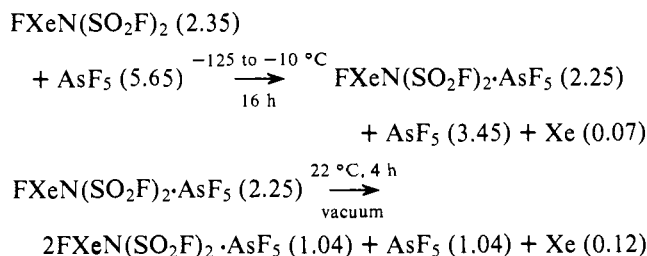1:1 adduct decomposes under dynamic vacuum at 22 °C very cleanly to a stable compound of the composition $2FXeN(SO_2F)_2 \cdot AsF_5$. The following equations (millimoles) indicate a typical reaction sequence:

$FXeN(SO_2F)_2$ (2.35)

$+ AsF_5$ (5.65) $\xrightarrow[16\ h]{-125\ to\ -10\ °C}$ $FXeN(SO_2F)_2 \cdot AsF_5$ (2.25)

$+ AsF_5$ (3.45) $+ Xe$ (0.07)

$FXeN(SO_2F)_2 \cdot AsF_5$ (2.25) $\xrightarrow[vacuum]{22\ °C,\ 4\ h}$

$2FXeN(SO_2F)_2 \cdot AsF_5$ (1.04) $+ AsF_5$ (1.04) $+ Xe$ (0.12)

Small amounts of other products, consisting mainly of SO_2F_2, $[N(SO_2F)_2]_2$, and $Xe_2F_3{}^+AsF_6{}^-$, are observed in the material pumped out at 22 °C, but only Xe and AsF_5 could be effectively measured. These results are very close to the expected values allowing for minor side reactions and some volatility of the 1:1 and 2:1 adducts. No reasonable alternative stoichiometry could be found.

The 1:1 adduct, which we believe is most probably $(FO_2S)_2NXe^+AsF_6{}^-$, is a bright yellow solid, whereas the 2:1 compound is a pale yellow solid. The Raman spectrum of a small sample (~0.1 mmol) of the 2:1 adduct contained in a glass apparatus for low temperature Raman had not changed after 4 days under dynamic vacuum at 22 °C. This indicates a low vapor pressure and thermal stability at 22 °C. Analysis of the compound for xenon by reaction with H_2O gave an average of 1.967 mol of Xe/mol of compound, very close to the expected 2:1 ratio.

The formulation of the 2:1 adduct as $[(FO_2S)_2NXe]_2$-$F^+AsF_6{}^-$ is supported by Raman and ^{19}F NMR spectroscopy. The Raman spectrum taken at ca. −100 °C shows strong bands at 1494, 1236, 906, 832, 647, 333, 289, 261, and 226 cm^{-1}, which can readily be assigned to covalently bound $-N(SO_2F)_2$ groups.[2] The relatively high frequency for the $\nu(SO)$ symmetric and $\nu(SO)$ antisymmetric frequencies at 1236 and 1494, compared with those of $FXeN(SO_2F)_2$, are in harmony with the $-N(SO_2F)_2$ groups being more covalent in the cation than in the neutral compound. The most striking difference between $FXeN(SO_2F)_2$ and the 2:1 spectrum is the complete absence of $\nu(XeF)$ at 504 cm^{-1} and the absence of any other intense Raman bands in the 500–620-cm^{-1} region. This clearly indicates the absence of terminal xenon-fluorine bonds.[3] With regard to $\nu(XeN)$ and $\nu(XeFXe)$ a moderately strong band at 486 cm^{-1} and a very weak band at 408 cm^{-1} may be tentatively assigned to these modes.[4] Finally, ν_1 of $AsF_6{}^-$ is clearly evident as a moderately intense band at 683 cm^{-1}.

The ^{19}F NMR of $[(FO_2S)_2NXe]_2F^+AsF_6{}^-$ was obtained in BrF_5 at ca. −45 °C. The compound is quite soluble forming a clear yellow solution, which undergoes little or no change after several hours at −45 °C. The initial interpretation of the NMR spectrum was difficult. Only two resonances are observed (external $CFCl_3$) at −61.2 $[N(SO_2F)_2]$ and 61.0 $(AsF_6{}^-)$ along with the expected AX_4 spectrum of BrF_5. The relative areas are 4.0:6.0 as expected for $[(FO_2S)_2NXe]_2$-$F^+AsF_6{}^-$, but no signal could be found for the bridging fluorine.[5] Either there is no bridging fluorine or that the resonance is unobservable because of some exchange process.

We summize that $[(FO_2S)_2NXe]_2F^+$ ionizes in the following way:

$$[(FO_2S)_2NXe]_2F^+ = FXeN(SO_2F)_2 + XeN(SO_2F)_2{}^+$$

Such a process could broaden the Xe–F resonance to a point where it could not be observed. This is supported by our finding that a ^{19}F NMR spectrum of a BrF_5 solution of a mixture (~1:1) of $FXeN(SO_2F)_2$ and $[(FO_2S)_2NXe]_2F^+AsF_6{}^-$ shows no F on Xe resonance, whereas resonance for $FXeN(SO_2F)_2$ is easily observed under identical conditions for the pure compound. The S–F resonance of $FXeN(SO_2F)_2$ and $[(FO_2S)_2NXe]_2F^+AsF_6{}^-$, which are different in the pure compounds by ~400 Hz, coalesce into a single peak, essentially at the midpoint of the two original signals. The relative area of this signal to that of the $AsF_6{}^-$ is ~1:1.

The above data clearly establishes the existence of $[(FO_2S)_2NXe]_2F^+AsF_6{}^-$ and further amplifies the similarity between XeF_2 and $FXeN(SO_2F)_2$. Whereas XeF_2 forms both 1:1 and 2:1 adducts with AsF_5, the 1:1 adduct $FXe^+AsF_6{}^-$ is unstable at 22 °C to form the 2:1 adduct $Xe_2F_3{}^+AsF_6{}^-$.[3,6] Interestingly, none of the xenon esters of the type FXeOR exhibit the same chemical behavior. While $FXeOSO_2F$ forms an unstable 1:1 adduct with AsF_5, decomposition results in the formation of $Xe(OSO_2F)_2$ and $(FXe)_2SO_3F^+AsF_6{}^-$.[7] The latter compound has been prepared in various ways using HF solvent.[8,9] On the other hand, $FXeOTeF_5$ is reported to form a stable 1:1 adduct with AsF_5 which is said to be $XeOTeF_5{}^+AsF_6{}^-$.[10]

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(4) The Xe–N stretch in $FXeN(SO_2F)$ is believed to be at 474 cm^{-1}, but this assignment remains tentative. The weak bridging fluorine–xenon stretch is at 420 cm^{-1} in $Xe_2F_3{}^+SbF_6{}^-$ and 401, 417 cm^{-1} in $Xe_2F_3{}^+AsF_6{}^-$ (ref 3).
(5) The only reported ^{19}F NMR of a Xe(II) compound containing an XeFXe bridge is that of the $Xe_2F_3{}^+$ cation in $BrF_5(I)$. The chemical shift was 184 ppm relative to external $CFCl_3$. R. J. Gillespie, A. Netzer, and G. J. Schrobiligen, *Inorg. Chem.,* **13**, 1455 (1974).
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Stereochemistry of Free-Radical Substitution at Trivalent Phosphorus. Permutational Processes Available for Stereochemically Nonrigid Phosphoranyl-Radical Intermediates

Sir:

The rapid pairwise exchange of substituents attached to pentacovalent phosphorus ($1 \rightleftarrows 2$) has been well established.[1] In trigonal-bipyramidal SF_4[2] and related sulfuranes,[3] where the lone pair can be considered a fifth ligand, DNMR studies suggest that an analogous process with the electron pair as pivot is operative. Such pairwise ligand permutations have been classified as mode 1[4] for which Berry[5] and turnstile[6] processes have been postulated as mechanistic alternatives. Phosphoranyl radicals, $X_4P\cdot$, bear at least superficial similarity to the above intermediates in that they are near-trigonal-bipyramidal in

Table I. Reaction of **5** with Alkoxy Radicals[a]

| reactant[b]	R'O·	cis/trans **5** initial	cis/trans **5** consumed	cis/trans **7** formed[d]	% **5**, consumed	% yield[e] of **7**
5a	EtO·	37/63	40/60	62/38	24	49
5a	EtO·	37/63	39/61	61/39	45	52
5a	sec-BuO·	37/63	40/60	61/39	15	76
5a	sec-BuO·	37/63	40/60	62/38	35	71
5b	EtO·	20/80	24/76	76/24	32	85
5b	EtO·	19/81	23/77	75/25	50	71
5b	sec-BuO·	20/80	27/73	76/24	16	79
5b	sec-BuO·	20/80	24/76	75/25	32	69

[a] In degassed C_6H_6 at 20–25 °C. [b] [**5**] = 0.25–0.36 mol/L. [c] Initial [ROOR]/[**5**] = 2–5. [d] Sensitivity calibrated ratio of corresponding sulfides following S_8 oxidation. [e] Based on **5** consumed.

geometry[7] with the vacant position equatorial, as represented by **3** and **4**. The potential interconversion of **3** and **4** via the same sort of pairwise exchange is depicted. However, there is no a priori reason that all trigonal–bipyramidal species need undergo rapid mode 1 isomerizations. A nonpairwise scrambling of carbonyls in $Fe(CO)_4$ has recently been proposed.[8]
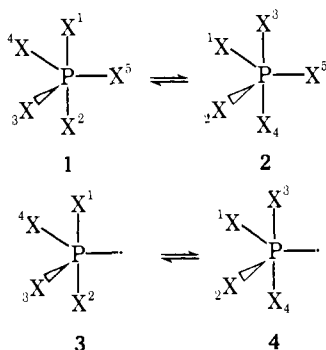
Two experimental approaches available for the classification of permutation mode in the rearrangement of a pentacovalent or pseudopentacovalent intermediate are dynamic magnetic resonance studies (NMR and ESR) and stereochemical investigations. These methods give complementary information; e.g., the overall stereochemistry of a given reaction may distinguish between modes which cannot be differentiated by spectroscopic means.[4]

We report here the results of the study of the overall stereochemistry of the substitution process depicted in eq 1. This is an especially favorable reaction system for study in that the geometries of postulated intermediate five-membered-ring phosphoranyl radicals like **6** have been well characterized by ESR.[9] The normally irreversible[10] reaction of alkoxy radicals with trivalent phosphorus derivatives removes the complications involved in mechanistic interpretation which would result if reactants were re-formed. The results that we report allow us to conclude that the sort of mode 1 isomerization process given by **3** ⇌ **4** is slow relative to other isomerizations available to intermediate **6**.
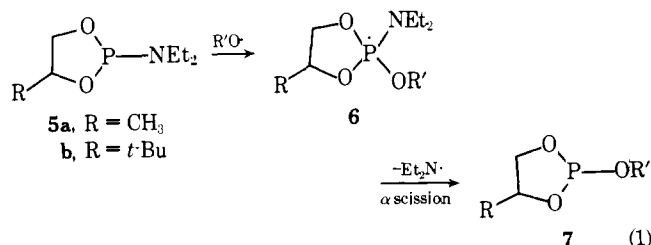
As recorded in Table I, the reactions of ethoxy and sec-butoxy radicals with the five-membered-ring phosphoramidites **5a** and **5b** give reasonable yields of phosphites (**7**) resulting

from substitution at phosphorus. The cis/trans geometries of the series of **5** and **7** were reported earlier.[11] The alkoxy radicals were generated by photolysis of the precursor peroxides. The phosphites were converted to the corresponding sulfides by stereospecific retentive reaction with S_8 prior to GLC analysis.[12] The product ratios resulted from kinetic control conditions as they are invariant with time and are far from the equilibrium cis/trans ratios[11] of the phosphites, **7** (~35/65 for R = CH_3, 20/80 for R = t-Bu). At higher conversions than those of Table I, the phosphites themselves intercepted some of the alkoxy radicals and yielded phosphates. Otherwise, <8 area % of side products was formed in any case. No oxidation of **5** was observed to accompany substitution. Within experimental error, the cis/trans ratio of product **7** formed corresponds to the inverse of the cis/trans ratio of consumed **5**. Thus the reactions all occur with *inversion of configuration about phosphorus*.

In earlier ESR work on reactions of non-ring-substituted five-membered-ring phosphoramidites like **5** with alkoxy radicals, the Roberts group observed[9] phosphoranyl radicals of structure **8**. The alkoxy group is in the thermodynamically
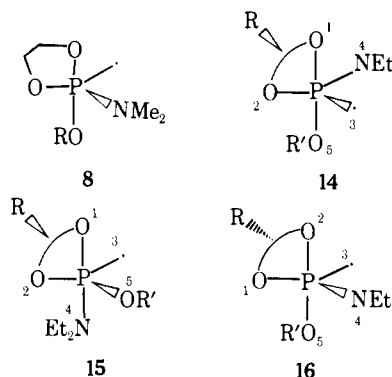
more favorable apical position with the ring apical–equatorial in attachment and the Me_2N and odd electron equatorial. It is reasonable as well to presume that the attacking alkoxy radical should *initially* enter the trigonal–bipyramidal phosphoranyl radical apically. This is indicated by ab initio calculations[13] for formation of H_4P·, by kinetic ESR studies[14] concerned with the stereospecificity of α scission (the microscopic reverse of radical attack on trivalent phosphorus) and by the apical introduction of R'O· in the T-shaped radicals, $(RO)_2\dot{S}OR'$.[15] On this basis the formation of the cyclic phosphoranyl radicals (**9**) involved in the reactions of Table I is shown in Scheme I for reaction of a cis phosphoramidite isomer. It is then reasonable that α scission (the reverse of radical attack) occurs from the apical position. This could be accomplished by the mode 1 (Berry or turnstile) permutation **9 → 10**, which keeps the ring apical–equatorial and the odd electron equatorial and is analogous to **3 → 4**. Loss of Et_2N· from **10**, however, gives phosphite with *retention* of configu-

Scheme I

cis-phosphoramidite

9   10   11 (retention) cis phosphite

12   13 (inversion) trans phosphite
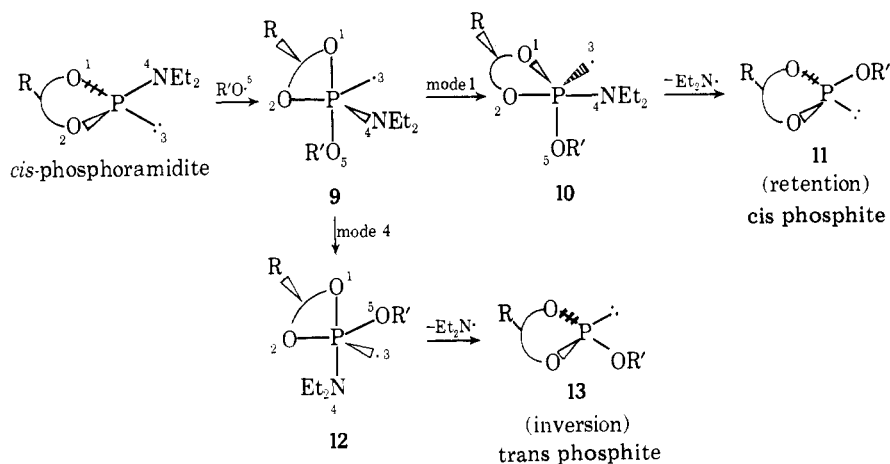
ration, which is contrary to fact (Table I).

ESR work[16] has led to the postulation that radicals like **8** and **9** undergo extremely rapid mode 4 isomerizations of the type **9 → 12** of Scheme I. α scission of **12** yields **13** and results in a reaction proceeding with overall *inversion* of configuration at phosphorus as required by the results of Table I. Thus the present stereochemical work and earlier ESR results are entirely consistent. Both confirm the notion that the sort of mode 1 isomerization shown in Scheme I, which one would have expected by analogy to pentacovalent phosphorus and sulfuranes to be favored,[1] *is not the most rapid permutation available to thoese phosphoranyl radicals.* Furthermore, the inversion pathway observed excludes a mode 3 permutation exchanging ligands 3 and 4 to give **14**, which would lead to loss of stereospecificity. Certain of the ESR results would have allowed for such an isomerization. A mode 2 exchange of ligands 4 and 5 gives **15**, resulting in retention on apical loss of Et_2N, which is again ruled out stereochemically. The only other permutation process which can give inversion is the mode 5 isomerization **9 → 16**, an anti-Berry[4] step involving exchange of substituent **1** with **2** and **4** with **5**. The ESR work excludes this.[9,16]

Since any mode 4 permutation can be attained by two successive mode 1 (Berry or TR) steps,[17] it should be stressed that the isomerization **9 → 12** could proceed through intermediate **17** as a higher energy minimum in the reaction profile. This

17
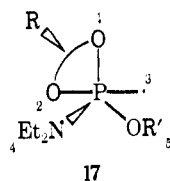
would require that mode 1 formation of an intermediate with odd electron apical be a more rapid process than the mode 1 alternative in which the odd electron serves as pivot ligand. That such might be the case is indicated by ab initio[13] and $CNDO/2$[18] calculations as well. Whether isomerizations of phosphoranyl radicals proceed by a one-step mode 4 processes or the equivalent in successive mode 1 rearrangements, it is clear that to regard phosphoranyl radicals as simple analogues of pentacovalent phosphorus species with the odd electron as an electropositive substituent is incorrect so far as their permutational properties are concerned. This is related to the fact that the structures like **3** and **4**, while accurate depictions of geometry, do not accurately represent electronic structure.[13,18,19,20]

The construction of Scheme I and the conclusions based thereon presume that product formation proceeds predominantly via the observed radicals (**9**). It is not possible to exclude

the possibility of reaction through *undetectable* intermediates or transition states of geometry which would lead to inversion stereochemistry. An obvious example would be a phosphoranyl radical with ring attachment diequatorial and R'O and Et_2N apical.

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