at appropriately timed intervals, immediately cooled in ice water, and titrated as previously described (see Tables III–IV).

In each case an ampoule was allowed to remain in the heated bath for a period of at least 10 half-lives. The sample was then titrated as above to give the infinity point.

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Stereoisomerism in Some Derivatives of the 2-Substituted 3-Phospholene System[1]

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Abstract: *trans*-1,3-Pentadiene and *trans,trans*-2,4-hexadiene form cycloadducts with phosphonous dihalides (CH_3PCl_2 or $C_6H_5PBr_2$) which on reduction with magnesium give mixtures of *cis,trans*-1,2-disubstituted 3-phospholenes. Hydrolysis of the cycloadducts gives the *cis,trans*-3-phospholene oxides. The configuration of the 3-phospholenes has been deduced from their nmr properties. For the 1-phenyl-2-methyl systems, the *cis* configuration was assigned to that isomer showing an upfield 2-CH_3 signal, occasioned by phenyl shielding. This isomer had a much smaller value for J_{PCCH} (10 Hz) than the *trans* isomer (18 Hz). Similar values were obtained for other isomer pairs; configurations were assigned on this basis and were supported by other data. Assignments were also made to the isomeric benzyl bromide salts and oxides of the phospholenes. The nmr spectra of the cycloadducts, which are largely ionic, do not show the presence of *cis,trans* isomers, and this was attributed to a rapid equilibration through pentacovalent structures (intermediates or transition states).

In 1965, we announced the first instance of the separation of stable *cis,trans* forms of a five-membered ring (3-phospholene) where trivalent phosphorus provided one chiral center.[2] In this paper, other cases of isomeric 3-phospholenes are reported, and assignment of structure to the *cis* and *trans* forms is made. Consideration is also given to the structure of the diene–phosphonous dihalide cycloadducts, from which the isomeric pairs are formed by reduction (dehalogenation).

Synthesis. The cycloaddition of dienes and phosphonous dihalides[3] was used to construct the 3-phospholene ring. The reactions and structures prepared are summarized in Chart I.

Methylphosphonous dichloride has been used extensively in earlier cycloadditions, and the products of hydrolysis or reduction of the adducts have been proven to contain the 3-phospholene ring.[4] When 1,3-pentadiene is used in the cycloaddition and the adduct **1a** reduced, a mixture of *cis*- and *trans*-1,2-dimethyl-3-phospholenes is possible. This isomerism is due to the configurational stability of trivalent phosphorus.[5] That an isomer mixture was obtained was readily apparent from the gas chromatogram, which contained two peaks in a 3:1 ratio, and the proton nmr spectrum, which had two P–CH_3 doublets and two C–CH_3 signals (four lines, due to coupling with the methine proton and ^{31}P). The isomer mixture was separated by preparative gc as well as by fractional distillation. The isomers were analyzed as their more readily handled benzyl bromide salts. As will be discussed below, the major isomer, having the lower boiling point and shorter gc retention time, proved to be the *trans* form of **3a**.

In the first synthesis[2] of the isomeric phospholenes, a commercial mixture of *trans*(73%)- and *cis*(27%)-1,3-pentadiene had been used in the cycloaddition. The individual dienes have now been subjected to the reaction and it has been found, as predicted on steric grounds,[3] that only the *trans* isomer reacted. The *cis* isomer failed to give any cycloadduct even after several months.[6]

Hydrolysis of adduct **1a** has already been reported[2] to give a mixture of stereoisomeric 3-phospholene oxides. Gc analysis of the distilled product indicated the ratio *cis*-**2a**:*trans*-**2a** to be 1:2. Fractional distillation provided a sample of the lower boiling (*trans*) isomer of good purity; however, some rearrangement to the higher boiling 2-phospholene oxide[4] isomer accompanied the distillation, and the best sample of the *cis* form obtained was of 85% purity. Other experiments have indicated a *cis*:*trans* ratio of about 1:1 to be more descriptive of the steric outcome of the hydrolysis.

(1) From the Ph.D. Dissertation of T. P. Barket, Duke University, Durham, N. C., 1969. Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969. Supported in part by Public Health Service Research Grant No. CA-05507 from the National Cancer Institute, and the National Science Foundation through a Traineeship to T. P. B.

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

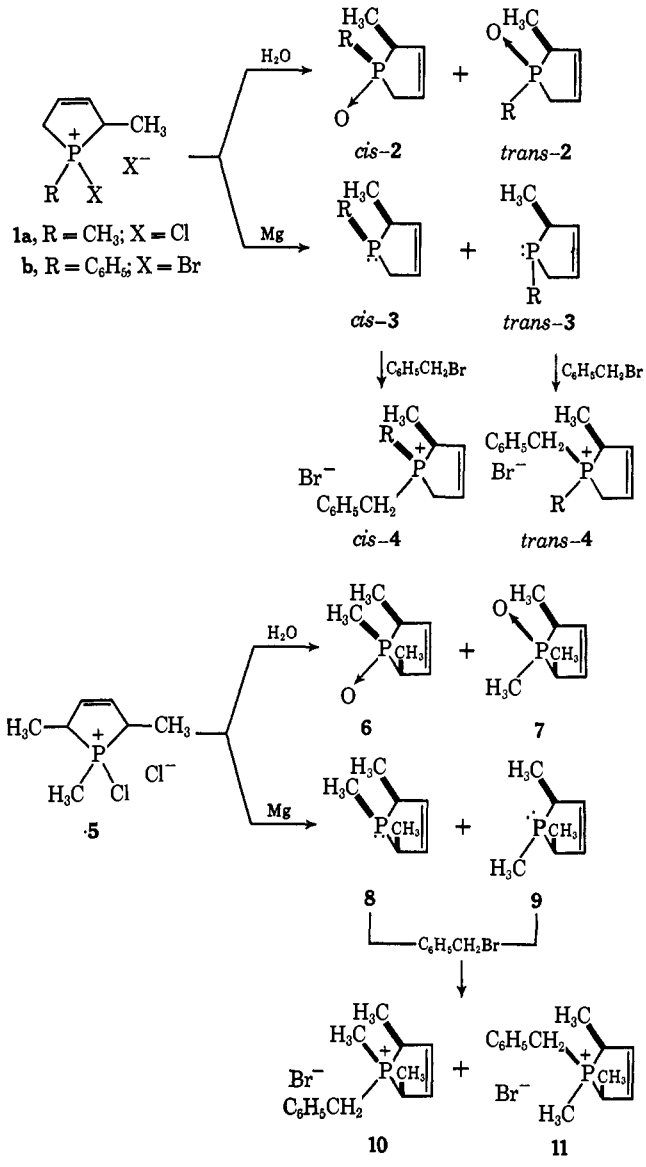
(3) W. B. McCormack, U. S. Patents 2,663,736 and 2,663,737 (1953); for a review, see L. D. Quin, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

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

(5) (a) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, 161 (1961); (b) for a recent review of phosphorus stereochemistry, seem M. J. Gallagher and I. D. Jenkins, "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 1.

(6) An earlier suggestion[2] that the isomeric dienes might give different cycloadducts, thus accounting for the isomerism in the reduction product, may now be discarded.

Chart I



For the synthesis of a suitable P-phenyl adduct, it was necessary to use phenylphosphonous dibromide, since it has been established[4] that the dichloride leads to the 2-phospholene system. Adduct **1b** was therefore prepared. Magnesium reduction gave a poor yield of phosphine mixture, consisting of about 80% *trans*-**3b**, 20% *cis*-**3b**, again with the *trans* isomer of lower boiling point and gc retention time. Neither preparative gc nor fractional distillation provided adequate separation of the isomers.

Hydrolysis of P-phenyl adduct **1b** provided an oxide mixture consisting of 33% *trans*-**2b**, 67% *cis*-**2b**. Small quantities of the mixture could be separated by silica gel column chromatography, but for larger amounts successive rapid distillations with a spinning band column were more effective. Prolonged reflux during distillation caused considerable rearrangement to the 2-phospholene oxide.

Once separated, the isomeric P-phenyl oxides **2b** proved valuable as precursors of the corresponding phosphines. The oxides were reduced in good yield with trichlorosilane,[7] a reaction known to proceed largely with retention of configuration.[8] The present reactions provide additional proof of the stereospecificity of this process as will be discussed. The original mixture of *cis,trans* oxides was also reduced with trichlorosilane to obtain a mixture of the isomers of phospholene **3b** in 78% yield. Since magnesium reduction of the adduct had proved unsatisfactory, this represented a useful source of the mixed phospholenes. It was noted in these reductions that the presence of triethylamine had no effect on the stereochemistry of the reduction; for acyclic oxides, the presence of the amine has led to inversion about phosphorus,[8] but in another cyclic system (a phosphetane derivative), retention has also been noted.[9]

The condensation of *trans,trans*-2,4-hexadiene with methylphosphonous dichloride gave adduct **5**, which was reduced with magnesium to give a product consisting of two isomers (**8** and **9**) in 1:9 ratio (by gc). From the nmr spectrum of the mixture, it was evident that a *cis* relation existed for the C–CH_3 groups in both isomers; only one four-line C–CH_3 signal was present for each isomer, proving the identity of environments for these groups in each isomer. A third possible isomer would have a *trans*-2,5-dimethyl structure; there would then be two four-line signals for each (nonequivalent) methyl. This stereospecificity in the cycloaddition has been observed previously;[10] the same diene on condensation with dimethylphosphinous chloride gave products of only *cis*-2,5-dimethyl structure, and the cycloaddition was considered to be concerted and disrotatory. No attempt was made in our work to separate the small amount of **8** accompanying **9** from the magnesium reduction.

Assignment of Configuration to Phosphines. Two nmr effects have been observed which together permit assignment of structure to the stereoisomeric phospholenes.

(a) Strong phenyl shielding of 2-CH_3 occurs for one P-phenyl isomer (**3b**). The difference between the chemical shifts of the 2-CH_3 groups in the two isomers is 0.46 ppm, with the upfield signal at δ 0.71 ppm. That the effect is due to phenyl shielding is clear from consideration of the P-methyl isomers; here the isomers have 2-CH_3 signals at δ 1.06 and 1.10 ppm. That P-phenyl isomer with upfield C-CH_3 is assigned the *cis* structure, as only in this isomer will the phenyl ring be in a position for its shielding area to influence the methyl group. There is ample precedent for this assignment.[11]

(b) The *trans*-P-phenyl compound (**3b**) has a significantly higher coupling constant (18 Hz) for interaction between ^{31}P and 2-CH_3 (J_{PCCH}) than does *cis*-**3b** (10 Hz). The same large difference holds for the two isomers of **3a** (18 and 10 Hz) and for the pair **9** (17.5) and **8** (9.5). This correlation permits the assignment of the *trans* configuration to the isomers of high J_{PCCH}, and *cis* to those of a low value. The origin of this effect is obscure, although a dependence of coupling constant on geometry has been observed for other trivalent

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

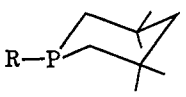
(8) L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).

(9) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 32, 4066 (1967).

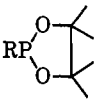
(10) A. Bond, M. Green, and S. C. Pearson, *J. Chem. Soc., B*, 929 (1968).

(11) See, for example, the case of 1,2-dimethyl-2-phenylcyclopentanol [T. D. Hoffman and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 1000 (1969)]; for 1-methyl, the signal is at δ 0.88 ppm when *cis* oriented to phenyl, and at 1.13 when *trans* oriented.

phosphorus compounds. For example, the axial and equatorial protons in 4,6 positions of the cyclic phosphites **12** have values of J_{POCH} of 11 and 3 Hz, respectively, even with considerable variation in the nature of R.[12,13] A similar effect was noted for the ring protons



12



13

of various compounds of structure **13**.[14] An apparent relation between J_{PCH} and the orientation of the proton relative to the lone pair of electrons of tertiary phosphines has also been detected.[15] The present case is somewhat different from those studied by others, in that the protons of the rotating methyl group are not fixed in a definite dihedral angle relationship with the phosphorus electrons. Nevertheless, the average position of the methyl protons will be quite different with respect to the phosphorus electrons in the *cis* and *trans* isomers, and the observed effect of considerably different value for J_{PCCH} is not inconsistent with the observations of others already cited. The effect is also apparently present in four-membered rings; Cremer and Chorvat[9] have observed significant differences (19.5 and 6–6.5 Hz) for the methyls on carbons α to phosphorus in 2,2,3,4,4-pentamethyl-1-phenylphosphetane.

Preliminary results show little tendency for the isomeric 1,2-dimethyl-3-phospholenes to equilibrate through inversion about phosphorus. Thus, heating pure *trans*-**3a** at 170° in a sealed capillary for 24 hr produced almost none of the *cis* isomer. Similar high stability of trivalent phosphorus when incorporated in cyclic systems has been observed by others.[16] In contrast, acyclic optically active phosphines racemize readily at 130°,[5] with half-lives of 3–4 hr.

Configurational Effects among Benzyl Bromide Salts. When *cis*-**3b** was converted to its benzyl bromide salt, the P-phenyl and 2-CH_3 retained their relative position, as indicated by the upfield (by 0.77 ppm) position of the 2-CH_3 signal relative to that from the salt of *trans*-**3b** (see Table I). This provides unambiguous proof that earlier suggestions[5a] that quaternization of phosphines occurs with retention of configuration are correct. As recently pointed out,[5b] this assumption, while reasonable, has required proof, and we offer this observation in this regard.

Table I. Nmr Spectra of Benzyl Bromide Salts of 3-Phospholenes[a]

Compd	P-CH_3 δ	P-CH_3 J_{PCH}	C-CH_3[b] δ	C-CH_3[b] J_{PCCH}	=CH δ	=CH J_{PCCH}	C_6H_5-CH_2 δ	C_6H_5-CH_2 J_{PCH}
trans-**4a**	2.13	13.5	1.65	17	6.00	26	4.33–4.90	*c*
cis-**4a**	2.26	13.5	1.36	17	5.80	27	4.71	17
trans-**4b**			1.87	17	6.04	27	4.91	16
cis-**4b**			1.10	19	5.81	28	4.91	16
10	2.06	14	1.57	17	6.06	27	4.46	16
11	2.13	13.5	1.33	17	5.67	27	4.81	16

[a] Chemical shifts in parts per million from TMS; J values in hertz. Taken in $CDCl_3$ solution with internal TMS. [b] J_{HCCH} was about 7 Hz for all compounds. [c] ABX signal.

The nmr spectra of the benzyl bromide salts of *cis*-**3b** and *trans*-**3b** possess another useful feature. The vinyl proton signal of the *cis* isomer is considerably (0.23 ppm) more upfield than that of the *trans* isomer. This difference is lacking in the phosphines themselves as well as in the phosphine oxides. It seems reasonable, then, to attribute the effect to the phenyl ring of the benzyl group; in the salt of the *cis* phosphine, this ring can easily be rotated to present its shielding cone to the vinyl protons, and indeed *cis*-**4b** has the more upfield vinyl signal. Models of the *trans* form show that the conformation which the benzylic phenyl must adopt to shield the vinyl protons has considerable interaction with the 2-CH_3 on the same face; the resulting diminished population of this conformation relative to the similar one of *cis*-**4b** would lead to a smaller shielding effect.

The same effect holds for the 1,2-dimethyl compounds; the benzyl bromide salt of *cis*-**3a** has the vinyl signal 0.20 ppm upfield of *trans*-**3a**. It is even more pronounced for the 1,2,5-trimethyl system, where the difference is 0.39 ppm. This large value may reflect even greater hindrance to the positioning of phenyl in the *trans,trans* salt in such a manner as to shield the vinyl protons. The effect provides further support for the assignment of *cis,trans* configurations of these isomers.

The 2-CH_3 signal of the salts also shows a shielding effect to be operative on this group; the 2-CH_3 signal of *cis*-**4a** is shielded by 0.29 ppm relative to that of the *trans* form. In *cis*-**4a**, models show that the benzylic group can achieve a conformation with the phenyl ring presenting its shielding cone to 2-CH_3 on the opposite face of the ring. Steric hindrance prevents a suitable conformation to be achieved readily in *trans*-**4a** (where benzyl and 2-CH_3 are *cis*) for shielding to occur.

The 2-CH_3 signal of the salts shows a similar shielding effect to be operative on this group; the 2-CH_3 signal of *cis*-**4a** is shielded by 0.29 ppm relative to that of the *trans* form. For the P-phenyl compounds, the difference in the chemical shifts of 2-CH_3 is increased to 0.77 ppm (from 0.45 ppm for the phosphines), presumably a result of combined shielding from both phenyl groups.

The nmr spectra of the benzyl bromide salts of the 1,2,5-trimethyl-3-phospholenes support the assignment of *cis* orientation for the 2- and 5-methyls. As noted in the preceding paragraph, a methyl *trans* to benzyl will be shielded, while one *cis* to benzyl will not. This effect would make the 2- and 5-methyls nonequivalent if they were *trans* oriented to each other. The spectrum should therefore show two C-CH_3 signals for each isomer in this case. In fact, the C-CH_3 signals remain of similar number in the phosphine isomers as in the salt isomers, consistent with the *cis*-2,5-dimethyl assignment.

The rates of quaternization for *cis,trans*-phosphine pair might be expected to be different, since approach of the halide to phosphorus of the *trans* isomer would be more hindered than to the *cis* isomer. Qualitative experiments suggest this to be the case; the isomer of **3b** assigned the *trans* configuration from the nmr study

(12) D. Gagnaire and J. B. Robert, *Bull. Soc. Chim. Fr.*, 2240 (1967).
(13) D. Gagnaire, J. B. Robert, and J. Verrier, *ibid.*, 2392 (1968).
(14) D. Gagnaire, J. B. Robert, and J. Verrier, *ibid.*, 3719 (1966).
(15) J. P. Albrand, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 1469 (1968).
(16) K. L. Marsi, *J. Amer. Chem. Soc.*, **91**, 4724 (1969), and references cited therein.

did indeed react more slowly than the *cis*-**3b**. Further study of this rate effect will be performed.

The benzyl bromide salt (**4a**) of *trans*-1,2-dimethyl-3-phospholene in $CDCl_3$ exhibits an ABX pattern for the benzylic protons, while the *cis* isomer gives an A_2X doublet. The ABX signal persists at 150°, suggesting that the nonequivalence arises from proximity of the benzyl group to an asymmetric center rather than to restricted rotation, the other common cause of such nonequivalence. However, this difference is lacking in the 1-phenyl-2-methyl series; both isomers gave A_2X doublets. We cannot account yet for the inconsistency of this effect. The benzyl bromide salts of both 1,2,5-trimethyl isomers (**10** and **11**) also had A_2X doublets for the benzylic protons. This is to be expected, since both isomers have a plane of symmetry perpendicular to the ring and passing through phosphorus. Identity of the benzylic protons is ensured by this symmetry.

Configurations of Phosphine Oxides. The shielding effect of the P-phenyl group in the isomeric 1-phenyl oxides (**2b**) readily permitted assignment of the *cis* structure to that isomer with the upfield (by 0.45 ppm) 2-CH_3 signal (see Table II). However, no useful difference existed in the spectra of the isomeric P-methyl oxides (**2a**). Their configuration was established by obtaining them independently from the stereospecific (retention)[17] oxidation with hydrogen peroxide of the isomeric phosphines of known structure. The validity of this approach was established in the P-phenyl series, where the phenyl shielding effect offers a simple means of following the stereochemistry of the reactions. Thus, the silane reduction of the *cis*-oxide (**2b**) occurred with retention and gave the *cis*-phosphine **3b**; this in turn re-formed *cis*-**2b** with hydrogen peroxide. The same cycle occurred in the *trans* series. The stereochemistry of 1,2,5-trimethyl-3-phospholene oxide has been established by others.[10] We have duplicated their results and confirm their assignments.

Table II. Nmr Spectra of 3-Phospholenes and Their Oxides[a]

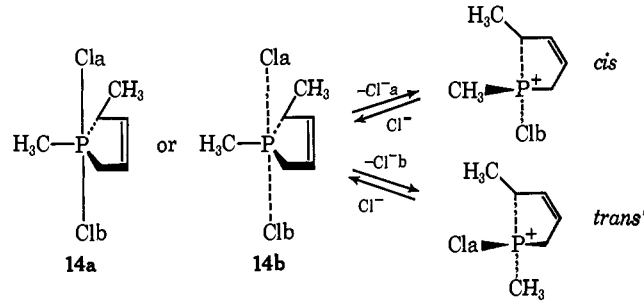
Compd	P-CH_3 δ	P-CH_3 J_{PCH}	C-CH_3[b] δ	C-CH_3[b] J_{PCCH}	=CH δ	=CH J_{PCCH}
			A. 3-Phospholenes[c]			
trans-**3a**	0.83	4	1.10	18	5.70	6
cis-**3a**	0.73	4	1.06	10	5.40–5.93	*d*
trans-**3b**			1.17	18	5.73	7
cis-**3b**			0.71	10	5.33–6.16	*d*
9[e]	0.91	4	1.16	17.5	5.63	6
8[e]	0.64	4	1.06	9.5	5.43–5.83	*d*
			B. 3-Phospholene Oxides[f]			
trans-**2a**	1.34	12.5	0.93	14	5.51	26
cis-**2a**	1.33	12.5	1.04	16	5.74	25.5
trans-**2b**			1.38	15	6.00	29
cis-**2b**			0.93	17.5	5.98	28

[a] Chemical shifts in parts per million from TMS; *J* values in hertz. [b] J_{HCCH} was about 7 Hz for all compounds. [c] Neat sample, internal TMS. [d] Complex multiplet. [e] Spectrum obtained on a mixture of **8** and **9**. [f] In $CDCl_3$ solution, internal TMS.

Stereochemistry of the Cycloadducts. Since the cycloadducts produce isomeric phosphines on reduction or isomeric phosphine oxides on hydrolysis, it might seem logical to expect the cycloadducts to possess geometrical isomerism. The striking observation has been made, however, that isomerism is lacking in the cycloadducts, at least in solution. The nmr spectra of adducts **1a** and **1b** were obtained in $CDCl_3$ and in each case only one four-line 2-CH_3 absorption was present. Also, **1a** as well as **5** exhibited only one P-CH_3 doublet. Duplicity of these signals, as noted before, is a clear indicator of the presence of the isomerism in the phosphines, their oxides, and their quaternary salts. In addition, adduct **5** possessed a single set of signals for the 2- and 5-methyls. It has furthermore been found that addition of chlorine to phosphorus of either the *cis* or the *trans* forms of phosphine **3a** resulted in re-formation of the cycloadduct **1a**, of identical proton nmr spectrum to the original material.

The structure about phosphorus in the cycloadducts must be considered to explain these results. We have suggested earlier[4] that in solution these compounds are better represented by ionic than covalent structures. This is readily apparent from their nmr properties in $CDCl_3$ solution. The protons are strongly deshielded, consistent with a positive charge on phosphorus. In **1a**, for example, the P-CH_3 group absorbs at δ 3.37 ppm, and vinyl signals appear at 6.14 ppm. More convincing are the ^{31}P spectra. For **1a**, this occurs at −121 ppm relative to 85% H_3PO_4; such a large negative value for a tertiary phosphine dihalide is a clear indication of the presence of positively charged phosphorus.[18,19] Similar ^1H and ^{31}P properties were found for cycloadducts **1b** and **5**, and for adducts we have studied previously.[4] Describing the adducts as simple tetrahedral derivatives, however, fails to account for the lack of isomerism. This can be accomplished if the *cis,trans*-ionic forms are equilibrated rapidly (on the nmr scale) through pentavalent structures, either intermediates or transition states. Good evidence exists for describing acyclic phosphine dihalides in these terms.[17] If an intermediate (**14a**), the pentacovalent form would very likely have trigonal-bipyramidal structure at phosphorus, possibly with the electronegative halogens occupying the apical positions.[20] Either halogen may be eliminated on ionization, thus forming the tetrahedral phosphonium ion in both *cis* and *trans* forms (Chart II).

Chart II



However, the nmr spectrum will not reveal this isomerism and will exhibit a single type of 2-methyl and P-methyl signal, if the process of halide loss and gain is rapid on the nmr time scale.[19] The same reasoning applies if a transition state (**14b**), lacking fully covalently

(17) L. Horner and H. Winkler, *Tetrahedron Lett.*, 455 (1964).

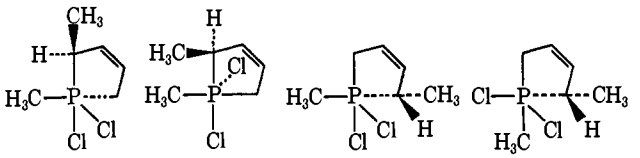
(18) G. A. Wiley and W. R. Stine, *ibid.*, 2321 (1967).

(19) D. B. Denney, D. Z. Denney, and B. C. Chang, *J. Amer. Chem. Soc.*, 90, 6332 (1968).

(20) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

bonded chlorines, is visualized for the pentavalent structure.

If the pentavalent structure is an intermediate, then another possibility exists for the construction of the trigonal bipyramid, with the ring occupying an apical and an equatorial position (*e.g.*, **15** or **16**). These structures would result from apical[21] approach of the chloride ion to the *trans,cis*-tetrahedral ions, respectively. While the 90° angle between apical and equatorial positions may be more compatible with the requirements of the five-membered ring,[21] these structures have the undesirable feature of a carbon atom in an apical position and chlorine in an equatorial position. These dispositions violate the generality that the most electronegative substituents preferentially occupy apical positions.[21] A single pseudorotation does not change this situation (*e.g.*, **16** to **17**, with CH_3 as pivot). Furthermore, it is a requirement that the group leaving the bipyramid do so from an apical position. Loss of the apical chlorine from **15** or **16** (and its isomer **17**) simply restores the original tetrahedral ion with the same *trans* or *cis* relation of the methyls. However, **15** can be transformed to **16** by two consecutive pseudorotations, passing through form **18**. Since **18** has two equatorial chlorines and two apical alkyl groups, the energy barrier to its formation would appear to be sizable. It is not possible with the data now available to assess the magnitude of this barrier to the equilibration relative to that involving a diequatorial ring, as has recently been done for some oxyphosphoranes,[22] and the true nature of the equilibration process remains unknown.



15 **16** **17** **18**

The magnesium reduction of the cycloadducts has in every case produced a mixture of phospholenes with the *trans* isomer predominant. The *trans* structure should be the more stable, having less steric interaction between substituents. As expected, the *trans*:*cis* ratio increases with greater interaction. Thus, for the methyl–methyl case **3a** the *trans*:*cis* ratio is 3:1, while for the phenyl–methyl case **3b** the ratio is 5:1. The interaction of P-methyl with two adjacent methyls leads to an even greater ratio (9:1) for *trans* (**9**) to *cis* (**8**).

The data so far available suggest that the hydrolysis of the cycloadducts proceeds with different stereochemistry than reduction. Thus, twice as much of *cis* form (**2b**) of 1-phenyl-2-methyl-3-phospholene oxide as the *trans* form was obtained on hydrolysis of adduct **1b**. The hydrolysis of the P-methyl adduct **1a** has given less clear-cut results. In the first experiments,[2] *trans*-**2a** predominated over *cis*-**2a**, but it now appears that a ratio of about 1:1 is more probable for this reaction. Further study of the mechanism and stereochemistry of the hydrolysis is clearly called for.

(21) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).
(22) D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1970); D. Gorenstein, *ibid.*, **92**, 644 (1970).

Table III. Nmr Spectra of Cycloadducts[a]

Compd	P-CH_3 δ	P-CH_3 J_{PCH}	C-CH_3[b] δ	C-CH_3[b] J_{PCCH}	=CH δ	=CH J_{PCCH}	^{31}P δ
1a	3.37	14.5	1.60	21	6.14	33.5	−121
1b			1.55	23	6.29	35	−81
5	3.37	13.5	1.56	21.5	6.10	32	−125

[a] Proton signals referenced to TMS, ^{31}P to 85% phosphoric acid. Shift values are in parts per million; J values in hertz. Taken in $CDCl_3$ solution with internal TMS. [b] J_{HCCH} was about 7.5 Hz for all compounds.

Experimental Section

Melting points were taken on a Mel-Temp apparatus and are corrected. Boiling points are uncorrected. Proton nmr spectra were run on a Varian A-60 spectrometer. Proton nmr chemical shifts are expressed in parts per million from internal TMS. ^{31}P nmr spectra were obtained on a Varian V-4300B spectrometer at 19.3 MHz. ^{31}P nmr are expressed in parts per million from 85% phosphoric acid. Gas chromatograms were prepared with a Varian-Aerograph Model 202-B instrument. Commercial piperylene was obtained from Aldrich Chemical Co. *trans,trans*-2,4-Hexadiene was obtained from Chem. Samples Co. Methylphosphonous dichloride[23] and phenylphosphonous dibromide[4] were available from published procedures. Mallinckrodt magnesium powder was used in the reduction reactions. It was freed of oxide coating by washing with 1 *N* hydrochloric acid, followed by distilled water, 95% ethanol, and finally ether. It was then dried in a vacuum oven. Fisher reagent tetrahydrofuran (THF) was used as received. All operations involving trivalent phosphorus or phosphorus halides were conducted in a nitrogen atmosphere.

Preparation of Cycloadducts. As described previously,[4] the diene and phosphonous dihalide were allowed to stand at room temperature for several weeks in the presence of copper stearate as polymerization inhibitor. For **1a**, 130 g (1.9 mol) of 1,3-pentadiene, 175 g (1.52 mol) of methylphosphonous dichloride, 50 ml of pentane, and 1 g of copper stearate were used; after 6 weeks, the crystalline adduct was filtered and washed with pentane. The yield was 0.97 mol. For **1b**, 46.0 g (0.675 mol) of 1,3-pentadiene, 117 g (0.44 mol) of phenylphosphonous dibromide, and 1 g of stearate set to a solid mass after 1 month. Adduct **5** was obtained from 25 g (0.303 mol) of *trans,trans*-2,4-hexadiene, 38.6 g (0.27 mol) of methylphosphonous dichloride, and 0.5 g of copper stearate. The mixture was a solid mass after 6 weeks. The nmr spectra of all three adducts (in $CDCl_3$) are given in Table III.

Magnesium Reduction of Cycloadducts.[4] Adduct **1a** (175 g, 0.945 mol) suspended in 2 pints of THF was stirred vigorously while a small amount (of a total of 35 g, 0.945 g-atom) of magnesium was added. The mixture was brought slowly to reflux to initiate the reaction. With intermittent heating as required to maintain reflux, the rest of the magnesium was added over a 2-hr period. The mixture was then refluxed 10 hr; it was diluted with another pint of THF and refluxed for 3 hr more. With ice-bath cooling, the mixture was slowly hydrolyzed with 250 ml of concentrated hydrochloric acid. The mixture was distilled to a head temperature of 100° to remove THF; it was then chilled and treated slowly with a solution of 200 g of sodium hydroxide in 500 ml of water. The final pH was 12. The mixture was steam distilled. The organic layer was collected from the distillate, dried over Drierite, and distilled (bp 127–133°; 130–134° was obtained in an earlier experiment[2]). The yield of **1,2-dimethyl-3-phospholene** (**3a**) was 40.4 g (37.2%). Gc on a 5-ft column of SE-30 (1:4 on Chromosorb W) at 75° showed the product to contain 75% *trans*, 25% *cis* isomers.

In a similar manner, adduct **5** (52 g, 0.26 mol) was reduced with 8 g (0.33 g-atom) of magnesium in 500 ml of sodium-dried THF, using a total reflux time of 3 hr. Work-up as above gave 13.7 g (42.3%) of **1,2,5-trimethyl-3-phospholene** (**8** and **9**), bp 132–136°. The nmr spectrum (Table I) revealed the product to be a 9:1 mixture of *trans,trans* isomer (**9**) and *cis,cis* isomer (**8**). A benzyl bromide salt was prepared from the **8,9** mixture in benzene solution and after three recrystallizations from methanol–ethyl acetate had mp 209–210°. It was revealed by its nmr spectrum (Table II) to have retained approximately the same isomer ratio (10:1).

(23) J. A. Pianfetti and L. D. Quin, *ibid.*, 84, 851 (1962).

Anal. Calcd for $C_{14}H_{20}BrP$: C, 56.20; H, 6.74; P, 10.35. Found: C, 56.65; H, 6.80; P, 10.63.

A methiodide (for which no isomers are possible) prepared in benzene solution and recrystallized from methanol–ethyl acetate decomposed about 320°.

Anal. Calcd for $C_6H_{16}IP$: C, 35.57; H, 5.97; P, 11.47. Found: C, 35.55; H, 5.97; P, 11.69.

The reduction of dibromide adduct **1b** was not very successful; from 260 g of adduct, only 5 g of **1-phenyl-2-methyl-3-phospholene (3b)**, bp 110–115° (6 mm), was obtained. The *trans–cis* ratio was 5:1 [by gc on a 10-ft DC-710 column (1:4 on Chromosorb W) at 190°]. A better procedure for preparing the phospholenes is the trichlorosilane reduction of the oxides, described in a later section.

Separation of *cis*- and *trans*-1,2-Dimethyl-3-phospholene (3a). By Gc. Thirty 100-μl samples of a 3:1 *trans–cis* **3a** mixture were injected on a 10 ft × 3/8 in. SE-30 column (1:4 on Chromosorb W, 60–80 mesh) at 57° with a helium flow of 60 ml/min. The phosphines were collected separately in 6 *N* hydrochloric acid, and were released on basification. After drying over Drierite, the nmr spectra were taken (Table I). **By Fractional Distillation.** Using a Nester-Faust annular Teflon column, 35 ml of 3:1 *trans–cis* mixture was distilled at atmospheric pressure. Pure *trans*-**3a** (20 g) was obtained at 132°; *cis*-**3a** (5 g) containing 1% of unidentified impurity (by gc) was obtained at 142°. The nmr spectra were identical with those from the gc separation. Benzyl bromide salts were prepared for each isomer from gc-collected samples in benzene solution. The salt of *trans*-**3a** had mp 206–208°; of *cis*-**3a**, 202–203°.

Anal. Calcd for $C_{13}H_{18}BrP$: P, 10.86. Found for *cis*-**3a**: P, 10.43; for *trans*-**3a**: P, 10.46.

The nmr spectra of both salts are reported in Table II.

***cis*- and *trans*-1,2-Dimethyl-3-phospholene Oxide (2a).** A 25-g (0.13 mol) sample of adduct **1a** was added to water with ice-bath cooling. The mixture was neutralized with sodium hydroxide, and the solution then saturated with sodium chloride and extracted several times with chloroform. The extracts were dried over magnesium sulfate and distilled, yielding 10.5 g (62%) of the isomeric oxides (**2a**) at 58–64° (0.17–0.25 mm). Gc indicated a *trans–cis* ratio of 2:1, with the *trans* form eluted first (1 m × 8 mm column of 15% DC-710 on Chromosorb W, 155°). The *trans* isomer was isolated by preparative gc on a 2 m × 10 cm column of PEG-20,000 on 30–60 mesh Chromosorb P, 1:4, at 195°. Its nmr spectrum is reported in Table I; it had $\gamma_{C=C}$ 1610 cm^{-1}.

Anal. Calcd for $C_6H_{11}OP$: C, 55.38; H, 8.52; P, 23.80. Found: C, 55.40; H, 8.46; P, 23.87.

The *cis* isomer was not readily obtained by gc, since it was not adequately separated from some 1,2-dimethyl-2-phospholene oxide formed by thermal rearrangement.[4] It was therefore obtained by fractional distillation with a spinning band column. A sample of 85% purity (with 8% *trans*-**2a** and 7% of the 2-phospholene derivative) was obtained. The nmr spectrum is recorded in Table I; $\gamma_{C=C}$ 1613 cm^{-1}.

Found: C, 55.21; H, 8.40; P, 24.02.

Several hydrolyses have been performed on small (1 g) samples of adduct **1a**. The products were not distilled; chloroform extracts were subjected directly to gc, with a *trans–cis* ratio of about 1:1 generally being obtained.

***cis*- and *trans*-1-Phenyl-2-methyl-3-phospholene Oxide (2b).** Cycloadduct **1b** (117 g, 0.44 mol) was added in portions to a slurry of 100 g of sodium bicarbonate and 200 g of ice. After stirring for 1–2 hr, the liquid was decanted from the inorganic matter and extracted with five 100-ml portions of chloroform. The residue left from vacuum stripping of the chloroform solution was distilled, giving 63.4 g (74.7% based on phenylphosphonous dibromide used in preparing **1b**), bp 136–142° (0.18 mm). Gc at 225° on a 5-ft SE-30-Chromosorb W (1:4) column revealed the mixture to consist of 25% *trans*-**2b**, 75% *cis*-**2b**.

Anal. Calcd for $C_{11}H_{13}OP$: C, 68.74; H, 6.82; P, 16.12. Found: C, 68.98; H, 6.96; P, 16.36.

Separation of a small amount of the isomers was accomplished by chromatography on a silica gel column. The column (1-in. i.d.) was prepared from 200 g of W. R. Grace silica gel grade 923 in chloroform. **2b** (1g) in chloroform was placed on the column and elution was performed with this solvent. The first fractions were enriched in *trans*-**2b**, the final fractions in *cis*-**2b**. Several passes through the column gave quite pure specimens of the two isomers but in small amount. Their nmr spectra are given in Table I.

Larger quantities were prepared by fractional distillation on a spinning band column. The final 5 g to distill from a 40-g sample was 95% *cis*-**2b** (bp 117° at 0.05 mm). The first five (of nine) fractions were enriched in *trans*-**2b**. Further enrichment was obtained on a second fractionation, and a third distillation of the best fractions finally gave 4 g of 98% *trans*-**2b**, bp 112° (0.04 mm). Prolonged exposure to high temperatures caused rearrangement to the 2-phospholene oxide isomer.

Trichlorosilane Reduction of *cis*- and *trans*-1-Phenyl-2-methyl-3-phospholene Oxide (2b). To 555 ml of dry benzene was added 62 g (0.323 mol) of the 3:1 *cis–trans* mixture of **2b**. Some benzene was distilled off to remove traces of water. Triethylamine[8] (35.4 g, 0.35 mol) was added, and after chilling the solution, 47.5 g (0.35 mol) of trichlorosilane was dropped in slowly. The mixture was then brought to reflux, which was maintained for 2 hr. The mixture was cooled, some ice was added, and then 300 ml of 20% sodium hydroxide was slowly added. After standing overnight, the organic layer was recovered, washed twice with 75-ml portions of 10% hydrochloric acid, and then twice with 75-ml portions of water. The organic layer was dried over sodium sulfate, stripped of solvent, and the residue distilled. There was obtained 44.5 g (78.1%) of a mixture (*cis–trans* ratio of 2:1) of the isomeric 1-phenyl-2-methyl-3-phospholenes (**3b**) at 138–156° (22 mm).

Attempts to separate the isomers on a 20 ft × 3/8 in. column of Dow-Corning silicone oil 710 on Chromosorb W (60–80 mesh) at 167° were not successful. Distillation with a Teflon annular column also failed to accomplish a significant degree of separation.

Synthesis of *trans*-1-Phenyl-2-methyl-3-phospholene (*trans*-3b). To 400 ml of dry benzene was added 2 g of *trans*-1-phenyl-2-methyl-3-phospholene oxide. The mixture was cooled and treated slowly with 10 g of trichlorosilane in 10 ml of benzene. After refluxing for 2 hr, the mixture was chilled, some ice added, and then made basic with 150 ml of 20% sodium hydroxide. The organic layer was separated, washed with water, and dried over sodium sulfate. A 125-ml portion of the benzene solution (175 ml) was freed of solvent and distilled. There was obtained 0.7 g of *trans*-1-phenyl-2-methyl-3-phospholene (*trans*-**2b**) at 120° (10 mm). Gc revealed its purity to be about 95%. The nmr spectrum is reported in Table I. The remainder of the benzene solution was treated with 3 ml of benzyl bromide; the precipitated salt was thrice recrystallized from ethyl acetate, mp 172–175°. Its nmr spectrum is given in Table II.

Anal. Calcd for $C_{18}H_{20}BrP$: C, 62.26; H, 5.80; P, 8.92. Found: C, 62.29; H, 6.01; P, 8.91.

Synthesis of *cis*-1-Phenyl-2-methyl-3-phospholene (*cis*-3b). The same procedure as above was followed, using 3 g of *cis*-**2b** in 200 ml of benzene and 12 g of trichlorosilane. The final volume of the organic layer was 150 ml; 100 ml was stripped of solvent and distilled to provide 1.5 g of *cis*-1-phenyl-2-methyl-3-phospholene [*cis*-**3b** in 95% purity, bp 110° (9 mm)]. The nmr spectrum appears in Table I. The remainder of the benzene solution was treated with 3 ml of benzyl bromide and the product worked up as for the *trans* isomer. The salt had mp 209–210°; its nmr spectrum appears in Table II.

Anal. Calcd for $C_{18}H_{20}BrP$: C, 62.26; H, 5.80; P, 8.92. Found: C, 62.24; H, 5.99; P, 9.05.

Addition of Chlorine to the 1,2-Dimethyl-3-phospholenes. A total of 0.147 g (2.1 mmol) of chlorine was produced from 0.131 g of potassium permanganate and 0.812 ml of hydrochloric acid and passed into a dry pentane solution of 0.24 g (2.1 mmol) of *trans*-1,2-dimethyl-3-phospholene (*trans*-**3a**). The precipitated product was dissolved in $CDCl_3$ and its nmr spectrum taken. The spectrum was identical with that of cycloadduct **1a** (Table III). The hydrolysis of a small amount of the precipitate gave a 1.1:1 *trans–cis* ratio of 1,2-dimethyl-3-phospholene oxides.

The same procedure was applied to *cis*-1,2-dimethyl-3-phospholene (*cis*-**3a**). The nmr spectrum of the precipitate in $CDCl_3$ was identical with that obtained from cycloadduct **1a** and from the chlorination of *trans*-**3a**. An identical *trans–cis* ratio was obtained on hydrolysis to the oxide.

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