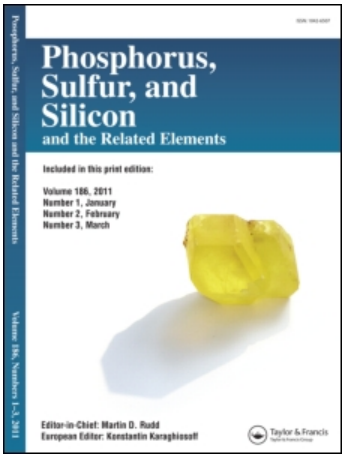

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STEREOCHEMICAL PROPERTIES OF THE 1-CHLORO-1- PHENYL-2,5-DIMETHYL-2-PHOSPHOLENIUM ION AND DERIVED OXIDE AND PHOSPHINE

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STEREOCHEMICAL PROPERTIES OF THE 1-CHLORO-1-PHENYL-2,5-DIMETHYL-2-PHOSPHOLENIUM ION AND DERIVED OXIDE AND PHOSPHINE[1]

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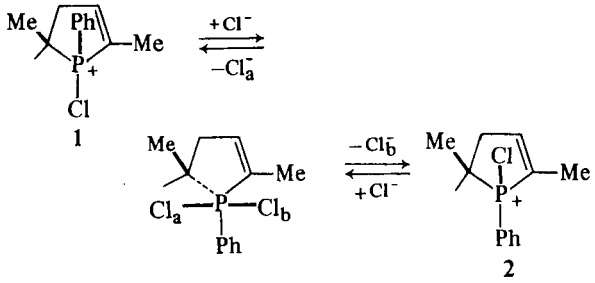
The cycloaddition of phenylphosphonous dichloride and *trans,trans*-2,4-hexadiene, or the addition of chlorine to *trans*-1-phenyl-*cis*-2,5-dimethyl-3-phospholene, gave 1-chloro-1-phenyl-2,5-dimethyl-2-phospholenium chloride. This compound shows no evidence in its ^{31}P and ^{1}H nmr spectra for the existence of *cis, trans* isomers, yet on hydrolysis or dehalogenation with magnesium the resulting oxide and phosphine, respectively, are seen to be isomer mixtures. This phenomenon is explained by a rapid equilibration of the *cis, trans* form of the 1-chloro ion through a pentacovalent species. Structures of the oxides and phosphines were assigned by ^{1}H and ^{13}C nmr relations. The 1-phenyl-*cis*-2,5-dimethyl-3-phospholenium ion and related compounds were also characterized.

3-Phospholene derivatives with 2-methyl[2] or *cis*-2,5-dimethyl substituents[2b,3] can possess *cis, trans*-isomerism with respect to the substituent(s) on phosphorus. This isomerism is readily observable for the tertiary phosphines and their oxides and quaternary salts by proton nmr techniques. However, the dihalo derivatives of the phosphines, the ionic 1-halo-3-phospholenium halides, give no spectral indications of the presence of the isomers, even though they must be present since hydrolysis and dehalogenation (with magnesium) give the oxide and phosphine, respectively, in isomeric forms. We have advanced[2b] an explanation for this phenomenon that rests on the rapid (on the nmr time scale) equilibration of the *cis, trans* forms through a pentacovalent intermediate, which dissociates to either of the two isomeric ionic forms. This explanation has since been experimentally verified[4] and used to account for similar nmr observations in dichlorides of phosphetanes[4] and of a phosphatetracyclooctane.[5]

2-Phospholene derivatives that contain 5-substituents are also potentially capable of exhibiting *cis, trans* isomerism, but this has not been demonstrated experimentally. The 1-halo-2-phospholenium halides would be of particular interest, since it is conceivable that the π-electrons of the adjacent double bond might interact with positive phosphorus (through *d*-orbitals); this might so reduce the tendency to form a pentacovalent dihalide that direct observation by nmr techniques of the *cis*(1) and *trans* (2) forms of the 1-halophospholenium ion might be possible. Recently,[6] some new evidence for $d\pi$-$p\pi$ interaction

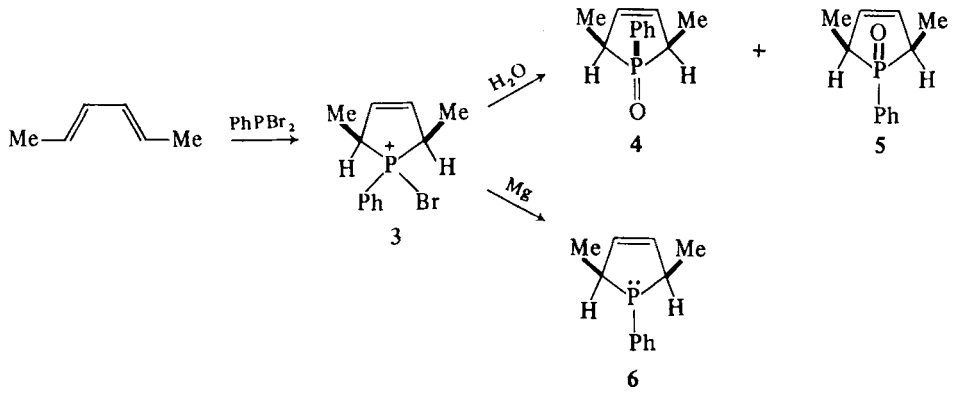


1 2

in quaternary vinylphosphonium salts has been obtained by comparing their ^{13}C and ^{31}P nmr properties to the saturated counterparts; pronounced downfield shifts of β-carbons of the vinyl groups and upfield shifts of phosphorus are consistent with this type of overlap. Indeed, the ready rearrangement of the 1-chloro-3-phospholenium to the 1-chloro-2-phospholenium system[7] has already pointed to the possible importance of such a delocalization effect. In the present paper, we consider the possibility of *d–p* stabilization of *cis, trans* isomers through examination of the 1-phenyl-2,5-dimethyl-2-phospholene system. (Throughout this paper, the relation between the carbon substituent on phosphorus and that on C-2 (or C-5) forms the basis for the isomer designation).

The 1-Phenyl-cis-2,5-dimethyl-3-phospholene System

It was first necessary to obtain derivatives of the 3-phospholene system for use as precursors to the 2-series (Scheme I). The disrotatory[2b,3] cycloaddition



SCHEME I

of phenylphosphonous dibromide and *trans,trans*-2,4-hexadiene gave the 1-bromo-3-phospholenium bromide **3** with *cis* methyls; on hydrolysis this provided a mixture of oxides **4** (*cis*, 73%) and **5** (*trans*, 27%). On dehalogenation with magnesium, only the *trans* phosphine **6** was obtained.

The strong preference for the *trans* form on dehalogenation has been found for other phospholene derivatives;[2b] for the related 1-phenyl-2-methyl system, the *trans* to *cis* ratio is 9 : 1. Hydrolysis gives the appearance of being less specific as the isomer ratio is rather sensitive to the experimental conditions. The *cis* isomer has been found to predominate also in the 1-phenyl-2-methyl system, however.[2b] Another feature of the oxides is that the isomer ratio can change on standing. Thus, after several weeks, the sample originally of composition 73% **4**, 27% **5** was found spectroscopically to have become entirely *trans* (**5**). It is quite possible that water picked up on standing is responsible for this isomerization; a pentacovalent dihydroxy form might develop which would then break down to the more stable oxide, presumably *trans*. This mechanism has been proposed[8] for the similar isomerization and O-exchange of phosphetane oxides when exposed to $H_2^{18}O$.

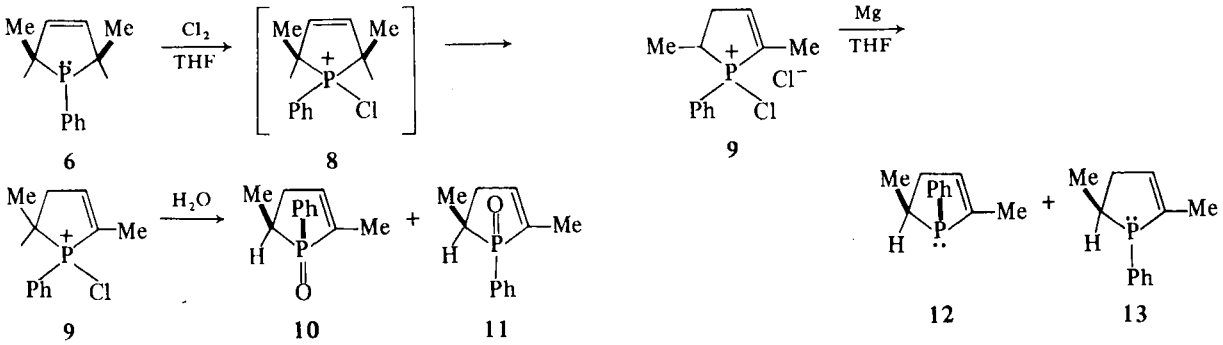
The expected[2b] loss of stereochemical integrity in the 1-halophospholenium ion was easily demonstrated by adding bromine to the pure *trans* phosphine **6**; this regenerates the dihalide **3**, which on hydrolysis gives the same isomer mixture of **4** and **5** as observed for the original cycloadduct. Only the presence of an equilibration mechanism can account for this result.

Structure assignments in this series were made with the aid of ^1H nmr spectroscopy, making use of relations established previously.[2b] For both the oxide and the phosphine, a pronounced phenyl shielding effect on the ring methyls is observed in one isomer, and this is assigned the all-*cis* structure. This is supported by the size of the ^{31}P-coupling with the 2,5-methyl protons in the phosphine; the *trans* arrangement about phosphorus allows better coupling than *cis*, and the values seen here for the *trans* (**6**, $^3J_{PH}$ = 19 Hz) and *cis* (**7**, $^3J_{PH}$ = 11 Hz; measured on the trichlorosilane reduction product from the **4**, **5** mixture) are perfectly consistent with those reported for related compounds.[2b] Furthermore, the ^{13}C nmr spectra are fully in accord with the isomer assignments, as is discussed separately in a later section.

The 1-Phenyl-2,5-dimethyl-2-phospholene System

The 1-chloro-2-phospholenium chloride **9** can be made by the cycloaddition of *trans,trans*-2,4-hexadiene with phenylphosphonous dichloride. This reaction appears to involve the initial formation of the 3-phospholenium ion (**8**), which then rearranges to the 2-isomer. As noted above, the behavior of the dibromide is quite different and the 3-phospholenium ion character is retained. This route to **8** is not very practical, however, for the cycloaddition is quite slow and attempts to expedite it with heat lead to the formation of unwanted tarry materials. The preferred method (Scheme II) for forming **9** is to add chlorine to the 3-phospholene **6**. With careful control of the conditions, attack occurs exclusively at phosphorus. If conducted in tetrahydrofuran solution, the initially formed 3-phospholenium ion **8** rearranges virtually completely to the 2-isomer. When conducted in pentane solution, however, the product precipitates immediately and has the unrearranged structure (**8**).

2-Phospholenium chloride **9** as formed by either route underwent hydrolysis to give the same mixture of oxides **10** (*cis*) and **11** (*trans*). The major product (62%) was assigned the *cis* structure, on the basis of the phenyl shielding effect seen in the 3-phospho-



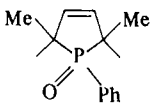
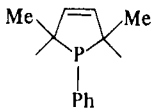
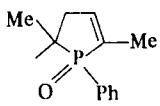
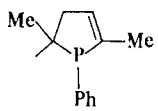
SCHEME II

lene system.[2b]. This isomer had δ 1.31 for its 5-methyl protons, whereas the minor isomer had δ 1.73.

Dehalogenation with magnesium of 2-phospholenium chloride **9** gave two phosphines, **12** (*cis*) and **13** (*trans*). The phenyl shielding effect pointed to the structure of the isomers; that isomer constituting 41% of the mixture had considerably shielded 5-methyl protons (δ 1.12) relative to the other (δ 1.60) and is assigned the *cis* structure **12**. This was supported by the coupling constant with ^{31}P; as for the 3-phospholene system,[2b] the *trans* isomer had a larger value (19 Hz) than the *cis* (11 Hz).

The above experiments therefore establish that the 1-halo-2-phospholenium ion **9** forms isomeric products on hydrolysis and dehalogenation just as the 3-phospholenium system does. The fact that the ion when formed by addition of chlorine to an isomerically pure phosphine (**6**) also gave a mixture of isomers is strong evidence for an equilibration mechanism. The crucial experiment was then to determine if the 1-halo-2-phospholenium ion itself gave spectra for the individual *cis* and *trans* isomers **1** and **2**. Both phosphorus and proton nmr spectroscopy showed conclusively that this was not the case. The ^{31}P nmr spectrum of **9** consisted of only one signal (+100.5 ppm, downfield from 85% H_3PO_4). The ^1H nmr spectrum contained only one signal for a C-5 methyl, a doublet ($^3J_{PH}$ = 23 Hz) of doublets ($^3J_{HH}$ = 7 Hz) at δ 1.54. These data leave no doubt that ions **1** and **2** are undergoing rapid

TABLE I
^{13}C Spectral data[a] for phospholenes and their oxides

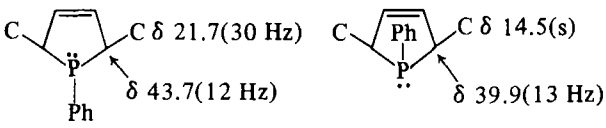
		C-2	C-4	C-5	2-CH_3	5-CH_3
	*cis* (**4**)	36.3(66)	–	36.3(66)	10.4(5)	10.4(5)
	trans (**5**)	37.3(67)	–	37.3(67)	13.8(4)	13.8(4)
	*cis* (**7**)	39.3(13)	–	39.9(13)	14.5(*s*)	14.5(*s*)
	trans (**6**)	43.7(12)	–	43.7(12)	21.7(30)	21.7(30)
	*cis* (**10**)	–	36.3(13)	32.1(72)	12.0(10)	11.7(*s*)
	trans (**11**)	–	36.2(11)	29.8(72)	11.5(11)	12.4(4)
	*cis* (**12**)	–	41.8(6)	33.5(6)	17.4(19)	15.1(*s*)
	trans (**13**)	–	42.3(*s*)	38.5(4)	16.8(18)	20.2(25)

[a] Aromatic and olefinic signals were not sufficiently resolved to permit assignments. Values are chemical shifts downfield from TMS internal standard; ^{31}P coupling constants (± 1 Hz) are given in parentheses.

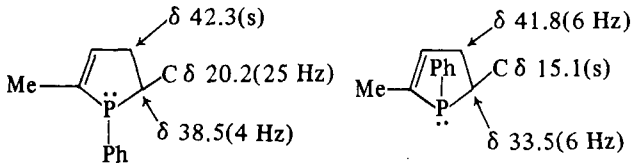
equilibration exactly as occurs in the 1-halo-3-phospholenium system. It must therefore be concluded that the presence of π-electrons on an adjacent C-C bond does not alter this fundamental property of the 1-halo ions to develop pentacovalent character in solution.

^{13}C nmr Spectra

The stereochemical assignments for the various phospholene derivatives were readily confirmed by their ^{13}C nmr properties (Table I). Among the phosphines, two effects were particularly helpful. (1) Relative to the *trans* structure, the steric crowding associated with the *cis* arrangement of phenyl and methyl substituents on adjacent atoms causes pronounced upfield shifts of the easily recognized methyl carbons. This crowding also causes the ring carbon bearing methyl to lie upfield in the *cis* isomer. These effects are apparent in the data for both the 3- and the 2-phospholenes. (2) Even more striking is the stereo-



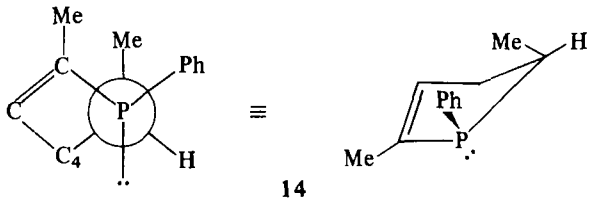
6 7



13 12

specificity of the two-bond P-C coupling,[9] which causes methyl in the *trans* isomers **6** and **13** (where the lone pair on phosphorus is *cis* to methyl) to have much larger values (30 and 25 Hz, respectively) than in the corresponding *cis* isomers **7** and **12** ($^2J_{PC} \sim 0$).

The two-bond coupling to ring carbon 4 in the 2-phospholene system also shows a steric dependence on the relation to the phosphorus lone pair, being larger in the *cis* isomer **12** (6 Hz) than in the *trans* (**13**, a singlet). Such an effect has also been observed in the six-membered phosphorinane system;[10] where the ring is locked by an equatorial 4-*tert*-butyl, the $^2J_{PC}$ values differ for the cases of equatorial *vs.* axial substitution on phosphorus. In the 2-phospholene system, which can be assumed to have planarity about P–C=C–C and to undergo flipping at C-5, it is suggested that the $^2J_{PC}$ values differ because of a difference in the population of the conformers of each isomer that prevails at equilibrium. The larger value for the *cis* isomer thus suggests that there is a relatively higher concentration of the conformer with the *gauche* lone pair and C-4 relation (as in **14**) than there is for the corresponding *gauche* conformer in the *trans* isomer. This conclusion is consistent with the $^2J_{PC}$ values for methyl coupling; in conformer **14**, methyl and the lone pair are *anti*, and as is observed, minimal coupling is expected.



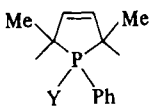
14

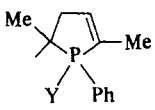
Among the 3-phospholene oxides the stereochemistry is revealed by the upfield shift (3.4 ppm) of the 2,5-methyls when in the *cis,cis* orientation (**4**) compared to the *trans,trans* (**5**) isomer. The oxides fail, however, to show pronounced stereospecificity of their two-bond P–C coupling. In the 2-phospholene oxides, the steric crowding effect is less pronounced, and the *cis* isomer (**10**) has its methyl signal only 0.7 ppm upfield of the *trans* (**11**).

^{31}P nmr Spectra

We have pointed out elsewhere[11] that substitution of ring hydrogens by methyls in five-membered cyclic phosphines produces reasonably additive effects on

TABLE II
^{31}P nmr spectral data[a] for phospholenes and their oxides





Y = Lone Pair		
cis-Ph	7, + 15.1	12, + 11.4
trans-Ph	6, + 8.5	13, + 24.2
Y = 0		
cis-Ph	4, + 72.9	10, + 63.1
trans-Ph	5, + 55.8	11, + 57.4

[a] The sign convention is the same as that used for ^{13}C and ^1H; downfield shifts from the reference (85% H_3PO_4) are positive, upfield are negative.

^{31}P chemical shifts. Data for the two new 3-phospholenes **6** and **7** (Table II) can be analyzed on this basis. Thus when 1-phenyl-3-phospholene (δ −25.3; see footnote a, Table II for a comment on the sign convention) is methylated to form the *trans*-2-methyl derivative (δ −9.2), a downfield shift of 16.1 ppm occurs.[11] Addition of a second *trans*-methyl at the 5-position, producing **6**, should cause a similar effect, leading to a predicted chemical shift of +6.9. In fact, a rather close value of +8.5 is observed for **6**. No data are available for the *cis*-1-phenyl-2-methyl-3-phospholene to allow a prediction of a value for **7**, but from observations on the effect of *cis*-α-methylation of 1-methyl-3-phospholene a significantly larger downfield shift should occur than was seen for **6**. This is indeed the case; the value for **7** is 6.6 ppm downfield of that for **6**.

We have analyzed ^{31}P nmr data for a number of families of acyclic compounds in terms of the familiar α, β, γ substituent effects of ^{13}C nmr spectroscopy and found the phosphorus compounds to lend themselves readily to such an interpretation.[12,13] The strong deshielding effect accompanying α-methylation of 3-phospholenes is a β-effect, and has a parallel in the acyclic trialkyl phosphines, where a similar substitution causes deshielding of 13.5 ppm. However, from our observations of *cis*-α-methylation of 3-phospholenes causing greater deshielding than *trans*-α-methylation, there would appear to be a steric factor operating to control the magnitude of the β-effect in cyclic compounds. Since the size of the β-effect of trialkyl phosphines matches that caused by *trans*-α-methylation, it is suggested that the extra crowding in the *cis* compounds may be the cause of the enhancement of the β-effect.

The chemical shifts of phosphine oxides are considerably less sensitive to substitution, and in acyclic trialkyl derivative the constant for the β-effect is only 4 ppm. The ^{31}P shift for 1-phenyl-3-phospholene oxide is +56.1 ppm,[14] and this value is hardly disturbed when two methyls are introduced in the 2,5-positions *trans* with respect to phenyl (**5**, δ +55.8). However, the more crowded *cis* isomer (**4**) undergoes a much more pronounced deshielding of 17.1 ppm.

The chemical shifts of the 2-phospholene system do not conform to these stereochemical generalizations; for the phosphines, the *trans* isomer (**13**) is more deshielded than the *cis* (**12**), while the opposite is true for the oxides. In this series, a new effect is present, the interaction of the double bond with the phosphorus functionality, and it is apparent that our simple treatment of chemical shifts is not useful in this situation.

EXPERIMENTAL

General

All manipulations involving trivalent phosphorus compounds were conducted in a glove bag with a nitrogen atmosphere. Boiling points are uncorrected. ^1H nmr spectra were taken on a Varian A-60 spectrometer; chemical shifts are relative to external tetramethylsilane. ^{13}C nmr spectra (Table I) were obtained on a Bruker HFX-10 system at 22.62 MHz; the Fourier transform method with proton-decoupling was used. Proton-decoupled Fourier transform ^{31}P nmr (Table II) were also obtained on the Bruker system, at 36.43 MHz, with 85% H_3PO_4 as standard. All nmr spectra were taken on $CDCl_3$ solutions.

Synthesis of the Isomeric 1-Phenyl-cis-2,5-Dimethyl-3-Phospholene Oxides (4 and 5) Phenylphosphonous dibromide and *trans,trans*-2,4-hexadiene were allowed to react at room temperature in pentane solution. Copper stearate was used as polymerization inhibitor. The cycloadduct (**3**) precipitated slowly; usually sufficient solid was obtained after 2–3 weeks to permit its collection. The solid was washed with pentane and added in portions to an ice-water slurry. After neutralization by slow addition of solid sodium carbonate, the mixture was filtered and the filtrate extracted continuously (12 hr) with chloroform. The extract was dried ($MgSO_4$), and on solvent stripping left an oil that solidified. This was purified by distillation, bp 115–117° (0.15 mm). GC on a 4% OV-17 column at 200° showed the presence of isomers with *trans* (**5**, 27%) at shorter retention time than *cis* (**4**, 73%); ^1H nmr for **4**, δ 1.45 (CH_3, d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.5 Hz), 3.60 (methine H, d of quartets, $^2J_{PH}$ = 3.6 Hz), 6.26 (olefinic H, d of d, $^3J_{PH}$ = 25 Hz); ^1H nmr for **5**, δ 1.71 (CH_3, d of d, $^3J_{PH}$ = 15 Hz), 6.38 (olefinic H, d, $^3J_{PH}$ = 28 Hz).

Synthesis of Trans-1-Phenyl-cis-2,5-Dimethyl-3-Phospholene (6) from **3** To 7.0 g (0.020 mol) of cycloadduct **3** in 150 ml of ice-cold dry THF was added 1.0 g (0.041 g-atom) of magnesium. The mixture was stirred for 30 min and then refluxed for 2 hr. Complete solution of **3** occurred during the reaction; excess magnesium was then removed and the solution was hydrolyzed with saturated ammonium chloride. An extract with benzene (3 × 50 ml) was prepared and dried ($MgSO_4$), and on distillation gave only the *trans* isomer **6** (0.98 g, 24.9%), bp 84–86° (1.2 mm); ^1H nmr δ 1.65 (CH_3, d of d, $^3J_{PH}$ = 19 Hz, $^3J_{HH}$ = 7.5 Hz), 3.2 (methine H, complex *m*), 6.09 (olefinic H, d of d, $^3J_{PH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz).

Silane Reduction of 1-Phenyl-cis-2,5-Dimethyl-3-Phospholene Oxides To 6.2 g (0.030 mol) of the oxide (73% **4**, 27% **5**) from hydrolysis of the cycloadduct **3** was added 150 ml of benzene and 5 ml of triethylamine. The solution was chilled in an ice bath and then treated over a period of 30 min with 4.05 g (0.030 mol) of trichlorosilane in 10 ml of benzene. The reaction was completed by refluxing for 1.5 hr and the mixture was then treated with 10N NaOH until all solid dissolved. A benzene extract on distillation gave 4.4 g (77%) of phosphines at 82–86° (1.1 mm). The ^1H nmr spectrum contained the expected signals (noted above) for the *trans* isomer (**6**) as the minor product (25%); the predominant *cis* isomer (75%, **7**) had δ 1.47 (CH_3, d of d, $^3J_{PH}$ = 11 Hz, $^3J_{HH}$ =

7.5 Hz), 3.02–4.35 (methine H, complex *m*), 6.27 (olefinic H, d of d, $^3J_{PH}$ = 6.0 Hz, $^4J_{PH}$ = 1.2 Hz).

Elemental analysis of the phosphine was effected through the methiodide. The reaction was conducted in benzene and the salt recrystallized from methanol-ethyl acetate.

Anal. Calcd for $C_{13}H_{18}IP$: C, 46.99; H, 5.47; P, 9.33. Found: C, 46.86; H, 5.59; P, 8.96.

Hydrolysis of the Chlorine Addition Product from Trans-1-Phenyl-cis-2,5-Dimethyl-3-Phospholene To a solution of 1.32 g (6.88 mmol) of **6** in 100 ml of pentane at 0° was introduced one molar equivalent of chlorine gas prepared from $KMnO_4$ and HCl. The precipitate (**8**) was collected by filtration; it was hydrolyzed by addition to ice water, and the mixture neutralized with solid sodium carbonate. Recovery of the oxide in the usual way gave 1.3 g (92%), bp 115–116° (0.15 mm). The product as seen from nmr was a *cis, trans* mixture of unrearranged 3-phospholene oxides (**4**, 73%; **5**, 27%).

The chlorination was also carried out by adding an equivalent of chlorine to a solution of 4.9 g (20.9 mmol) of **6** in 200 ml of THF at 0°. The resulting solution was stirred for 2 hr at room temperature and then hydrolyzed by addition of an ice-water slurry. THF was stripped and the water solution extracted with chloroform. From the extract on distillation there was obtained 3.47 g (86.8%) of oxide, bp 133–136° (0.25 mm), indicated by GC (200°) to be a mixture of rearranged products **11** (38.5%, shorter retention time) and **10** (61.5%); ^{1}H nmr of **10**, δ 1.29 (5-CH_3, d of d, $^3J_{PH}$ = 17.3 Hz, $^2J_{HH}$ = 7 Hz), 2.23 (2-CH_3, d, $^3J_{PH}$ = 10.5 Hz with additional small splitting), 7.08 (olefinic H, d, $^3J_{PH}$ = 40 Hz); ^{1}H nmr of **11**, δ 1.76 (5-CH_3, d of d, $^3J_{PH}$ = 15.3 Hz, $^2J_{HH}$ = 7 Hz), other signals not clearly resolved from **10**.

Magnesium Reduction of 1-Chloro-1-Phenyl-2-Phospholenium Chloride (9) The salt was obtained from the addition of chlorine to the 3-phospholene (2.0 g, 10.4 mmol) in 100 ml of THF. The solution was cooled to 0°, and 1.0 g of cleaned (by HCl) magnesium was added. The mixture was stirred at 0° for 30 min, and then refluxed for 7 hr. Treatment at room temperature with 40 ml of satd. ammonium chloride solution followed, and the organic layer was separated. The aqueous layer was washed with benzene; the organic layers were combined, dried ($MgSO_4$) and distilled to yield 0.76 g (38%) of a mixture of **12** and **13** distilling at 85–94° (1.0 mm); ^{1}H nmr of the major member (**13**, 59%) had δ 1.60 (5-CH_3, d of d, $^3J_{PH}$ = 19 Hz, $^3J_{HH}$ = 7 Hz) and of the minor isomer (**12**, 41%) had δ 1.12 (5-CH_3, d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 6.3 Hz). The methiodide formed from the isomer mixture in benzene was recrystallized from methanol-ethyl acetate.

Anal. Calcd for $C_{13}H_{18}IP$: C, 46.99; H, 5.47; P, 9.33. Found: C, 47.15; H, 5.48; P, 9.13.

Spectral Properties of 1-Chloro-1-Phenyl-2,5-Dimethyl-2-Phospholenium Chloride (9) Cycloaddition of phenylphosphonous dichloride and *trans,trans*-2,4-hexadiene in refluxing pentane produced a dark gummy solid having essentially the same spectral properties as the white solid precipitating from addition of chlorine to a mixture of phosphines **12** and **13** in pentane. This product (**9**) had a single ^{31}P nmr signal, +100.5 ppm ($CDCl_3$); its ^{1}H nmr spectrum ($CDCl_3$, internal TMS) contained a doublet (δ 2.14, $^3J_{PH}$ = 15 Hz) for the 2-CH_3 and a doublet of doublets (δ 1.54, $^3J_{PH}$ = 23 Hz, $^3J_{HH}$ = 7 Hz) for the 5-CH_3. Hydrolysis of **9** from either source provided a mixture of 2-phospholene oxides of composition 65% **10**, 35% **11**.

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REFERENCES

1. Supported by Public Health Service Research Grant CA-05507, National Cancer Institute.
2. (a) L. D. Quin, J. P. Gratz and R. E. Montgomery, *Tetrahedron Lett.* 2187 (1965) (b) L. D. Quin and T. P. Barket, *J. Am. Chem. Soc.* **92**, 4303 (1970).
3. A. Bond, M. Green and S. C. Pearson, *J. Chem. Soc. B*, 929 (1968).
4. S. E. Cremer, F. L. Weitl, F. R. Farr, P. W. Kremer, G. A. Gray and H. Hwang, *J. Org. Chem.* **38**, 3199 (1973).
5. S. E. Cremer, F. R. Farr, P. W. Kremer, H. Hwang, G. A. Gray and M. G. Newton, *J. Chem. Soc. Chem. Commun.* 374 (1975).
6. T. A. Albright, W. J. Freeman and E. E. Schweizer, *J. Am. Chem. Soc.* **97**, 2946 (1975).
7. L. D. Quin, J. P. Gratz and T. P. Barket, *J. Org. Chem.* **33**, 1034 (1968).
8. D. Gorenstein, *J. Am. Chem. Soc.* **94**, 2808 (1972).
9. L. D. Quin, S. G. Borleske and R. C. Stocks, *Org. Magn. Resonance* **5**, 161 (1973).
10. S. E. Featherman, S. O. Lee and L. D. Quin, *J. Org. Chem.* **39**, 2899 (1974).
11. J. J. Breen, J. E. Engel, D. K. Myers and L. D. Quin, *Phosphorus* **2**, 55 (1972).
12. L. D. Quin and J. J. Breen, *Org. Magn. Resonance* **5**, 17 (1973).
13. L. D. Quin, M. D. Gordon and S. O. Lee, *Org. Magn. Resonance* **6**, 503 (1974).
14. C. E. Roser and L. D. Quin, unpublished results.