation, the product was received at 69–72° (0.23 mm). This was redistilled with a spinning-band column to give 15.9 g (33.6% yield) of **11**, bp 65° (0.75 mm) (lit.[22] bp 117–119° (10 mm)). Its pmr spectrum ($CDCl_3$, internal standard) contained a vinyl proton doublet (J_{PCCH} = 35.5 cps) at δ 5.87 (lit.[10] J = 36.5 cps).

Synthesis of 1-Chloro-3-methyl-2-phospholene Oxide (10).—A solution of 9.27 g (0.0715 mol) of 1-methoxy-3-methyl-2-phospholene oxide (**9**) in an equal volume of carbon tetrachloride was placed in an ice bath and treated with 77.5 ml of a 12% solution of phosgene (0.078 mol) in benzene. After standing overnight, phosgene and solvents were removed by vacuum distillation. Continued distillation gave 5.53 g of **10** at 100° (0.3 mm), 51.2% yield. A boiling point of 91° (0.07 mm) has been reported[6] previously.

Synthesis of 1-Chloro-3-methyl-3-phospholene Oxide (12).—The procedure was similar to that used for the synthesis of **10**, and employed 9.57 g (0.073 mol) of 1-methoxy-3-methyl-3-phospholene oxide (**11**) and 0.10 mol of phosgene (100 ml of 12% solution). Distillation gave 4.74 g (43% yield) of **12**, bp 77° (0.5 mm). Analysis was not attempted.

Synthesis of 1-Phenyl-3-methyl-2-phospholene Oxide (7b) from 1-Chloro-3-methyl-2-phospholene Oxide (10).—Phenylmagnesium bromide solution (from 4.5 ml (0.044 mol) of bromobenzene and 1.08 g (0.044 g-atom) of magnesium) in 50 ml of dry THF at 5–10° was treated with 5.53 g (0.0366 mol) of 1-chloro-3-methyl-2-phospholene oxide (**10**) dissolved in a few milliliters of THF. Immediately after the addition was complete, excess Grignard reagent was decomposed by adding 20 ml of ice water, followed by 100 ml of 6 *N* hydrochloric acid. After drying over sodium sulfate, the extract was distilled to give 1.45 g (22.4% yield) of a low-melting solid product having bp 150° (15 mm); bp 173–174° (0.7 mm) has been reported in a different synthesis.[16] Spectral properties are reported in Table III.

Synthesis of 1-Phenyl-3-methyl-3-phospholene Oxide (8b) from 1-Chloro-3-methyl-3-phospholene Oxide (12).—The Grignard reagent from 3.6 ml (0.035 mol) of bromobenzene and 0.89 g (0.037 g-atom) of magnesium in 20 ml of dry THF was added to a chilled mixture of 4.74 g (0.0314 mol) of 1-chloro-3-methyl-3-phospholene oxide (**12**) in THF. As soon as addition was complete, there were added a few small pieces of ice and then 100 ml of 6 *N* hydrochloric acid. The mixture was then extracted with five 30-ml portions of chloroform and the extract dried over sodium sulfate. The solvent was stripped off, and the residue was distilled with a spinning-band column. There was obtained 3.24 g (53.5% yield) of liquid product, bp 136° (2.0 mm). This is the first authenticated synthesis of this compound. Spectral and analytical data are given in Tables III and IV, respectively.

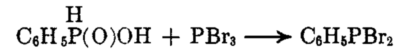
Synthesis of 1-Phenyl-3-methyl-2-phospholene Oxide (7b) by Adduct Hydrolysis.—The procedure of McCormack[16] was followed. To 1 l. of ice water was added 38.6 g (0.156 mol) of phenylphosphonous dichloride–isoprene adduct which had been washed with petroleum ether (30–60°). A 10-ml aliquot of the

---

(22) A. O. Vizel, M. A. Zvereva, K. M. Ivanovskaya, I. A. Studentsova, V. G. Dunaev, and M. G. Berim, *Dokl. Akad. Nauk SSSR*, **160**, 826 (1965).

solution was titrated and the required amount of concentrated sodium hydroxide was added to neutralize 90% of the acid in the bulk of the solution. It was then brought to pH 7 (Hydrion paper) with solid sodium bicarbonate. The chloroform was stripped off and the residue distilled to provide 16.4 g of **7b** at 149° (0.26 mm). A modified procedure was also used. To the solution of 200 ml of ice water and 75 g of sodium bicarbonate was added 38.6 g (0.156 mol) of adduct. After the hydrolysis was complete the pH was found to be about 7. The solution was saturated with salt and extracted with a large quantity of chloroform. The extract was dried and the chloroform was stripped off. Gc indicated the crude product to contain 4.5% of isomer **8b**. The residue was distilled giving 18.7 g of **7b** at 149° (0.26 mm). These preparations of **7b** were identical in spectral properties with **7b** from the Grignard reaction of **10**. The compound is a solid for which mp 60–65° has been reported.[16]

Synthesis of Phenylphosphonous Dibromide.—A new method for the preparation of phenylphosphonous dibromide was employed.



$$C_6H_5\overset{H}{P}(O)OH + PBr_3 \longrightarrow C_6H_5PBr_2$$

The reaction is similar to that described by Frank for phenylphosphonous dichloride synthesis.[23] The new method compares favorably in its simplicity with other methods. To 160 ml of phosphorus tribromide (1.6 mol) was added in portions 99 g (0.696 mol) of Eastman practical-grade phenylphosphinic acid. The addition required no external cooling. A viscous oil formed on the surface as the reaction proceeded. After 24 hr with occasional agitation, the lower liquid layer was separated and distilled with a Vigreux column (8 in.) under reduced pressure. Excess phosphorus tribromide was recovered at 50° (11 mm) and phenylphosphonous dibromide (143 g, 76.7%) then distilled at 121–123° (11 mm) (lit.[24] 124–126° (11 mm)). The P^{31} chemical shift was -151.8 ± 0.5 ppm.[25] (This new method has also been successfully used to synthesize *m*-bromophenylphosphonous dibromide from *m*-bromophenylphosphinic acid;[26] a yield of 38.2% was obtained using 2.3 g of phosphinic acid: bp 164° (11 mm); P^{31} signal at -147 ± 0.5 ppm).

Synthesis of 1-Phenyl-3-methyl-3-phospholene Oxide (8b) by Adduct Hydrolysis.—To 300 ml of ice water was added 18.46 g (0.055 mol) of phenylphosphonous dibromide–isoprene adduct. The mixture was neutralized with solid sodium bicarbonate to a pH of 7. This solution was extracted with 250 ml of chloroform and the extract dried over sodium sulfate. The solvent was stripped off and the residue distilled to give 3.74 g of **8b** at 136° (0.26 mm). The product was identical with that from the Grignard route on **12**.

Rearrangement of 1-Phenyl-3-methyl-3-phospholene Oxide (8b). By Acid.—A mixture of 1 g of **8b** and 25 ml of 3 *N* hydrochloric acid was allowed to stand overnight at room temperature. An aliquot was neutralized with sodium bicarbonate, and a benzene extract was gas chromatographed (5-ft SE-30 column, 4:1 on Chromosorb W, 275°). Only **8b** was detected. A similar extract after 29 hr of reflux contained **8b** and **7b** in the approximate ratio 1:10.

By Base.—A mixture of 1 g of **8b** and 25 ml of 3 *N* sodium hydroxide was allowed to stand overnight at room temperature. A benzene extract contained only **8b** by gc. After 48 hr of reflux, an extract contained both **8b** and **7b**, in the ratio 1:3.5.

Rearrangement of 1-Phenyl-3-methyl-2-phospholene Oxide (7b).—Both acid and base treatments at reflux were performed as for the 3-phospholene oxide isomer (**8b**). After 29 hr in acid, a mixture of **7b** and **8b** (about 10:1) was formed. After 48 hr in base, the mixture contained **7b** and **8b** in the ratio 5.5:1.

Preparation of 1-Phenyl-2-methyl-2-phospholene Oxide (7a).—The adduct from 3 months' standing of a mixture of 12.2 g (0.179 mol) of *trans*-piperylene, 39.7 g of phenylphosphonous dichloride, and 0.5 g of cupric stearate, after washing with pentane, was added in portions to 200 ml of ice-cold water. The mixture was neutralized with sodium bicarbonate, and the product extracted with chloroform. After drying over sodium sulfate, the solution was stripped of solvent and the residue distilled. Oxide **7a** (9.34 g, 27% yield on piperylene used) was received at 131–133° (0.32 mm). Spectral properties are given in Table III; analyses are in Table IV.

Preparation of 1-Phenyl-2-methyl-3-phospholene Oxide (8a).—The adduct from 15.5 g (0.228 mol) of *trans*-piperylene, 58 g (0.217 mol) of phenylphosphonous dibromide, and 0.5 g of cupric stearate was treated in the manner used for preparation of oxide **7a**. The product (30.7 g, 88% yield on phenylphosphonous dibromide) had bp 124–132° (0.16 mm). The wide boiling point is probably due to the presence of *cis* and *trans* isomers, which were evident on the pmr spectrum (Table III). The isomers have not yet been separated. Analyses are in Table IV.

Synthesis and Characterization of 1-Phenyl-3-methyl-3-phospholene (14).—To 200 ml of THF (sodium dried) and 52.1 g (0.155 mol) of phenylphosphonous dibromide–isoprene adduct was added slowly with vigorous stirring 5.4 g (0.2 g-atom) of freshly cleaned magnesium. The mixture was refluxed for 5 hr and then neutralized with excess saturated sodium bicarbonate solution. The resulting emulsion was continuously extracted with benzene for 24 hr. The benzene was removed and the residue distilled to give 12.3 g (45.1% yield) of **14** at 125° (13 mm). Spectral data appear in Table III. A sample (in benzene) was converted into the benzyl bromide salt, which was recrystallized from methanol–ethyl acetate (spectral data, Table III; analytical data, Table IV.)

Another sample was converted into the oxide. To 30 ml of 10% hydrogen peroxide solution was added a few milliliters of 1-phenyl-3-methyl-3-phospholene. After 24 hr, excess peroxide was decomposed with a small amount of reduced Adams catalyst. Water was stripped off and the residue distilled. Infrared spectroscopy and gc of the product confirmed it to be primarily 1-phenyl-3-methyl-3-phospholene oxide (**8b**) with a few per cent of 1-phenyl-3-methyl-2-phospholene oxide (**7b**).

Characterization of 1-Phenyl-3-methyl-2-phospholene (17).—This compound was available from a previous[13] reduction of the isoprene–phenylphosphonous dichloride adduct. Spectral properties are now reported in Table III. A sample was converted to the benzyl bromide salt; data are provided in Tables III and IV. Another sample on hydrogen peroxide oxidation was seen by infrared and gc studies to be converted into oxide **7b**.

Registry No.—**1a**, 930-38-1; **1b**, 15450-79-0; **1c**, 15450-80-3; **2a**, 872-45-7; **2b**, 15450-68-7; **2c**, 15450-82-5; **3a**, 872-37-7; **3b**, 15450-84-7; **3c**, 14410-05-0; **4a**, 1130-42-3; **4b**, 15450-87-0; **4c**, 14409-96-2; **7a**, 15450, 89-2; **7b**, 707-61-9; **8a**, 15450-91-6; **8b**, 7564-51-4; **14**, 15450-93-8; **15**, 15450-94-9; **17**, 1445-83-6; **18**, 15450-96-1.

Acknowledgments.—We are grateful to Mr. Stephen W. Dale of this department for obtaining the P^{31} nmr spectra and to Dr. C. E. Griffin, University of Pittsburgh, for the preparation and discussion of some of the pmr spectra in the early phases of the work. T. P. B. was supported by a National Science Foundation Traineeship.

---

[23] A. Frank, *J. Org. Chem.*, **26**, 850 (1961).

[24] W. Kuchen and W. Grünewald, *Angew. Chem.*, **75**, 576 (1963).

[25] K. Moedritzer, L. Maier, and L. C. D. Groenweghe [*J. Chem. Eng. Data*, **7**, 307 (1962)] reported −152 ppm.

[26] L. D. Quin and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, **83**, 4124 (1961).