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(23) M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins", Wiley-Interscience, New York, N.Y., 1971.
(24) P(4), P(5), P(6) = tetra-, penta-, and hexacoordinate phosphorus compound.
(25) The stereochemistry of the reaction P(5) → P(6) → P(5)′ is not considered in the present discussion.
(26) (a) P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971); (b) F. Ramirez and I. Ugi, *Bull. Soc. Chim. Fr.*, 453 (1974).
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(28) The kinetic picture may be more complicated in the reactions of the highly reactive X=P(O)OAr, where step P(4) → P(5) may not be rate controlling.
(29) The behavior of $C_6F_5O^-$ and p-$NO_2C_6H_4O^-$ in the reaction R^2OH + X=P(O)OR^1 (Table IV) can be interpreted along the same lines with reference to **27**.
(30) D. A. Usher, D. I. Richardson, Jr., and D. G. Oakenfull, *J. Am. Chem. Soc.*, **92**, 4699 (1970).
(31) S. J. Benkovic and K. J. Schray, "The Enzymes", Vol. III, 3 ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1973, p 201.
(32) W. Stillwell, G. Steinman, and R. L. McCarl, *Bioorg. Chem.*, **2**, 1 (1972).
(33) S. Pantremoli, E. Grazi, and A. Accorsi, *J. Biol. Chem.*, **242**, 61 (1967).
(34) D. E. Watts, "The Enzymes", Vol. VIII, 3d ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1973, Chapter 12.
(35) **Note Added in Proof.** This mechanism—P(4) → P(5) → P(4)′ → P(5)′ → P(4)″—is inconsistent with the following data: $t_{1/2} \sim 15$ h for the reaction R^2OH + (ArO)(R^1O)P(O)OCH(CH_3)$COCH_3$ + R_3N → (R^2O)(R^1O)P(O)OCH(CH_3)$COCH_3$ + $ArO^-R_3NH^+$, at 25 °C in 0.2 M $CDCl_3$, while $t_{1/2}$ = 3 min for R^2OH + X=P(O)OR^1 → (R^2O)(R^1O)P(O)OCH(CH_3)$COCH_3$, under comparable conditions (Table IV), when R^2 = $(CH_3)_2CHCH_2$, R^1 = c-C_5H_9, Ar = p-$NO_2C_6H_4$, R = C_2H_5. It is clear that the acyclic P(4)′ intermediate, that should have been formed from the cyclic triester according to this mechanism, reacts at a much slower rate (~15 h) than the cyclic triester itself (~3 min). Hence the latter reaction must proceed by a different mechanism, possibly that postulated here: P(4) → P(5) ≡ **27** → P(6) ≡ **28** → P(5)′ ≡ **31** → P(4)″. Moreover, the reaction ROH + (ArO)P(O)(OC_6H_5)$_2$ → (RO)P(O)(OC_6H_5)$_2$ + ArOH is *effectively catalyzed* by $ArOR_3NH^+$, as well as by $ArO^-R_4N^+$, in either $CDCl_3$ or CD_3CN (0.2 M, 25 °C), although it is evident that in this case the intermediate P(4)′ postulated by the mechanism P(4) → P(5) → P(4)′ → P(5)′ → P(4)″ is identical with the starting triester, P(4), and therefore the catalysis must be exerted via a different mechanism (F. Ramirez and J. Marecek, *Tetrahedron Lett.*, submitted for publication).

Synthesis, Structure Analysis, and Stereochemistry of Some Reactions of *cis*- and *trans*-2,2,5-Trimethyl-3-phenyl-1,3-oxaphospholane

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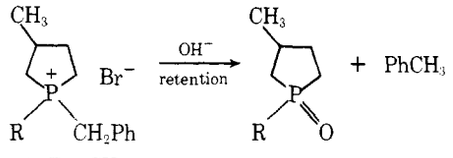
The syntheses of *cis*- and *trans*-2,2,5-trimethyl-3-phenyl-1,3-oxaphospholane are reported and a detailed analysis of the NMR spectra given from which stereochemical assignments were made and conformational structure suggested. Hydroxide cleavage of *cis*- and *trans*-3-benzyl-2,2,5-trimethyl-3-phenyl-1,3-oxaphospholanium bromide occurred stereospecifically with retention of configuration at phosphorus to yield the corresponding diastereomers of 2,2,5-trimethyl-3-phenyl-1,3-oxaphospholane 3-oxide.

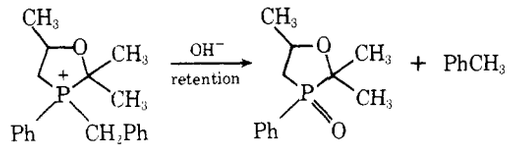
Stereochemistry of nucleophilic displacement at a phosphonium phosphorus atom confined to a five-membered ring (phospholanium salts) has been the subject of a number of investigations which are briefly summarized in a recent paper.[1] One of the most significant findings in this system is the hydroxide-induced displacement of benzyl from both the cis and trans isomers of **1** and **2** with complete retention of configuration at phosphorus.[2a-d]



1, R = CH_3
2, R = Ph

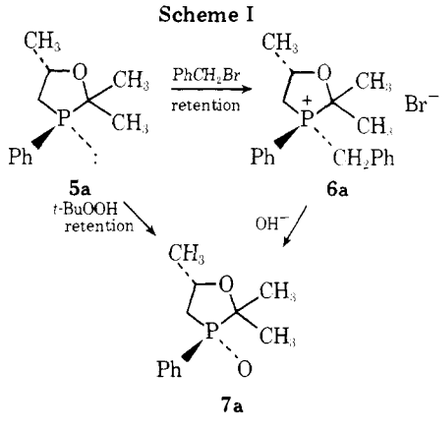
3

The possible influence of any "element effect" of a second heteroatom on the stereochemistry of this reaction has prompted us to synthesize the cis and trans isomers of 3-benzyl-2,2,5-trimethyl-3-phenyl-1,3-oxaphospholanium bromide (**4**). The 1,3-oxaphospholane system is a newly synthesized one,[3a] and its chemistry has been essentially limited to a few NMR studies.[4-6] Also no pure geometric isomers have been isolated until this report. With this appropriately substituted 1,3-oxaphospholane system in hand, chosen especially for its relatively simple NMR spectra, we have now discovered that the presence of oxygen in the ring provokes no stereochemical change. Indeed, **4** behaves precisely as **1** and **2** toward base cleavage, which again occurs with complete retention of configuration. The stereochemistry for eq 1 was demonstrated by completion of the stereochemical cycle shown in Scheme I for which the stereochemistry of reduction[2,7] and oxidation[8]



4 (1)

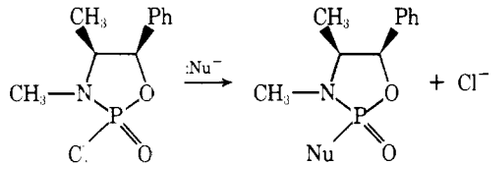
Scheme I



is known. Stereospecific oxidation of **5a** produces the same isomer as cleavage of **6a**. Although racemic mixtures of both cis and trans isomers were used, the cycle is illustrated with one enantiomer of the trans phosphine **5a**.

Since the completion of this work, Cooper and others[9] have

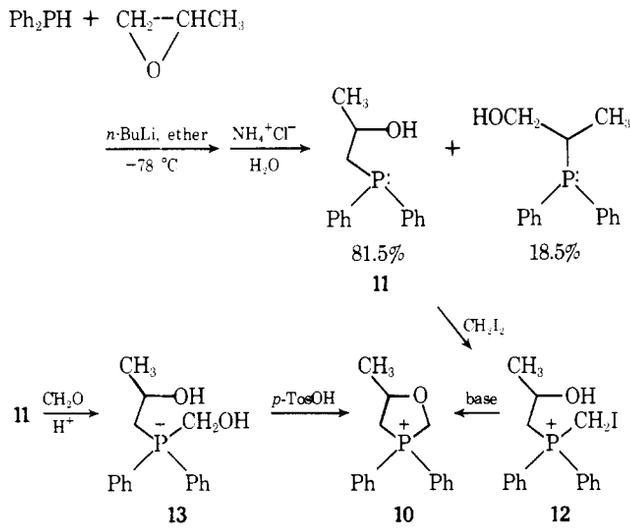
reported that for the two isomers of **8**, epimeric at phosphorus, retention accompanies displacement of chloride by methoxide or phenoxide to give **9**. Retention of configuration at phos-



8 **9**

phorus resulting from nucleophilic displacement of leaving groups for the cis and trans isomers **1**, **2**, **4**, and **8** is presently best explained by apical attack at phosphorus by the nucleophile to produce a trigonal bipyramidal intermediate with one ring bond and the nucleophile occupying apical positions in order to minimize ring strain. The leaving group is then expelled following one Berry pseudorotation.[1] We are now investigating the effect of incorporation of larger heteroatoms in place of oxygen in structures similar to **4**. This could conceivably lead to some inversion of configuration at phosphorus if the larger atom alleviates some ring strain during the course of nucleophilic substitution.[10]

Synthesis of Cis and Trans Isomers of 2,2,5-Trimethyl-3-phenyl-1,3-oxaphospholane (15). A preliminary attempt was made to synthesize **10**, by the route shown.



11 **13** **10** **12**

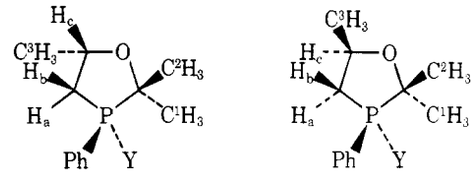
However, difficulty was experienced in the ring closure steps.

It was proposed that **10** could be cleaved by base[2c] to 5-methyl-3-phenyl-1,3-oxaphospholane 3-oxide which could in turn be reduced[7] to 5-methyl-3-phenyl-1,3-oxaphospholane, the immediate precursor for the oxa analogue of **2**. However, protonation of **13** is evidently retarded by the presence of the positively charged phosphonium atom since only unreacted phosphonium salt was recovered from acid treatment of **13**. No exhaustive study was made to cyclize **12**. The use of Me_2SO[11] or 2,4,6-collidine also failed to effect ring closure of **13** or **12**, respectively.

By modification of Oehme's procedure,[3a] in order to enable the use of a volatile ketone such as acetone, it was possible to prepare a mixture of the cis and trans isomers of **5** in yields surpassing literature reports for the use of ketones in such cyclizations.

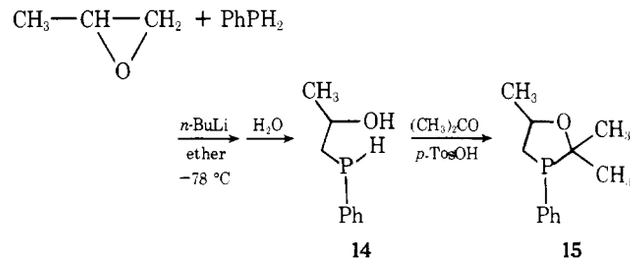
The mixture of isomeric cyclic phosphines **15** was subjected to fractionation on a spinning band column and the lower boiling isomer of bp 95 °C (3.5 mm) was obtained pure. This isomer was assigned a trans configuration (**5a**) based upon its NMR spectrum as discussed below. The tail fraction of bp 97 °C (3.0 mm) was found to be a mixture consisting of 80% cis isomer and 20% trans isomer. These two fractions were separately subjected to the reactions illustrated in Scheme I. It was possible to show that the isomeric composition of the phosphonium salt and phosphine oxide derived from the phosphine mixture was identical within experimental error with that of the original phosphine mixture.

Table I. Chemical Shifts and Coupling Constants for *trans*- and *cis*-2,2,5-Trimethyl-3-phenyl-1,3-oxaphospholane and the Corresponding Oxides[a]



	5a[b] (Y = lone pair)	**7a**[c] (Y = O)	**5b**[d] (Y = lone pair)	**7b**[e] (Y = O)
	Chemical Shift (δ, ppm from Me_4Si)			
δH_a	2.50	2.42	1.91	2.12
δH_b	1.89	2.04	2.43	2.72
δC^1H_3	1.37	1.57	1.53	1.56
δC^2H_3	1.03	1.07	1.02	1.00
δC^3H_3	1.51	1.47	1.36	1.49
δC_6H_5	7.44		7.44	
δH_c	4.10	4.47	4.45	4.34
	Coupling Constant, Hz			
$J_{H_aCH_b}$	14.2	14.9	14.4	15.2
$J_{H_aCCH_c}$	6.9	6.3	9.6	9.9
$J_{H_bCCH_c}$	8.3	8.7	5.6	6.0
$J_{C^3H_3CH_c}$	6.3	6.2	6.0	5.9
J_{PCH_a}	24.4	14.9	19.5	19.0
J_{PCH_b}	6.2	9.9	2.7	6.0
J_{PCCH_c}		1.4		2.8
$J_{PCC^1H_3}$	17.6	10.9	18.2	11.0
$J_{PCC^2H_3}$	7.6	13.5	6.4	13.6
$J_{PCCC^3H_3}$		1.8		1.8

[a] Determined at ambient temperature using a 100-MHz Varian Associates Model XL-100-15 spectrometer. Chemical shifts were measured from tetramethylsilane as an internal standard in a neat sample for the phosphines and in $CDCl_3$ for the oxides. [b] Registry no., 61009-58-3. [c] Registry no., 61009-59-4. [d] Registry no., 61009-60-7. [e] Registry no., 61009-61-8.

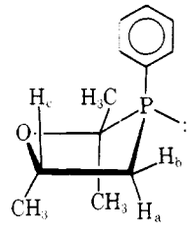


14 **15**

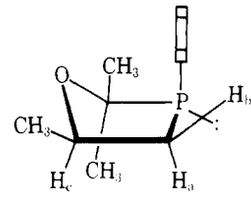
Assignment of Cis, Trans Structure to 5. The ^1H NMR spectra obtained for the phosphines were completely analyzed and the analysis verified using the computer program LAOCOON III.[12] The chemical shifts and coupling constants are presented in Table I. Data supporting configurational assignments are summarized as follows:

1. H_c would be expected to be found further downfield than either H_a or H_b because of deshielding by oxygen.[2d] The protons of the methyl group to which H_c is coupled resonate

at 1.51 ppm for one isomer and at 1.36 ppm for the other. The methyl group is designated as C^3H_3 in each case. Where C^3H_3 is cis to phenyl, an upfield shift would be expected because of the shielding effect of the aromatic ring. Where C^3H_3 is cis to the lone pair on phosphorus (trans isomer) a downfield shift[4,13] would be expected for the methyl group. Thus the lower boiling isomer having δC^3H_3 1.51 ppm is assigned the structure **5a**. The isomer of δC^3H_3 1.36 ppm is given the structure **5b**.



5a



5b

2. H_a in each structure should exhibit a larger coupling constant than H_b because of the cis relationship of H_a with the lone pair on phosphorus.[13] Once identified, H_a is seen to be trans to H_c in **5a** and cis to H_c in **5b**. These spatial relationships are borne out by the values of the coupling constants for $J_{H_aCCH_c}$ and $J_{H_bCCH_c}$ for the two isomers; e.g., the Karplus equation would predict a larger value for $J_{H_aCCH_c}$ for the cis isomer than for the trans. This is indeed the case as shown in Table I. The values for $J_{H_aCCH_c}$ and $J_{H_bCCH_c}$ for the two isomers suggest dihedral angles consistent for phosphorus at the flap of an envelope for **5a** and with oxygen at the flap position in **5b** in the principal conformers. In both conformations Courtauld models show *cis*-1,3-dimethyl and *cis*-1,2-methylphenyl interactions to be optimized and the lone pair on phosphorus oriented pseudoequatorially.[14] These models also strongly suggest a highly rigid system for both **5a** and **5b** around the phosphorus atom. For **5b** H_b is downfield with respect to the same proton in **5a**, possibly owing to the conformational preference of the phenyl group as shown in **5b** which minimizes interaction with the two cis methyl substituents. Of course, unequivocal assignment of H_a and ring conformation await x-ray analysis which we have planned.

The spectra of the corresponding oxides **7a** and **7b** are also given in Table I. The ring geometry for the oxides, as indicated by the coupling constants $J_{H_aCCH_c}$ and $J_{H_bCCH_c}$, has evidently not changed significantly as a result of oxidation of the phosphines **5a** and **5b**. The values of $J_{H_aCH_b}$ for both the phosphines and the phosphine oxides indicate a nearly normal tetrahedral angle and thus considerable ring puckering.

Table II gives NMR data for the diastereomeric phosphonium salts **6a** and **6b**. It is interesting to note that the benzyl protons are nonequivalent owing to the adjacency of the benzyl methylene to an asymmetric phosphorus atom in each case. This is in marked contrast to the behavior of benzyl protons in the isomers of **1** and **2** which appear as one set of doublets.[2a-c]

Experimental Section

2-Hydroxypropyldiphenylphosphine (11). To 42.6 g (0.23 mol) of diphenylphosphine dissolved in 1 l. of anhydrous ether was added dropwise with stirring 159 ml of 1.45 M butyllithium. The reaction was conducted at 0 °C under nitrogen. The yellow reaction mixture was cooled to −78 °C using a dry ice–acetone bath and an equimolar amount of a 0.25 M solution of propylene oxide[15] in ether was added with stirring. After addition, the mixture was allowed to come to room temperature and 107 ml of 4 M ammonium chloride solution was added whereupon the earlier formed precipitate dissolved and the solution became colorless. The ether layer was removed and the aqueous layer was extracted twice with two portions of 200 ml of ether. The ether layer and extracts were combined. The residue, after concentration of the ether solution, was fractionally distilled and two principal fractions were obtained. The first fraction of bp 147 °C (0.05 mm) accounted for 51% of the product and was identified as **11**.

Anal. Calcd for $C_{15}H_{17}OP$: C, 73.76; H, 7.01; P, 12.68. Found: C, 73.76; H, 7.11; P, 12.54. NMR (neat) δ 1.27 (d, 3 H, J = 6 Hz, CCH_3), 2.29 (d of d, 2 H, PCH_2), 3.54–4.00 (m, 1 H, CHOH), 7.1–7.6 (m, 5 H, C_6H_5), 3.70 (s, 1 H, OH).

The infrared spectrum of a neat sample of **11** showed an intermolecular hydrogen bonded band at 3325 cm^{-1} which disappeared on dilution with chloroform. No appearance of a distinctive free OH stretching vibration could be observed upon dilution, but a band appeared at 3150 cm^{-1} which may be attributed to intramolecular association between phosphorus and the hydroxyl hydrogen.

A second fraction (13.4% yield) distilling at 153–154 °C (0.07 mm) was found to be enriched in $Ph_2PCH(CH_3)CH_2OH$: NMR (neat) δ 0.95 (d, 3 H, J = 6 Hz, $CHCH_3$), 4.23 (d, 2 H, J = 5 Hz, CH_2OH).

Anal. Calcd for $C_{15}H_{17}OP$: C, 73.76; H, 7.01; P 12.68. Found: C, 73.48; H, 7.12; P, 12.96.

NMR analysis of the reaction product prior to fractional distillation showed 81.5% of the hydroxyphosphine product to be **11** and 18.5% its isomer, $Ph_2PCH(CH_3)CH_2OH$.

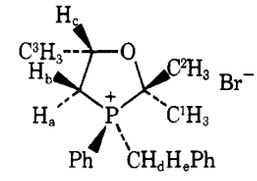
Preparation of 2-Hydroxypropyliodomethyldiphenylphosphonium Iodide (12). A benzene solution (50 ml) containing 1.2 g of **11** was treated with 2.8 g of methylene diiodide to yield 1.34 g of pure **12** after recrystallization from ethanol, mp 200.5–201 °C.

Anal. Calcd for $C_{16}H_{19}I_2OP$: C, 37.52; H, 3.74. Found: C, 37.57; H, 3.88.

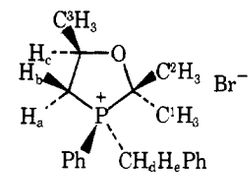
Attempted ring closure reactions with **12** using 2,4,6-trimethylpyridine failed to bring about cyclization and resulted in recovery of starting materials.

Hydroxymethyl-2-hydroxypropyldiphenylphosphonium Chloride (13). Equimolar amounts of **11** and 37% formaldehyde were allowed to react in concentrated hydrochloric acid at 0 °C. After 1 h the solution was extracted continuously for a period of 3 days with chloroform. The resulting glassy product was recrystallized from ethanol–ethyl acetate to give a 60% yield of **13** of mp 130.5–132.5 °C. Equivalent weight: calcd for $C_{16}H_{20}ClO_2P$, 310.7; found, 312.7.

Table II. NMR Data for Diastereoisomeric 3-Benzyl-3-phenyl-2,2,5-trimethyl-1,3-oxaphospholanium Bromides[a]



6a[c]



6b[d]

	6a	6b
Chemical Shifts (δ, ppm from Me_4Si)		
C^1H_3	2.06 (d)	2.03 (d)
C^2H_3	1.48 (d)	1.30 (d)
C^3H_3	1.56 (d)	1.53 (d)
H_a	2.34 (d of d)	*b*
H_b	2.46 (pent)	*b*
H_c	4.04 (pent)	3.98 (m)
H_d	5.00 (t)	4.88 (t)
H_e	5.50 (t)	5.41 (q)
Coupling Constants, Hz		
$J_{PCC^1H_3}$	13.7	14.7
$J_{PCC^2H_3}$	15.9	14.1
$J_{H_2CC^3H_3}$	7.11	6.74
$J_{H_aCH_b}$	14.0	*b*
$J_{H_bCCH_c}$	7.33	*b*
$J_{H_dCH_e}$	14.7	13.3
J_{PCH_a}	4.3	*b*
J_{PCH_b}	8.2	*b*
J_{PCH_d}	15.0	15.3
J_{PCH_e}	14.7	19.3

[a] Data measured at ambient temperature using a 60-MHz Perkin-Elmer R12-B spectrometer with Me_4Si as an internal standard in $CDCl_3$ solution. [b] The spectrum of **6b** could not be completely analyzed. [c] Registry no., 61009-62-9. [d] Registry no., 61009-63-0.

Anal. Calcd for $C_{16}H_{20}ClO_2P$: C, 61.79; H, 6.44; Cl, 11.41; P, 9.98. Found: C, 61.57; H, 6.72; Cl, 11.44; P, 9.80. NMR ($CDCl_3$) δ 1.5 (unresolved d, 3 H, J = 6 Hz, CCH_3), 3.5 (m, 3 H, $CHCH_3$ and PCH_2OH), 5.25 (d of d, 2 H, PCH_2), 6.26 (s, 1 H, OH), 7.75 (m, 5 H, C_6H_5).

Attempted cyclization of **13** with catalytic quantities of *p*-toluenesulfonic acid, dimethyl sulfoxide,[11] or cyclohexylcarbodiimide were unsuccessful.

2-Hydroxypropylphenylphosphine (14). Phenylphosphine (41.1 g, 0.374 mol) was made to react with 260 ml of 1.45 M *n*-butyllithium in the manner described above for the preparation of **11**. The resulting solution was treated with 22.0 g of propylene oxide and the product worked up as for **11** to yield 70% of **14**: bp 103 °C (0.5 mm); NMR (neat) δ 1.25 (d, 3 H, J = 6 Hz, CCH_3), 1.66–2.66 (m, 2 H, CH_2), 3.56–4.16 (m, 1 H, CH), 4.62 (s, OH), 5.8–6.2 (d, 1 H, J = 216 Hz, PH), 6.93–7.66 (m, 5 H, C_6H_5). There was no NMR evidence for the formation of appreciable amounts of $PhPHCH(CH_3)CH_2OH$. Compound **14** was further characterized by reaction with cyclopentanone following the procedure for the synthesis of **5** given below to yield 50% of 5-methyl-3-phenyl-2,2-tetramethylene-1,3-oxaphospholane, bp 174 °C (0.4 mm).

Anal. Calcd for $C_{14}H_{19}OP$: C, 71.77; H, 8.17. Found: C, 72.0; H, 8.26.

***cis*- and *trans*-3-Phenyl-2,2,5-trimethyl-1,3-oxaphospholane (5).** 2-Hydroxypropylphenylphosphine (**14**, 11.3 g, 0.0673 mol), dissolved in approximately 350 ml of benzene, was mixed with 100 ml of acetone and 0.2 g of *p*-toluenesulfonic acid added as a catalyst. The reaction mixture was refluxed for 16 h and condensed vapors were passed through a Soxhlet extractor thimble filled with Linde 3A molecular sieves which had been dried at 140 °C for 60 h previous to use. At this point an additional 100 ml of acetone was added and the reaction mixture allowed to reflux in like manner for 6 h longer. The resulting solution was treated with sodium to precipitate unreacted phosphine as the sodium salt, and the precipitate was removed by filtration. After removal of the solvent, vacuum distillation of the residue yielded 9.80 g (70%) of product [bp 91 °C (1 mm)]. By NMR analysis, the product was shown to consist of 70% **5a** and 30% **5b** (Table I).

Fractionation of *cis*- and *trans*-2,2,5-Trimethyl-3-phenyl-1,3-oxaphospholane (15). A mixture of phosphines **5a** and **5b** (19.0 g) was subjected to fractional distillation on a spinning band column. The fraction boiling at 95 °C (3.5 mm) and consisting of 3.2 g was collected and shown by NMR to be isomerically pure. Based upon its NMR spectrum, this isomer is assigned the structure *r*-3-phenyl-2,2,*t*-5-trimethyl-1,3-oxaphospholane (**5a**).

***r*-3-Phenyl-2,2,*t*-5-trimethyl-1,3-oxaphospholane 3-Oxide (7a).** The pure isomeric oxaphospholane (**5a**) was oxidized with *tert*-butyl hydroperoxide in accordance with a literature procedure[8] to yield the corresponding oxide (**7a**) of bp 115 °C (0.07 mm) (Kugelrohr), mp 78–80 °C.

Anal. Calcd for $C_{12}H_{17}O_2P$: C, 64.27; H, 7.64. Found: C, 64.18; H, 7.88. NMR data are presented in Table I.

Cleavage of 3-Benzyl-*r*-3-phenyl-2,2,*t*-5-trimethyl-1,3-oxaphospholanium Bromide (6a). This salt (0.715 g) was cleaved with 1 N sodium hydroxide under previously described conditions except that the reaction time was limited to 1 h. GLC analysis of the cleavage product showed the formation of toluene to the exclusion of any benzene. The oxide **7a** was obtained in 93% yield and was identical in every respect with that prepared by *tert*-butyl hydroperoxide oxidation of **5a**. The NMR spectrum of the product, mp 78–80 °C, showed no trace of **7b**. The spectrum of **7b** was determined by *tert*-butyl hydroperoxide oxidation of a 60:40 mixture (trans:cis) of the isomeric oxaphospholanes and subtraction of the spectrum of **7a**.

Cleavage of 3-Benzyl-*r*-3-phenyl-2,2,*c*-5-trimethyl-1,3-oxaphospholanium Bromide (6b). A salt mixture consisting of 38% of **6b** and 62% of **6a** as determined by NMR analysis was treated with 1 N sodium hydroxide as described above for **6a**. Upon workup, a mixture of oxides consisting of 42% **7b** and 58% **7a** of bp 120 °C (0.2 mm) (Kugelrohr) was obtained in 93% yield. The composition of reactants and products is consistent with complete retention of configuration within the limits of error of NMR integration.

Anal. Calcd for $C_{12}H_{17}O_2P$: C, 69.21; H, 8.23. Found: C, 69.29; H, 8.31. NMR spectrum (see Table I).

All higher boiling fractions were combined and carefully redistilled. The final fraction (1.90 g) of bp 97 °C (3 mm) was collected and shown to consist of 80% of *r*-3-phenyl-2,2,*c*-5-trimethyl-1,3-oxaphospholane (**5b**) and 20% of the corresponding trans isomer (**5a**). Further separation was not achieved. The NMR spectrum of **5b** was obtained by difference (Table I).

Anal. Calcd for $C_{12}H_{17}OP$: C, 69.21; H, 8.23. Found: C, 69.30; H, 8.18.

3-Benzyl-*r*-3-phenyl-2,2,*t*-5-trimethyl-1,3-oxaphospholanium Bromide (6a). The pure phosphine **5a** (1.4 g, 0.0067 mol) was treated with 2.3 g of benzyl bromide in 50 ml of benzene. After 1 week at room temperature the resulting crystals were removed and recrystallized from ethanol–ethyl acetate to give 1.9 g of **6a**, mp 208–209 °C. For NMR spectrum see Table II.

Anal. Calcd for $C_{19}H_{24}OPBr$: C, 60.17; H, 6.38. Found: C, 59.91; H, 6.58.

Mixtures Enriched in 3-Benzyl-*r*-3-phenyl-2,2,*c*-5-trimethyl-1,3-oxaphospholanium Bromide (6b). A mixture consisting of 80% **5b** and 20% **5a** (1.19 g), dissolved in 50 ml of benzene, was treated with 1.96 g of benzyl bromide and, after 2 days, 1.855 g of crude product recovered. The crude material was recrystallized from ethyl acetate–ethanol to give a product of mp 200–202 °C.

Anal. Calcd for $C_{19}H_{24}OPBr \cdot C_2H_5OH$: C, 59.30; H, 7.11. Found: C, 59.41; H, 7.09. The NMR spectrum indicated the presence of 1 mol of ethanol per mole of phosphonium salt.

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Registry No.—**11**, 2652-63-3; **12**, 61009-64-1; **13**, 61047-25-4; **14**, 2328-18-9; diphenylphosphine, 829-85-6; propylene oxide, 75-56-9; $Ph_2PCH(CH_3)CH_2OH$, 61009-65-2; formaldehyde, 50-00-0; phenylphosphine, 638-21-1; cyclopentanone, 120-92-3; 5-methyl-3-phenyl-2,2-tetramethylene-1,3-oxaphospholane, 61047-24-3.

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