

The first process is that proposed by Olah. Lukas' data tend to support the second of the two possibilities.¹⁰ We do not wish to enter this controversy except to point out that the reaction is sufficiently complex so that it occurs in several steps; we feel more than two. A thorough kinetic analysis would be quite desirable and probably necessary to pin down the mechanism.

It is obvious that there exists a very rich and complicated chemistry of alkane oxidation in superacids. Thermodynamic calculations such as these represent only the first step in unraveling the reactions involved. A thorough kinetic study is needed. Extension of these calculations to other systems including the interesting TaF₅ system used by Siskin³⁰ is underway.³¹

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References and Notes

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Free-Radical Chemistry of Organophosphorus Compounds. 8.¹ Free-Radical Arbuzov Reaction Stereochemistries and the Question of Available Permutational Modes for Phosphoranyl Radicals

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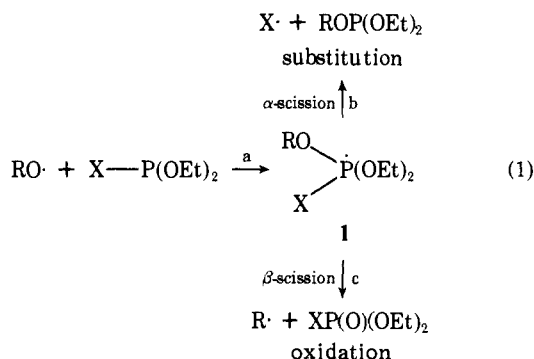
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Abstract: The stereochemistries of the reactions of Ph· and Me₂N· with *cis/trans* isomeric five- and six-membered ring phosphites have been determined. The reactions are nearly stereospecific with *cis* phosphite yielding *trans* phenylphosphonate and phosphoramidate. Reactions with the *trans* phosphites give the corresponding *cis* products. Toward Me₂N· the two isomers of the six-membered ring phosphite show a six- to eightfold difference in reactivity, the thermodynamically less stable *trans* isomer being the more reactive. It is argued that for these phosphoranyl radical intermediates permutational isomerization steps of mode I (Berry or turnstile mechanisms, e.g.) are unable to compete with product-forming β-scission. The reaction stereochemistries would allow but do not require mode 4 or mode 5 isomerizations to occur rapidly.

The oxidation and substitution processes which occur when a free radical attacks a trivalent phosphorus compound have been reasonably well explored.² Both ESR³ and chemical studies^{1a,4} support the postulation that many of these reactions proceed via an intermediate species, **1**, termed a phosphoranyl radical. Until very recently, however, only scant attention has been given to the question of possible permutational modes by

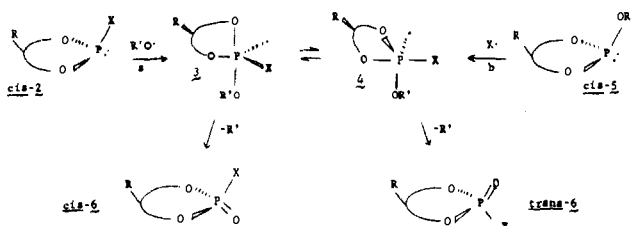
which these trigonal bipyramidal intermediates³ might undergo isomerizations in which equatorial and apical substituents are interchanged.^{1a,3m,n,4a}

Phosphoranyl radicals are superficially analogous to pentacovalent phosphoranes, PZ₅, if one views the odd electron as a phantom ligand. Stereochemical studies have proved to be very powerful tools in the investigation of the formation and



permutational isomerizations of PZ₅.⁵ In a recent paper,^{1a} we reported a study of the stereochemistries of alkoxy and thyl radical oxidations of a phosphine and certain five- and six-membered ring phosphites. Our results suggested that mode 1 (M₁; see Musher⁶) permutation processes (Berry⁷ and turnstile⁸ mechanisms, as examples) have high barriers relative to those for product formation (~10–11 kcal/mol). Specifically, we found no stereochemical evidence for the M₁ isomerization 3 → 4 for presumed intermediate 3 formed by reaction path a of Scheme 1. Only stereochemically retentive ox-

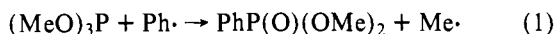
Scheme 1



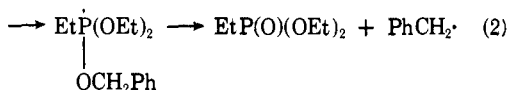
dation occurred (*cis*-2 → *cis*-6).

We here report our attempts to increase the rate of such an isomerization by introducing a group X (path b) which is of an electronic nature such that it should thermodynamically prefer to be in the equatorial position as in 3. A rapid isomerization of 4 to 3 prior to β-scission then would require a *change* in observed stereochemistry with formation of *cis*-6 rather than *trans*-6.

A process in which addition of a radical to trivalent phosphorus is followed by the β-scission of a group already attached to phosphorus in the starting material would be the free-radical equivalent of the familiar Arbusov rearrangement. Chemical^{9,10} and ESR^{3d} investigations have shown that such a sequence requires a reasonably reactive radical (step 1a) or, as an alternative, a rapid β-scission step. Thus, Ph· and (MeO)₃P give product quantitatively (eq 1),¹⁰ but Et·⁹ and Me·^{3d} give



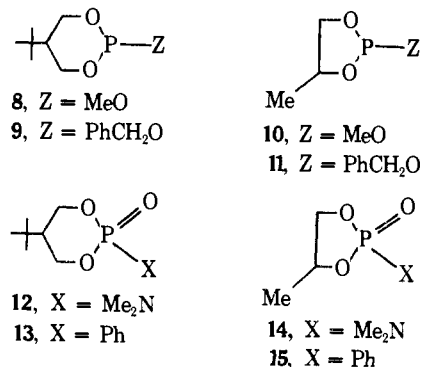
no overall reaction, although MeP(OEt)₃ is noted by ESR.^{3d} By contrast both Me· and Et· give alkyl phosphonate when a benzyloxy is attached to phosphorus (eq 2) because of the rapid



rate with which it undergoes β-scission.^{3d,9} The intermediate MeP(OEt)₂OCH₂Ph is still detectable by ESR,^{3d} however. Moreover, we find¹¹ that Me₂N· reacts efficiently with benzyl diethyl phosphite to yield correspondingly Me₂NP(O)(OEt)₂ and PhCH₂·. In this paper we report the results of stereochemical studies of the free-radical Arbusov reactions of certain five- and six-membered ring phosphites.

Results

Reactions of the radicals X· = Me₂N· and Ph· with the five- and six-membered ring phosphites 8–11 were investigated. Radicals were generated photochemically at 20 °C in degassed benzene from the initiator molecules tetramethyltetrazene (TMT, (Me₂N)₂N₂) and phenylazotriphenylmethane (PAT, PhN₂CPh₃). TMT photolysis is a well-known¹² source of dimethylamino radicals. The reaction of (MeO)₃P with thermally generated radicals from PAT has been thoroughly investigated.¹⁰ In Table I are found the products of these reactions. The formation of 1,1,1-triphenylethane, a product also seen when PAT is thermally decomposed in the presence of methyl phosphites,¹⁰ is to be expected for a free-radical process. The bibenzyl generated from the reactions of 9 and 11 is in-



dicative of benzyl radical formation. In confirmation, when reactions of Me₂N· with 9 and 11 were carried out in the cavity of an ESR spectrometer (benzene solvent at ca. 10 °C), signals were noted that could be readily assigned to the benzyl radicals (Figure 1). The low-field component of the methylene triplet hfs ($A_{\text{H}}^{\text{CH}_2} = 16.9 \text{ G}$) was completely broadened out presumably because of high viscosity of the sample. Also, the central component of the triplet hfs is broadened, so that the amplitude of the central component is less than that expected for 1:2:1 triplet hfs. (See Experimental Section for complete listing of hfsc values.)

All reactions were subjected to careful controls. Reactants were shown to be inert to photolysis in the absence of initiator molecule. No thermal reaction between initiator and phosphite could be detected at 20 °C. Prolonged irradiation of product mixtures failed to affect product distributions. Phosphite-TMT solutions were not decomposed in the gas chromatograph, although PAT solutions were and therefore had to be run to complete consumption of phosphite before analysis. The desire to avoid thermal equilibration of isomers of 8 and 10 was the reason for selecting photolytic rather than thermal decomposition of PAT.

The stereochemical outcome of each reaction listed in Table I was determined by methods we have published previously and which are well worked out. The *cis* and *trans* assignments to isomers of 8¹³ and 10¹⁴ have been reported. Those for 9 and 11 were deduced from analysis of the non-first-order ¹H NMR spectra with the aid of LAOCN3 (Experimental Section) and the ³¹P chemical shifts for the isomers in question in complete analogy to earlier work with 8 and 10. *Cis/trans* geometry assignments for the isomers of 12 also were reported earlier.¹⁵ For the isomer of 13, geometries were determined from the already known for the trivalent analogue, 2-phenyl-5-*tert*-butyl-1,3,2-dioxaphosphorinane,¹⁶ by stereospecific,¹⁷ retentive, N₂O₄ oxidation of the latter.

The *cis/trans* ratios of reactants were determined either directly from ¹H NMR integration of the 4-methyl or 5-*tert*-butyl resonances at 60 or 100 MHz as required to obtain good peak separations or by GLC following conversion of reactants to the sulfide with S₈ which involves retention of configura-

Table I. Free-Radical Arbuzov Reactions of X· with Cyclic Phosphites in C₆H₆ at 20 °C

Reactions	Phosphite, M	X·, M ^a	Phosphorus product	% yield ^f	Cis/trans ratio		Other products, %
					Reactant	Product	
1	8 , 0.4	Ph·, 0.8	13	96 ^b	96/4 ^b	6/94 ^b	PH ₃ CCH ₃ , 74 ^c
2	8 , 0.2	Ph·, 0.4	13	90 (2) ^{b,e}	7/93 (2) ^{b,e}	92/8 (2) ^{b,e}	Ph ₃ CCH ₃ , 79, 96 ^c
3	10 , 0.4	Ph·, 0.6	15	72 ^c	40/60 ^b	58/42 ^b	Ph ₃ CCH ₃ , 54 ^b
4	9 , 0.3	Me ₂ N·, 1.0	12	88 (3) ^c	13/87 (3) ^{b,d,e}	90/10 (3) ^{d,e}	(PhCH ₂) ₂ , 65 ± 2 (3) ^c
5	9 , 0.3	Me ₂ N·, 1.0	12	85 (3) ^c	97/3 (3) ^{b,d,e}	5/95 (3) ^{d,e}	(PhCH ₂) ₂ , 60 ± 2 (3) ^c
6	11 , 0.2	Me ₂ N·, 1.0	14	97 (3) ^c	46/54 (3) ^{b,e}	55/45 (3) ^{d,e}	(PhCH ₂) ₂ , 78 ± 3 (3) ^c
7	11 , 0.3	Me ₂ N·, 1.4	14	98 (3) ^c	35/65 (3) ^{b,e}	65/35 (3) ^{d,e}	(PhCH ₂) ₂ , 71 ± 2 (3) ^c

^a Refers to initial concentration of radical source, mol/L. See Results for radical source molecules. ^b By ¹H NMR. Internal standard added following reaction. ^c By GLC. Internal standard added after reaction. ^d By GLC following conversion by S₈ to sulfides. ^e Range of replicate runs ±2%. Number of replications given in parentheses.

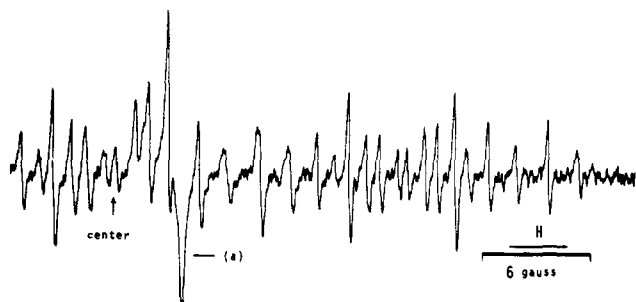
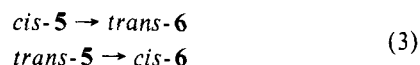


Figure 1. ESR spectrum of benzyl radical observed during in situ photolysis of tetramethyltetrazine in the presence of compound **11** at 10 °C (benzene). High field half of spectrum shown. (See Results.) Signal a from color center impurity in quartz tube.

tion.¹⁸ (Both methods were used in reactions 4–7 of Table I.) Likewise, product isomer ratios were monitored either by GLC or ¹H NMR. We have found generally^{13,15,16} that cis/trans ratios of such compounds can be determined either by ¹H NMR integrations of 4-methyl or 5-*tert*-butyl peaks or by GLC of oxides or sulfides with nearly identical results, i.e., percentages within a range of ±2. This applies whether the two techniques are used for a given pair of pentavalent isomers or whether isomer ratios for trivalent compounds are compared before and after conversion to oxide or sulfide with N₂O₄ or S₈. All products were identified by GLC even if ¹H NMR methods were used to determine cis/trans ratios.

The conclusions to be drawn from the data of Table I are the following. The reactions give high product yields, are nearly stereospecific, and proceed with the overall stereochemistry given by



Thus, the phosphoryl oxygen in the product phosphonates retains its original stereochemical relationship to the ring substituent, R.

Because of the concern that product ratios should reflect kinetic control of product formation, the reactions in Table I with one exception were run at more than one starting cis/trans ratio of phosphite, and one mixture which was not at thermodynamic equilibrium was used in every case. Reaction 2 was interrupted before completion. The cis/trans ratio of remaining reactant was unchanged, and that of the products (**13**) was the same as at completion of the reaction. This is consistent with the high reactivity¹⁰ of Ph· toward phosphites ($k \geq 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and demonstrates that reactants are not interconverted (cis = trans) under reaction conditions.

Similarly, the dimethylamino radical reactions were studied as a function of time, but somewhat more carefully. Reaction **11** was examined at five intermediate times between 0 and 2.6

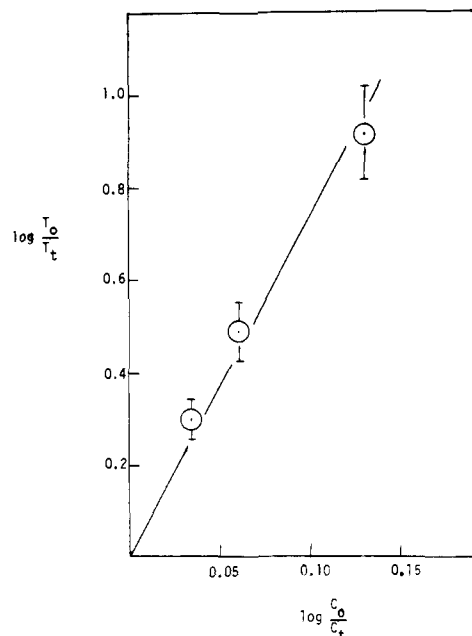


Figure 2. Kinetic plot of relative reactivities of *cis*- and *trans*-**9** toward Me₂N·.

h. Remaining phosphite was analyzed by GLC following S₈ treatment. Good zero-order plots of both reactant and product were obtained over the range 0–91% reaction. The starting cis/trans ratio of remaining **11** increased steadily from 65/35 to 78/22 (91% reaction), and the trans/cis ratio of product **14** increased overall from 60/40 to 65/35. This indicates that the cis phosphite is slightly (up to 40%) more reactive toward Me₂N· than is its trans counterpart. The ratio of rate constants for reactions of the cis (k_C) and trans (k_T) isomers is readily determined from the equation

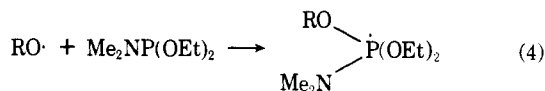
$$k_C/k_T = \log(C_0/C_t)/\log(T_0/T_t)$$

where C_0 , C_t and T_0 , T_t refer to the concentrations of cis and trans phosphite isomers at time zero and at time t during reaction. A lack of precision in k_C/k_T for **11** results from the small experimental changes in cis/trans ratio.

The reaction of a 95/5 cis/trans ratio sample of **9** also was zero order to 58% reaction after which all of the trans isomer had been consumed. A plot according to the above equation (Figure 2) to 88% consumption of *trans*-**11** shows the trans isomer to be about 7–9 times the more reactive. Here, error results from measurements of the small amount of *trans*-**11**. Each point in Figure 2 represents two or three measurements, and the error range represents the extremes in the experimental numbers.

Discussion

As indicated in the introduction to this paper, phosphoranyl radical species are readily detected when Me^{3d} or Ph^{31j} is generated in the presence of (RO)₃P. Furthermore, ESR shows the presence of similar species in certain alkoxy radical reactions with phosphoramidites, eq 4.^{3m} Therefore, we will discuss



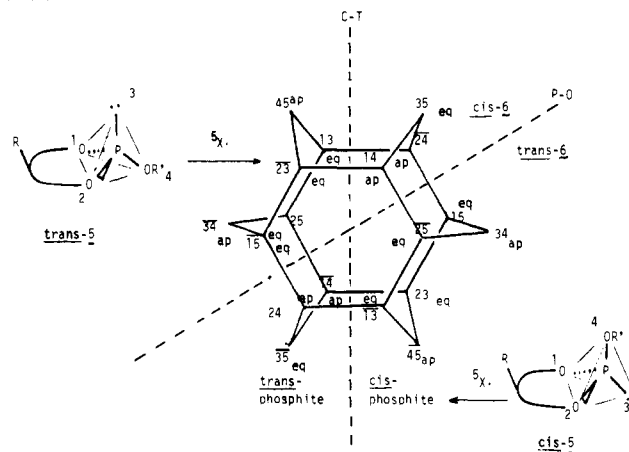
the results of the present studies of the stereochemistry of free-radical Arbusov reactions in terms of such intermediates.

In this discussion, the phosphites are considered to be tetrahedral species with the lone pair at one apex. The usual conventions applied in formation of pentacovalent phosphorus intermediates or transition states on attack of nucleophiles on tetrahedral phosphonium salts, phosphine oxides, phosphates, etc.,⁸ are then employed. Thus, facial approach of attacking radical results in its apical introduction into the trigonal bipyramidal phosphoranyl radical intermediate, whereas edge attack on the trivalent phosphorus reactant introduces the RO equatorially. (See Schemes II and III.)

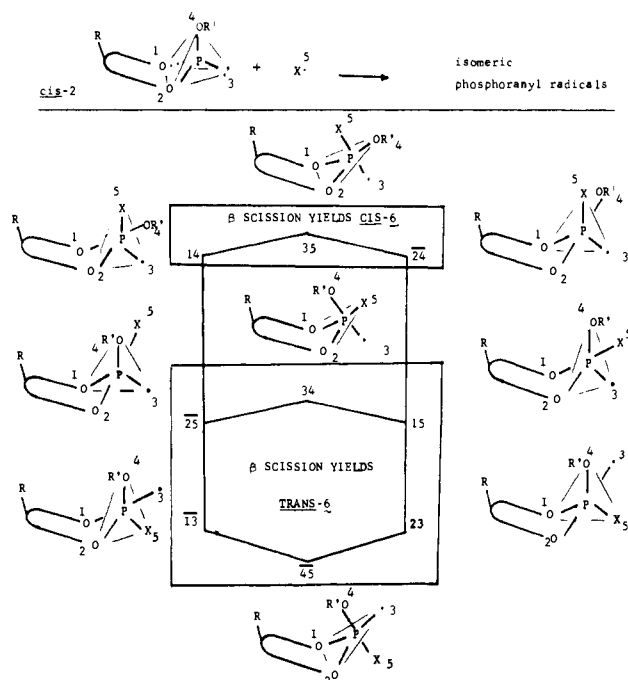
A Levi-Desauges graph similar to those used with pentacovalent phosphorus intermediates¹⁹ will prove extremely useful in systematizing the different initially formed phosphoranyl radicals and in keeping track of their isomerizations. Such a topological representation is given in Scheme II. As is the usual convention,^{8a} the vertices represent individual permutamers, and the lines interconnecting the vertices trace the available pathways for interconversion of Musher M₁ isomerizations⁶ (of which the Berry⁷ and turnstile⁸ processes are mechanistic examples). The numbers at the vertices designate configuration, by showing which two substituents are apical. Unbarred numbers are for isomers in which the remaining equatorial substituents increase numerically in clockwise order when viewed from the lowest numbered apical ligand. (Permutamers **15** and **15** are examples of cis/trans isomers.) Note that the odd electron in these isomers retains the number 3 given to the pair in reactant phosphite, and the attacking radical, X·, is substituent 5. The designation ap or eq, which appears at each vertex, tells the location (apical or equatorial) of R'O in which it potentially can undergo β-scission. The C-T plane (perpendicular to page) separates those phosphoranyl radicals formed initially from *cis*-**5** from those resulting from *trans*-**5**. On either side of the P-O plane are permutamers which on β-scission give either *cis*- or *trans*-**6** as designated.

What can be seen clearly in Scheme II are the effects on stereochemistry of a free-radical Arbusov reaction of (1) the direction of X· attack on pyramidal **5**; (2) possible isomerizations of an initial phosphoranyl radical prior to product-forming β-scission. Examining the reactions of *cis*-**5**, it is seen that approach of X· at a tetrahedral face or edge which includes the phosphorus lone pair results in one of six isomers which on β-scission yield *trans*-**6**. However, if for some reason attack were to take place away from the lone pair to give isomers **14**, **35**, or **24**, then the *cis* oxide would result. It is also evident that for five of the six initial adducts which arise from attack toward the lone pair, at most two permutational isomerizations prior to β-scission are required for *cis*-**6** to result. Therefore, the stereochemical outcome of the present studies as expressed in eq 3 means that *extensive amounts of M₁ permutation do not precede β-scission in these cases*. It also can be concluded that X· attack fails to give the sterically less probable initial adducts **14**, **35**, and **24** unless these forms undergo immediate isomerization to **25** and **15** prior to product formation. The above

Scheme II



Scheme III



conclusions become more clear on examination of Scheme III, which shows the detailed structure of the phosphoranyl radicals on the right-hand half of the diagram of Scheme II, i.e., those potentially formed initially from reaction of *cis*-**5**.

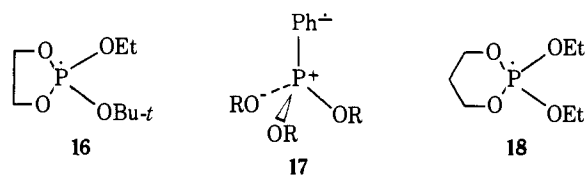
A simplification of Scheme III may be made as follows. Initial formation of **14**, **35**, and **24** was excluded above (and also by our work on oxidation stereochemistry in these systems.^{1a,20}) Furthermore, ESR measurements to date have detected only tetraalkoxyphosphoranyl radicals with odd electron (vacant site) equatorial.³ Thus any initial **34** or **13(23)** would be quickly converted to **25(15)** or **45**. (Note that **13** and **23** are mirror images as are **25** and **15**.) ESR measurements on (MeO)₃PH formation are interpretable in terms of *initial* apical introduction of H apical.²¹ Recent ab initio calculations of the energetics of H· attack on PH₃ strongly favor apical (facial) attack.²² In reactions of pentacovalent phosphorus species, one generally assumes apical entering and leaving of groups as well.⁵ The above all suggest that we may focus our attention on structures **25(15)** and **45**.

If all of the reactions being considered proceed via an initial adduct like **45** with ring diequatorial, then it is not surprising that only retention of phosphorus configuration is encountered. Inversion would require isomerization via **13(23)** which are expected to be high-energy intermediates since they have an odd electron on the apical position (see Schemes II and III).

However, if attack on phosphite to give $\overline{25}$, **15**, and $\overline{45}$ were merely statistical in nature, $\overline{25}$ (**15**) would result 67% of the time. In addition ESR investigations^{3d,e,m} of alkoxy radical attack on closely analogous five-membered ring compounds, containing at the 1 and 3 positions two oxygens, two nitrogens, or one each of oxygen and nitrogen, all show hyperfine splittings interpretable only in terms of an apical-equatorial attachment of the ring to phosphorus as in $\overline{25}$ (**15**). Even the radical resulting from reaction of RO· with a six-membered ring diamino compound, a 1,3,2-diazaphosphorinane, has the ring attached in apical-equatorial fashion.^{3m} For these reasons it is likely that a major portion of the free-radical Arbuzov reactions of the present study proceed via $\overline{25}$ (**15**) (intermediate **3** of Scheme I).

Direct β -scission of $\overline{25}$ (**15**) yields trans oxide product as is consistent with eq 3. Had $\overline{25}$ (**15**), however, undergone a permutational isomerization to $\overline{14}$ (**24**) prior to β -scission, then the cis oxide would have been formed. This sequence of events corresponds to $5 \rightarrow 4 \rightarrow 3 \rightarrow \text{cis-6}$ in Scheme I. The isomerization of $4 \rightarrow 3$ ($\overline{25}$ (**15**) \rightarrow $\overline{14}$ (**24**)) of Scheme III) exchanges the groups X and R'O between apical and equatorial positions while keeping the other substituents, the ring oxygens and odd electron, overall in the same positions. In our earlier investigations^{1a} of R'O oxidations of *cis*-**2** with X = RO (i.e., a phosphite) the isomerization $3 \rightarrow 4$ was found to be slower than β -scission since *cis*-**6** rather than *trans*-**6** was formed. The conversion $3 \rightarrow 4$ is nearly neutral energetically in such systems since two alkoxy groups are interchanged. However, in the free-radical Arbuzov reactions with X = Me₂N, this is not the case for *cis*-**5** \rightarrow **4** \rightarrow **3**. The apparent thermodynamic apicophilicity order RO > Me₂N is indicated by ESR work^{3a,e,m} on phosphoranyl radicals containing these substituents. (See below for comments on Ph·) Thus when X is Me₂N, **3** will be more stable than **4**, which fact could cause an acceleration of the isomerization rate for $4 \rightarrow 3$. In spite of this, there is no evidence from the nearly stereospecific nature of the free-radical Arbuzov processes we have studied that the isomerization $4 \rightarrow 3$ is even competitive with β -scission ($4 \rightarrow \text{trans-6}$).

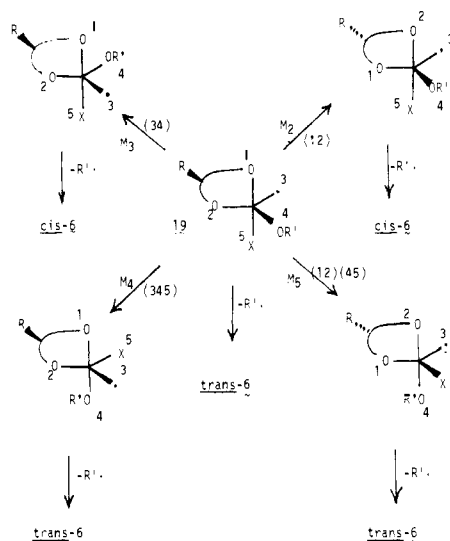
We are unable to make firm quantitative estimates of upper limit values of ΔG^\ddagger for the process $4 \rightarrow 3$ ($\overline{25}$ (**15**) \rightarrow $\overline{14}$ (**24**)), because that for the β -scission step with which it is in competition is not known for PhCH₂O. Although as noted above the intermediate MeP(OEt)₂OCH₂Ph has been detected by ESR,^{3d} the kinetics of its decomposition via β -scission have not been reported. Species such as PhCH₂O \dot{P} (OEt)₃ undergo β -scission too rapidly to be seen by ESR.^{3d} A lower limit value for ΔG^\ddagger for β -scission of **16**, available from known^{3d,23} *E_a* and *A* values,



is 11 kcal/mol at 20 °C. With benzyloxy in place of *tert*-butoxy, this value would be several kilocalories per mole lower, but we cannot say more than that. In these stereochemical studies it has been necessary to sacrifice the lifetime of the intermediate in order to gain a greater potential rate for the isomerization $4 \rightarrow 3$.

We have not included the case X = Ph· in this discussion. Since our work was completed, there have appeared several reports, both experimental^{3i,j,24} and theoretical,²⁵ which indicate that the Ph-substituted phosphoranyl radicals in the absence of other very electronegative substituents on phosphorus may very well have tetrahedral structures with the ddd electron distributed over the π and d orbital system as repre-

Scheme IV



sented by **17**. Nevertheless, the stereochemical outcome of the phenyl radical reactions reaffirms the conclusion that X· attacks **8** and **10** on a tetrahedral face or edge which includes the phosphorus lone pair, i.e., in the stereochemically least demanding fashion. We also find it surprising that apparently β -scission in the reactions of Ph· gives the relatively unstable Me·. This is especially true for the reactions with **8**. It is known from ESR^{3d} and chemical work¹¹ that phosphoranyl radical **18** yields little or no product of ethoxy C–O scission but ring opens instead. The rate of β -scission in radicals like **17** is unusually fast³ⁱ compared to nonphenyl systems, suggesting that these tetrahedral species have unusual features. In addition we showed earlier¹⁰ that the rate of addition of Ph· to (CH₃O)₃P was independent of any subsequent steps, and also that the β -scission process does not require participation of the trityl radical. Yet, the high yield of Ph₃CCH₃ could be the result of facile attack by Ph₃C· at the methyl carbon of the phosphoranyl radical precursor, a process expected to be more rapid than that at a ring carbon.

While our stereochemical results exclude extensive amounts of M₁ permutation prior to β -scission in free-radical Arbuzov processes, they do not exclude all other permutation modes by any means. Shown in Scheme IV are the effects of various permutation modes⁶ potentially available to initial adduct **19** (mirror image of **4** and equivalent to **15** of Scheme III) on the overall stereochemistry of reaction of X· with *cis*-**5**. In all cases the ring is restricted to being apical-equatorial^{3d,e,m} and the odd electron equatorial.³ Only a single representative of each mode is shown. The numbers given in parentheses are useful for keeping track of the changes in locations in ligands but should not be taken as an assignment of a specific physical mechanism for a particular isomerization. Other orderings of ligands within a mode could be given to designate the permutation. What is seen is that while M₂ and M₃ processes (like M₁) do not fit the stereochemical outcome of our experiments, the occurrence of a rapid M₄ or M₅ isomerization prior to β -scission would give the *same* stereochemical outcome as would β -scission directly from **19**. We are aware that combinations of successive rearrangements may be stereochemically equivalent to a single step of another mode⁶ (e.g., M₂ × M₂ = M₄), and make the above statements regarding allowed single permutational modes with due caution. The restrictions imposed on the ring attachments and position of the odd electron reduce this danger, however.

It has recently been proposed^{3m} that very rapid M₄ isomerizations (*k* = 10⁷–10⁸ s⁻¹ at –100 °C) may account for the temperature-dependent ESR spectra of intermediates like **16**

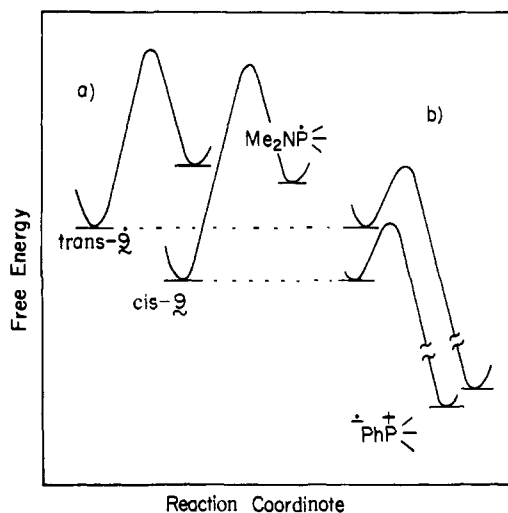
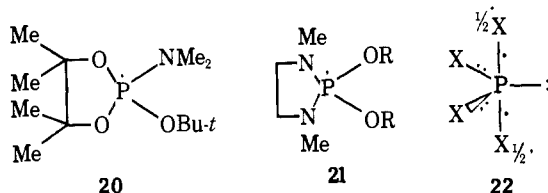


Figure 3. Possible energy profile diagrams for reactions of $\text{Me}_2\text{N}\cdot$ and $\text{Ph}\cdot$ with **9**.



and closely related species (**20**, **21**) containing nitrogen in place of oxygen at one or more positions. Such a rapid process also is allowed (*but not required*) by the results of our investigations of the stereochemistry of oxidation of cyclic phosphite systems by $\text{RO}\cdot$ ^{1a} and also by the inversion of stereochemistry which we observe accompanies certain free-radical substitutions at trivalent phosphorus.²⁶ Again, ESR work has shown that the fluorines of $\text{RO}\dot{\text{P}}\text{F}_3$ exchange rapidly³ⁿ by an undefined process, as do the Me_2N groups of $(\text{Me}_2\text{N})_2\dot{\text{P}}(\text{OEt})_2$ ^{3m} and hydrogen of $\text{RO}\dot{\text{P}}\text{H}_3$.^{3f}

Theoretical calculations involving PH_4 ,^{22,27} $\dot{\text{P}}\text{F}_4$,^{22,27} and PO_4^{4-} ²⁸ all show that a Berry-like isomerization mechanism involving a square pyramidal transition state with odd electron apical would be a much higher energy process than that for the truly pentacoordinate phosphorus analogue (PF_5 vs. $\dot{\text{P}}\text{F}_4$, or $\dot{\text{P}}\text{H}_4$ vs. PH_5). In fact any distortion from a distorted trigonal bipyramidal geometry for $\dot{\text{P}}\text{H}_4$ or $\dot{\text{P}}\text{F}_4$ with the electron equatorial involves an unusually high calculated amount of energy.²²

Interestingly, trigonal bipyramidal structures with odd electron apical are predicted^{22,27} to be of much lower energy than the square pyramidal odd electron apical species involved in a Berry-mechanism M_1 isomerization (**25** \rightarrow **14**). Possibly the apparent M_4 isomerizations^{3m} are consecutive M_1 processes ($\text{M}_1 \times \text{M}_1 = \text{M}_4$) via an energetically accessible odd electron apical trigonal bipyramidal intermediate, e.g. **25** \rightarrow **[34]** \rightarrow **15**. Clearly the factors which determine the modes and rates of exchange of substituents in phosphoranyl radicals are not thoroughly understood. Any conclusion that these species are simply analogues of their truly pentacoordinate phosphorus relatives is certainly premature.

The difference in reactivity of *cis* and *trans* isomers of **9** toward $\text{Me}_2\text{N}\cdot$ compared to those of **11** is worth comment. The equilibrium *trans/cis* ratio for **11** is about 65/35. The slightly greater reactivity of the *cis* isomer could reflect its ground state instability, ΔG° (*trans* \rightarrow *cis*) of 0.35 kcal/mol at 25 °C. Within this line of thought, the *cis/trans* equilibrium for **9** (95/5) corresponds to ΔG° (*cis* \rightarrow *trans*) of 1.7 kcal/mol. The relatively greater selectivity, k_T/k_C , of **9** toward $\text{Me}_2\text{N}\cdot$ then is not surprising. ($\Delta\Delta G^\ddagger$ for a k_T/k_C of 8 is 1.2 kcal/mol at

25 °C.) The ground state stability difference is not fully realized in $\Delta\Delta G^\ddagger$. The unselective nature of reaction 2 is predictable from the very reactive nature of $\text{Ph}\cdot$ and its irreversible,^{9,10} exothermic addition to trivalent phosphorus. By contrast, the $\text{Me}_2\text{N}\cdot$ reaction with benzyl phosphites is probably reversible, since when $\text{Me}_2\text{NP}(\text{OCH}_2)_2$ reacts with $\text{PhCH}_2\text{O}\cdot$, both $\text{PhCH}_2\text{OP}(\text{OCH}_2)_2$ and $\text{Me}_2\text{NP}(\text{O})(\text{OCH}_2)_2$ are formed.²⁶ The relative energetics of the $\text{Me}_2\text{N}\cdot$ and $\text{Ph}\cdot$ reactions are shown in Figure 3. The phosphoranyl radical intermediates in the $\text{Me}_2\text{N}\cdot$ reactions are depicted as being more nearly equal in energy than the reactants, compressing somewhat the transition state energies. The rapid $\text{Ph}\cdot$ reactions are little affected by reactant stabilities in an exothermic, irreversible reaction. These are probable but perhaps not unique energy profiles consistent with the observed reactivities.

Finally, it should be noted that both molecular orbital calculations^{22,27} and experimental data²⁹ show that phosphoranyl radicals are likely better represented electronically by a form (valence bond representation) like **22** which emphasizes that the odd electron is distributed to a large degree over the σ orbitals of the axial ligands. For simplicity in writing of structures, however, we have used the form with odd electron in the equatorial position. Geometrical considerations are unaffected by this choice.

Experimental Section

Gas chromatography was performed on F & M Model 810 and Hewlett-Packard 5830 instruments equipped with TC detectors. Aluminum columns (0.25 in.) packed with about 20% SE-30 on 60–80 mesh Chromosorb W and, more usually, 0.25-in. glass columns packed with 3–4% QF-1 on 100 mesh Gas Chrom Q were employed in temperature-programmed analyses. The glass columns proved especially applicable with sensitive five-membered ring products. No correction was made for small differences possible in sensitivities of isomers. ¹H NMR spectra were obtained on Varian A-60 and XL-100-15 instruments. ³¹P spectra were recorded on the XL-100 operating in the CW mode with proton-phosphorus splitting noise decoupled. Microanalyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y., and Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected.

PAT and **TMT** were prepared by standard literature procedures. Benzene was purified by washing with concentrated H_2SO_4 , 5% NaOH, and then H_2O before drying over CaCl_2 , and distillation from LiAlH_4 . The preparations of **8**,¹³ **10**,¹⁴ and **12**¹⁵ were reported earlier. New phosphorus compounds were synthesized by standard methods as summarized below.

Phosphite 9. This material, 2-benzyloxy-5-*tert*-butyl-1,3,2-dioxaphosphorinane, was synthesized from the phosphorochloridite, 2-chloro-5-*tert*-butyl-1,3,2-dioxaphosphorinane, by reaction with benzyl alcohol in the presence of triethylamine by a procedure exactly analogous to that for the preparation of **8**.¹³ Filtration and removal of solvent left a low-melting solid at least 90% pure by ¹H NMR. From integration of the well-separated 5-*tert*-butyl resonances the ratio of isomers, *cis/trans*, was determined to be 97/3. Stereospecific retentive S_8 oxidation¹⁸ followed by GLC analysis of the sulfides gave a ratio 95/5 *cis/trans*. This material (**9**) was used without further purification in reaction 5 of Table I.

In another reaction, crude **9** following filtration to remove the last traces of triethylamine hydrochloride was distilled through a small Vigreux column. A middle fraction was collected, bp 110 °C (0.02 mm). This material, a liquid, was shown by NMR and also GLC of the sulfide to be a 13/87 *cis/trans* mixture of isomers.

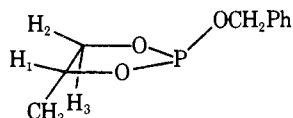
Detailed ¹H NMR analysis (aided by the LAOCN3 program) of the non-first-order spectra for the isomers of **9** confirmed the *cis* and *trans* assignments of geometries. In addition the relative $\delta^{31}\text{P}$ shifts (parts per million downfield from external 85% H_3PO_4) confirm^{16,30} the geometries: δ *cis*-**9**, 124.1; *trans*-**9**, 131.3. (See ref 16.) Key parameters in these assignments for the *trans* form were the vicinal J_{HH} values (Hz) for the $\text{CH}_X\text{CH}_A\text{H}_B\text{OP}$ grouping of 4.82 (J_{AX}) and 5.12 (J_{BX}) and J_{HP} values for $\text{CH}_A\text{H}_B\text{OP}$ of 8.61 (J_{BP}) and 4.65 (J_{AX}). For the *cis* isomer the analogous parameters (Hz) were 11.73 (J_{AX}), 3.96 (J_{BX}), 2.81 (J_{AP}), and 11.04 (J_{BP}). These values show the equatorial nature of the 5-*tert*-butyl of *cis*-**9**. (See ref 13 and 16 for

complete discussion of such assignments to **8** and other 1,3,2-dioxaphosphorinanes.)

^1H NMR for *cis*-**9**: δ (C_6D_6) 0.558 (s, *t*-Bu), 1.91 (m, methine H), 3.77 and 4.23 (m, CH_2), 4.78 (d, $J_{\text{HP}} = 8.9$ Hz, PhCH_2), 7.06–7.45 (m, Ph). ^1H NMR for *trans*-**9** δ (C_6D_6) 0.842 (s, *t*-Bu), 1.33 (m, methine H), 3.79 and 4.27 (m, CH_2), 4.81 (d, PhCH_2), and 7.06–7.45 (m, Ph).

Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{O}_3\text{P}$: C, 62.65; H, 7.89; P, 11.55. Found: C, 62.50; H, 7.70; P, 11.59.

Phosphite 11. 2-Benzyloxy-4-methyl-1,3,2-dioxaphospholane was prepared from benzyl alcohol and 2-chloro-4-methyl-1,3,2-dioxaphospholane by the method reported previously for **10** and similar compounds,¹⁴ bp 70–72 °C (0.02 mm), *cis/trans* ratio 46/54 (^1H NMR of 4- CH_3). After several days at room temperature, the *cis/trans* ratio of the sample had changed to 38/62 (true equilibrium ratio, 35/65). The ratio was determined by integration of the ^1H NMR 4-Me resonances or by GLC following conversion to the sulfide isomer mixture. The ^1H NMR spectrum (C_6D_6) was analyzed approximately for a 35/65 mixture by first-order methods using the cleanly separated H_1 and H_3 resonances for the *trans* (major) isomer (structure) to give $J_{13} = 6$, $J_{12} = 6$, $J_{23} = -8$, $J_{34} = 7.5$ Hz, δ_{H_1} 3.13, and δ_{H_3} 4.2. These



parameters are very similar to those for **10** and also 2-*tert*-butoxy-4-methyl-1,3,2-dioxaphospholane (ref 14). Confirmation of the assignment of geometries is given by the relative ^{31}P shifts (parts per million downfield from external 85% H_3PO_4) of 141.6 (*cis*-**11**) and 137.5 (*trans*-**11**). (See also ref 14.) Other ^1H NMR parameters: for *trans*-**11** (C_6D_6) δ 0.917 (d of d, $J_{\text{HH}} = 5.9$, $J_{\text{HP}} = 0.7$ Hz, CH_3), 4.64 (d, $J_{\text{HP}} = 8.6$ Hz, PhCH_2); for *cis*-**11** δ 1.07 (d of d, $J_{\text{HH}} = 5.9$ Hz, CH_3), 4.66 (d, $J = 9.0$ Hz, PhCH_2), ~ 7 (m, Ph), both isomers.

Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_3\text{P}$: C, 56.58; H, 6.18; P, 14.60. Found: C, 56.55; H, 6.40; P, 14.98.

Phosphonate 13. 2-Phenyl-2-oxo-5-*tert*-butyl-1,3,2-dioxaphosphorinane (**13**) was formed from the phosphonite, 2-phenyl-5-*tert*-butyl-1,3,2-dioxaphosphorinane, of known¹⁶ *cis/trans* isomer ratio by stereospecific N_2O_4 oxidation¹⁷ at 0–5 °C. Preparative scale amounts of **13** were synthesized routinely from reaction of $\text{PhP}(\text{O})\text{Cl}_2$ with 2-*tert*-butyl-1,3-propanediol in the presence of Et_3N . Separation of the geometric isomers of **13** was effected on Florisil. *cis*-**13** had mp 106–107 °C, while that of *trans*-**13** was 89.0–89.5 °C.

Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{PO}_3$: C, 61.41; H, 7.53; P, 12.18. Found (*cis*-**13**): C, 61.34; H, 7.56; P, 11.98. Found (*trans*-**13**): C, 61.23; H, 7.43; P, 12.23.

Phosphoramidate 14. Oxidation of 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane¹⁴ (*cis/trans*, 33/67, ^1H NMR) with N_2O_4 at 0 °C gave stereospecifically (GLC) the *cis/trans* mixture of 2-dimethylamino-1-oxo-4-methyl-1,3,2-dioxaphospholanes (**14**) in near quantitative amounts (*cis/trans*, 35/65, GLC). Distillation of the crude **14** mixture gave GLC-pure **14**, bp 110–112 °C (0.2 mm), a liquid.

Phenylphosphonate 15. Addition of a saturated solution of N_2O_4 in benzene to an ice-cooled solution of 2-phenyl-4-methyl-1,3,2-dioxaphospholane¹⁴ (*cis/trans*, 33/67) was followed (GLC) to completion of the reaction. Distillation through a Vigreux column of the residue from removal of the solvent gave a high yield of the viscous liquid 2-phenyl-2-oxo-4-methyl-1,3,2-dioxaphospholane (**15**), bp 146–152 °C (0.2 mm), *cis/trans* ratio about 35/65 by GLC. ^1H NMR δ (CDCl_3) 1.51 (d, $J_{\text{HH}} = 6.1$ Hz, CH_3 of *cis* isomer), 1.57 (d, $J_{\text{HH}} = 6.1$ Hz, CH_3 of *trans* isomer), 3.9–5.2 broad m, $\text{OCH}_2\text{CH}_2\text{O}$, 7.4–8.2 (m, Ph).

Photoreactions. Reactions were run on a very small scale with total volumes of 0.1–0.5 mL. Pyrex tubes were soaked in dichromate solution for 24 h, rinsed with distilled water, then with Et_3N or dilute NH_3 , rinsed again with distilled H_2O , and dried at 110 °C. (Careful removal of all traces of acid is necessary to prevent *cis*–*trans* isomerization of trivalent reactants.) Tubes were filled using syringe techniques and stock solutions of reactants and then sealed under vacuum after several (usually three) freeze–thaw degassing cycles (10^{-5} – 10^{-6} mm). Photolysis of these solutions was effected by a 450-W Hanovia medium-pressure lamp contained in a water-jacketed quartz thimble immersed in a water bath. The tubes were strapped directly to the

outside of the thimble. Reaction times varied with conditions and initiator from 1 to 24 h. Control reactions are described in the Results section.

Tubes were opened following reaction, and an appropriate internal standard and, in some instances, S_8 was added to convert any trivalent phosphorus reactant or product to the sulfide. GLC analysis was then carried out. In the runs in which consumption of **9** and **11** was followed as a function of time, tubes were pulled periodically. Sulfur and internal standard were added immediately. Amount of unreacted *cis* or *trans* isomer was measured relative to a zero time sample of **9** or **11** sulfide. All peaks were identified by doping samples with authentic materials, even when *cis/trans* ratios were determined by ^1H NMR. All GLC yields were obtained from carefully done sensitivity plots of area ratio vs. weight ratio or mole ratio with at least four points plus origin. Equal sensitivities for *cis* and *trans* isomers of oxides and sulfides were assumed.

ESR spectra were recorded on a Varian V-4502 X-band spectrometer equipped with a 100-kHz field modulation. A V-4557 variable temperature accessory was used to control the sample temperature during the direct photolysis in the microwave cavity, the actual sample temperature being monitored by a Cu–constantan thermocouple placed in a sample tube.

A 2500-W Hg–Xe short arc lamp enclosed in an Oriel lamp housing was used. A quartz condenser lens, water filter, iris diaphragm, and a quartz focusing lens were suitably mounted in the lamp housing to focus the light into the sample cavity.

Each sample tube was carefully freeze–thaw degassed and then filled with He at 1 atm to suppress bubbling caused by the formation of nitrogen gas in the photodecomposition of tetramethyltetrazine.

Hyperfine splitting constants were calibrated using anthracene cation radical in H_2SO_4 . For Figure 1 the observed values (G) are³¹ 16.9 (CH_2), 6.07 (*p*-H), 5.41 (*o*-Hs), 1.80 (*m*-Hs).

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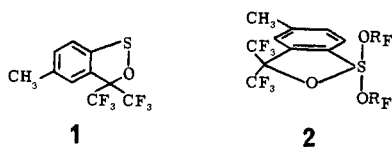
Oxidation of a γ -Sultene to a Cyclic Orthosulfinate.¹ Reactions of a Trialkoxysulfurane with Bifunctional Substrates as a Reflection of the Polarity Rules in Trigonal Bipyramidal Species

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Abstract: Trialkoxysulfurane **2**, the first reported orthosulfinate, is prepared by treatment of sultene **1** with bromine and KOR_F (R_F = C₆H₅C(CF₃)₂). Although the reactions of this sulfurane with water, tertiary alcohols, amines, and secondary amides give, respectively, a sultine, sulfinimides, and amide cleavage products in reactions analogous to those reported previously for dialkoxysulfuranes, **2** differs from them in its reactions with methanol, 1,2-diols, and 1,3-diols to give new trialkoxysulfuranes. The products from methanol, 2,2-dimethyl-1,3-propanediol, and ethylene glycol (**25**, **12**, and **13**) undergo intramolecular ligand exchange, shown by variable temperature ¹⁹F and ¹H NMR studies to have free energies of activation of ca. 11 kcal/mol (-68°C), 10 or 11 kcal/mol (-74 or -55°C) and 23 kcal/mol (163°C), respectively. A permutational isomerization mechanism of a type different from the pairwise exchange of the more usual Berry pseudorotation, a process involving a transition state with "tetrahedral" geometry at sulfur, is proposed to explain these results. In contrast to spiro-sulfuranes **10**, **11**, **12**, and **13** and dimethoxysulfurane **25**, sulfurane **2** is shown to exist in solution in a novel conformation having a diequatorial five-membered ring, on the basis of ¹H and ¹⁹F NMR chemical shift comparisons, the lack of any evidence for ligand exchange processes in the -90°C ¹⁹F NMR spectrum of **2**, and other arguments. The greater apicophilicity of the fluorinated alkoxy ligands of **2** over the methoxy ligands of **25** is suggested to be responsible for the difference in structure. The pyrolyses of spiro-sulfuranes **10**, **11**, and **13** are reported.

Cyclic sulfenates (sultenes) have never been prepared although acyclic analogues have been known for over 60 years.² Sultenes, however, have been proposed as reactive intermediates³ and suggested to explain mass spectral fragmentation.⁴ Molecular orbital calculations⁵ have predicted the orbital energies and interactions in small ring sultenes as well as similar acyclic sulfenates.^{5b} One example of a cyclic sulfenyl carboxylate is known although it polymerizes rapidly at room temperature.⁶ Here we report details⁷ of the synthesis of sultene **1** and its conversion to aryltrialkoxysulfurane **2**, a com-



pound whose reactions show important contrasts to those of the well-studied diaryldialkoxysulfuranes.⁸ This is the first reported aryltrialkoxysulfurane (or orthosulfinate) although thermally unstable trichlorosulfuranes⁹ and highly reactive

trifluorosulfuranes¹⁰ are well known. One fluorotrialkoxysulfurane has also been reported.¹¹

Synthesis and Reactions of Sultene 1. Thiol alcohol **3**, a key intermediate in the synthesis of sultene **1**, was prepared by two different methods. In method A (Scheme I), adapted from a procedure by Walker and Leib¹² for halogenating thiophenols, 4-methylthiophenol was protected by reaction with chloroacetic acid in the presence of aqueous NaOH before treatment with hexafluoroacetone in carbon disulfide solution at -10°C in the presence of aluminum chloride to yield ester alcohol **5**. At 40°C **5** was contaminated with small amounts of the product resulting from hexafluoroacetone substitution meta to the thioalkyl group. Since the spectra of these two isomers are very similar, the best proof of these assignments is the cyclization to sultene **1** of the thiol (**3**) made from **5**. However, more evidence comes from the lower frequency OH stretch in **5** (3320 vs. 3660 cm^{-1}) and the downfield NMR shift of the OH proton in **5** (δ 8.16 vs. 3.80) which support the idea of internal hydrogen bonding in **5** which is impossible in a 1,3-disubstituted structure. Ester **5** was saponified with aqueous KOH and the resulting carboxylic acid was cleaved to thiol **3**